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**SYNTHESIS, STRUCTURE AND  
PROPERTIES OF SOME  
DIHYDROTETRATHIAFULVALENES**

by

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B.Sc. (Hons), AMRSC

Thesis presented towards the degree of

**DOCTOR OF PHILOSOPHY**

University of St Andrews



November 2003

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## DECLARATION

I, Stephen Costello, hereby certify that this thesis is a record of my work, has been composed by myself and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Date. 26<sup>th</sup> Nov 2003

I was admitted to the Faculty of Science of the University of St Andrews under Ordinance General No. 12 on 1<sup>st</sup> October 2000 and as a candidate for the degree of Doctor of Philosophy on the 1<sup>st</sup> October 2001.

Date. 26<sup>th</sup> Nov 2003

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the degree of Doctor of Philosophy.

Date. 26<sup>th</sup> Nov 2003

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Finally I would like to thank the University of St Andrews for providing financial assistance through a studentship.

## LECTURE COURSES ATTENDED

The following is a statement of the courses attended during the period of research:

Organic Research Seminars	3 years attendance
School Colloquia	3 years attendance
Organic Problem Solving	Prof. D. O'Hagan and Dr. N. P. Botting
Molecular Rearrangements in Organic Chemistry	Prof. J. C. Walton
The Chemistry of Phosphorus and Related Elements	Dr. R. A. Aitken
The Chemistry of Sulfur and Related Elements	Dr. R. A. Aitken
Electrochemistry	Dr. J. A. Crayston

## ABSTRACT

A total of ten norbornene and norbornane-fused dihydrotetrathiafulvalenes have been prepared by reaction with  $\text{Bu}_3\text{P} \cdot \text{CS}_2$  and DMAD, two of them for the first time. Cyclic voltammetry was used to measure the oxidation potentials of the dihydrotetrathiafulvalenes. The data obtained showed two reversible oxidation processes for each dihydrotetrathiafulvalene group present with oxidation potentials being rather high compared to many standard electron donors.

A decarboxylation reaction was used to remove the ester groups giving a series of five new dihydrotetrathiafulvalenes which were fully characterised. Cyclic voltammetry measurements on these showed that removal of the ester groups had lowered the oxidation potentials considerably taking them into the range for useful electron donors.

The dihydrotetrathiafulvalenes were then reacted with various oxidants such as iodine, bromine, benzoquinone and TCNQ in an attempt to prepare charge transfer complexes. In some cases black crystalline solids were obtained from the reaction with iodine and on the basis of elemental analysis these appeared to be iodine Charge Transfer Complexes.

X-ray structures were obtained for four of the dihydrotetrathiafulvalenes and in two cases these represent a second crystalline form for the compound in question. Several interesting features occur in these structures and these are discussed in detail.

A donor- $\sigma$ -spacer-acceptor compound has been successfully synthesised and characterised. Cyclic voltammetry has shown two reversible oxidation and reduction processes and EPR spectroscopy shows the presence of a low concentration of the radical anion / radical cation species at room temperature, only the second time this has been observed. The X-ray structure shows a regular pattern consisting of infinite ladders of hydrogen-bonded dimer pairs.

A simple two-step method for converting aldehydes into 2-alkylidene-1,3-dithioles was developed and evaluated.

A novel compound was isolated from the reaction of  $\text{Bu}_3\text{P}$  with DMAD in the presence of various heterocumulenes, its structure determined by X-ray methods, and a mechanism proposed for its formation.

Finally a brief study was carried which showed that the "second generation" Grubbs catalyst could be used in the ring-opening metathesis co-polymerisation of norbornene-fused dihydrotetrathiafulvalenes thus opening the way for future work in the area.

## ABBREVIATIONS

BCS Theory	Bardeen, Cooper and Schrieffer theory
BEDT-TTF	bis(ethylenedithio)tetrathiafulvalene
BDA-TTP	2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene
BDH-TTP	2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene
CDW	charge density wave
CTC	charge transfer complex
CT	charge transfer
CV	cyclic voltammetry
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DHDA-TTP	2-(1,3-dithiolan-2-ylidene)-5-(1,3-dithian-2-ylidene)- 1,3,4,6-tetrathiapentalene
DMA	<i>N,N</i> -dimethylacetamide
DMAD	dimethyl acetylenedicarboxylate
DODHT	(1,4-dioxane-2,3-diyledithio)dihydratetrathiafulvalene
DTDAF	dithiadiazafulvalenes
EDO-TTF	ethylenedioxa-tetrathiafulvalene
FVP	flash vacuum pyrolysis
h	hour(s)
HPLC	high performance liquid chromatography
ICT	intramolecular charge transfer
IET	intramolecular electron transfer
IR	infra red
MDT-TTF	methylenedithio-tetrathiafulvalene
min	minute(s)

NMR	nuclear magnetic resonance
OP	oxidation potentials
pet. ether	light petroleum, boiling point 40-60 °C
RCS	radical cation salts
RIS	radical ion salt
RP	reduction potentials
RT	room temperature
SDW	spin density wave
T <sub>c</sub>	critical temperature
TCNAQ	tetracyanoanthraquinodimethane
TCNQ	tetracyano-p-quinodimethane
THF	tetrahydrofuran
TLC	thin layer chromatography
TMTTF	tetramethylthio-tetrathiafulvalene
TMTSF	tetramethyltetraselenafulvalene
TTP	tetrathiapentalene
TTF	tetrathiafulvalene

## INTRODUCTION

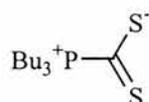
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## EXPERIMENTAL

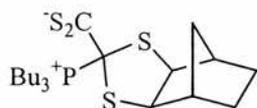
### A Instrumentation and General Techniques 48

### B Formation of Norbornane and Norbornene-Fused Dihydrotetrathiafulvalenes

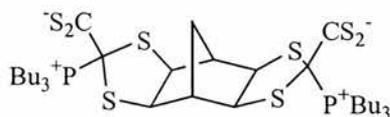
#### 1a Preparation of tri-n-butylphosphoniodithioformate **92** 53



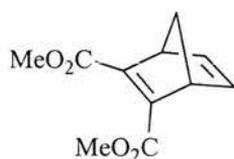
#### b Preparation of 2,6-exo-4-dithiocarboxylato-4-tri-n-butylphosphonio-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **94** 53



#### c Preparation of 4,10-bis(dithiocarboxylato)-4,10-bis(tri-n-butylphosphonio)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane **98** 53



#### d Preparation of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate **109** 54



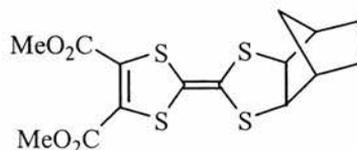
#### e Preparation of methyl phenylpropiolate in two steps

##### (i) Preparation of phenylpropionic acid 54

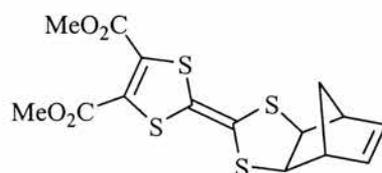
##### (ii) Conversion of phenylpropionic acid into methyl phenylpropiolate 55

#### f Alternative preparation of methyl phenylpropiolate 55

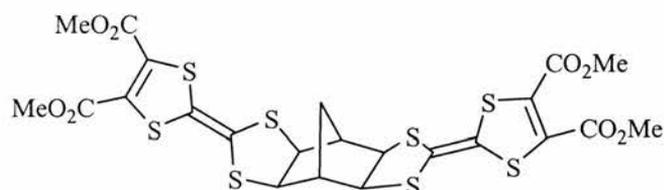
- 2 Preparation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99** 56



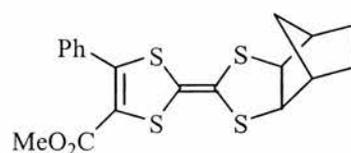
- 3 Preparation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **101** 57



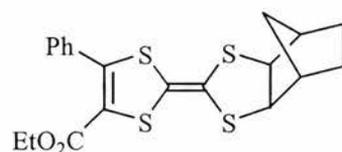
- 4 Preparation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>,0<sup>8,12</sup>]tridecane **102** 58



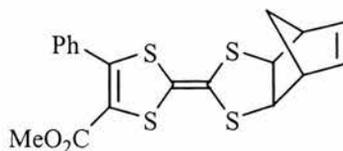
- 5 Preparation of 2,6-exo-4-(4'-methoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **103** 58



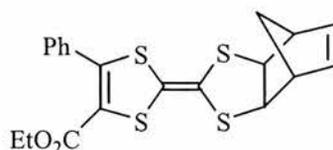
- 6 Preparation of 2,6-exo-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **104** 59



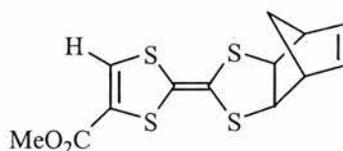
- 7 Preparation of 2,6-exo-4-(4'-methoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **105** 60



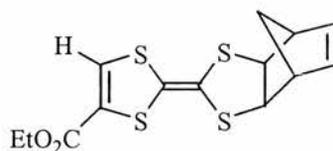
- 8 Preparation of 2,6-exo-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **106** 60



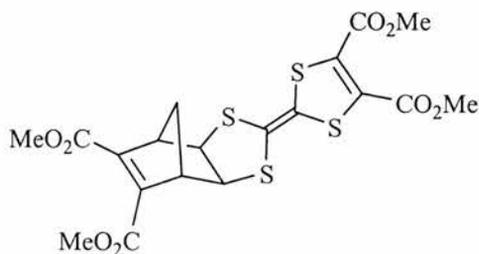
- 9 Preparation of 2,6-exo-4-(4'-methoxycarbonyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **107** 61



- 10 Preparation of 2,6-exo-4-(4'-ethoxycarbonyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **108** 62



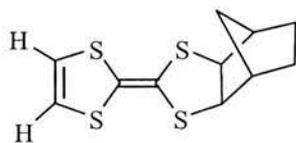
- 11 Preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **110** 63



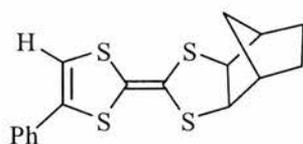
- 12 Attempted dehydrogenation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatriacyclo[5.2.1.0<sup>2,6</sup>]decane **99** using sulfur 63
- 13 Attempted dehydrogenation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatriacyclo[5.2.1.0<sup>2,6</sup>]decane **99** using selenium 64

### C Decarboxylation Reactions of Norbornane and Norbornene-Fused Dihydratetrathiafulvalenes

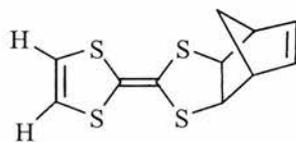
- 1 Preparation of 2,6-exo-4-(1',3'-dithiol-2'-ylidene)-3,5-dithiatriacyclo[5.2.1.0<sup>2,6</sup>]decane **117** 64



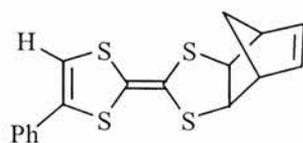
- 2 Preparation of 2,6-exo-4-(4'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatriacyclo[5.2.1.0<sup>2,6</sup>]decane **118** 65



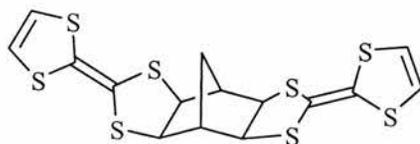
- 3 Preparation of 2,6-exo-4-(1',3'-dithiol-2'-ylidene)-3,5-dithiatriacyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **119** 65



- 4 Preparation of 2,6-exo-4-(4'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatriacyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **120** 66



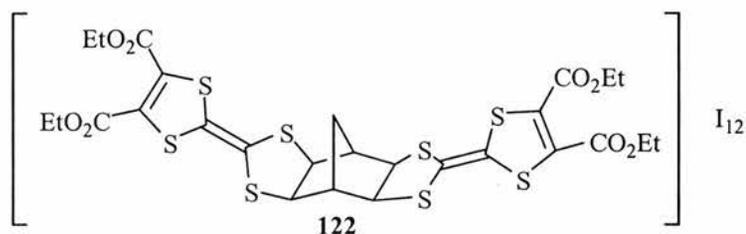
- 5 Preparation of 2,6-exo-8,9-exo-4,10-bis(1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiacyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridec-4-diene **121** 67



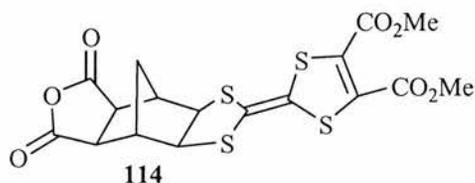
- 6 Attempted decarboxylation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **110** 67

#### D Preparation of Charge Transfer Complexes

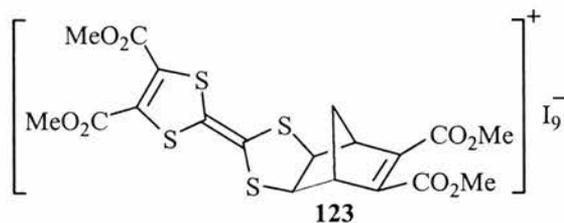
- 1 Formation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(ethoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane Iodine Charge Transfer Complex **122** 68



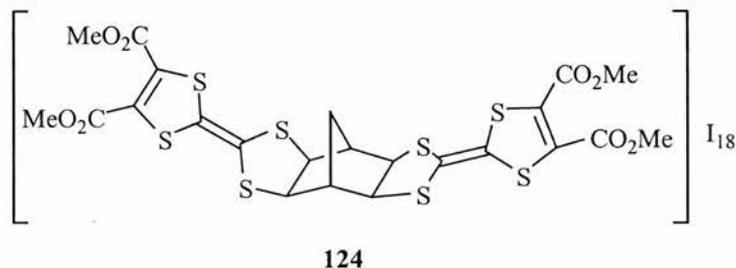
- 2 Attempted Formation of an Iodine Charge Transfer Complex with 2,6-exo-8,12-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10-oxa-3,5-dithiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane-9,11-dione **114** 69



- 3 Formation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene Iodine Charge Transfer Complex **123** 69

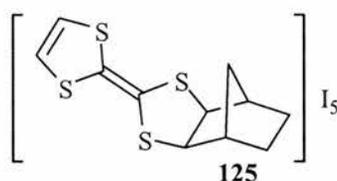


- 4 Formation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane Iodine Charge Transfer Complex **124** 70



- 5 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(ethoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane **112** 70
- 6 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,12-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10-oxa-3,5-dithiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane-9,11-dione **114** 71
- 7 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **110** 71
- 8 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane **102** 72

- 9 Attempted formation of a charge transfer complex involving TCNQ and 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane **102** 72
- 10 Attempted formation of a charge transfer complex with TCNQ and 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99** 73
- 11 Formation of 2,6-exo-4(1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane Iodine Charge Transfer Complex **117** 73



- 12 Attempted preparation of a quinone charge transfer complex with 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane **102** 74
- 13 Attempted preparation of a quinone charge transfer complex with 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99** 74

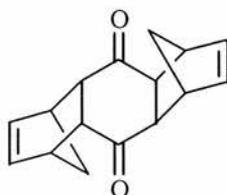
## E X-ray Structure Determination

- 1 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99** 75
- 2 2,6-exo-4-(1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **117** 75
- 3 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99** 76

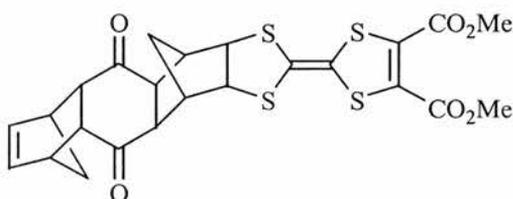
- 4 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiacyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane **102** 76
- 5 11-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10,12-dithiahexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradec-2(7),4(5)-diene-3,10-dione **91** 77
- 6 2-tri-n-butylphosphonio-2-methoxy-3,4,5-tri(methoxycarbonyl)cyclopent-2-en-1-ion-4-ide **203** 77

## F Construction of Norbornane-Fused Dihydrotetrathiafulvalene-Quinone Compounds

- 1 Formation of a Donor- $\sigma$ -Acceptor Compound
- a Preparation of 2,11-endo-4,9-endo-pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]hexadeca-6,13-diene-3,10-dione **132** 78

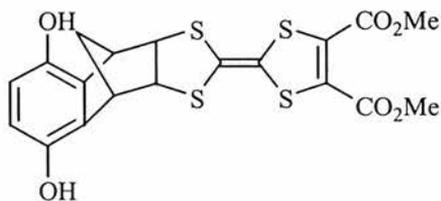


- b Preparation of 15-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-14,16-dithiahexacyclo[10.5.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]nonadec-6-ene-3,10-dione **134** 78



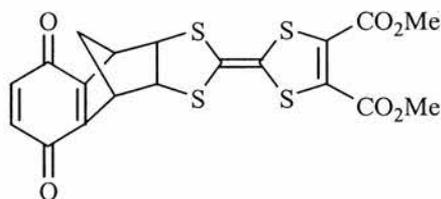
- c Attempted retro-Diels Alder reaction of compound **134** using FVP 79

- d** Preparation of 11-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10,12-dithiatetracyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradeca-2,4,6-triene-3,6-diol **135** using a retro Diels Alder reaction 79

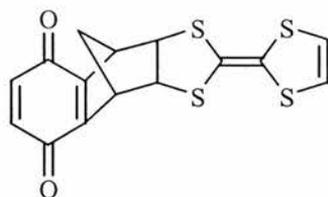


- e** Attempted oxidation of compound **135** using silver oxide 80
- f** Attempted oxidation of compound **135** using CrO<sub>3</sub> 80
- g** Attempted oxidation of compound **135** using benzoquinone 81

- h** Preparation of 11-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10,12-dithiatetracyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradeca-2(7),4-diene-3,6-dione **91** 81

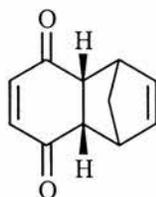


- i** Preparation of 11-(1',3'-dithiol-2'-ylidene)-10,12-dithiahexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradeca-2(7),4-diene-3,6-dione **143** 82

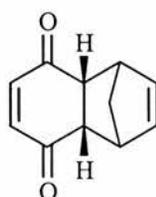


**2 Attempted formation of the donor- $\sigma$ -acceptor compound using alternative routes**

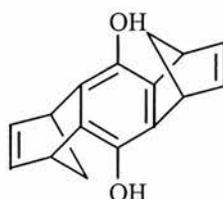
- a** Preparation of endo-tricyclo[6.2.1.0<sup>2,7</sup>]undeca-4,9-diene-3,6-dione **148** 83



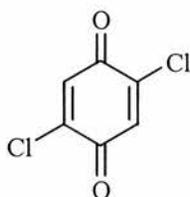
- b** Improved preparation of endo-tricyclo[6.2.1.0<sup>2,7</sup>]undeca-4,9-diene-3,6-dione **148** 83



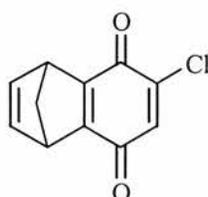
- c** Attempted formation of an unsaturated quinone adduct **150** 84



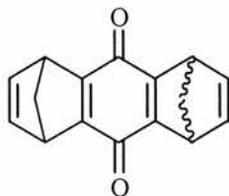
- d** Preparation of 2,5-dichloro-1,4-benzoquinone **152** 85



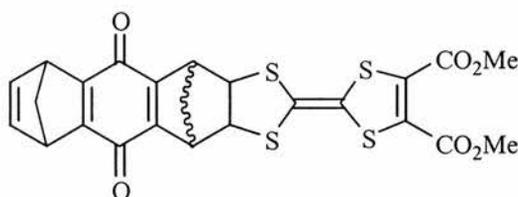
- e** Synthesis of 4-chlorotricyclo[6.2.1.0<sup>2,7</sup>]undeca-2(7),4,9-triene-3,6-dione **154** 85



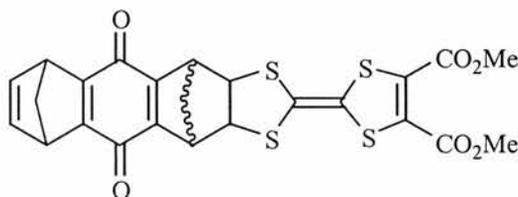
- f** Synthesis of pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]hexadeca-2(11),4(9),6,13-tetraene-3,10-dione **144** 86



- g** Attempted preparation of 8-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-7,9-dithiahexacyclo[13.2.1.1<sup>5,11</sup>.0<sup>2,14</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>]nonadeca-2(14),4(12),16-triene-3,13-dione **146** 87

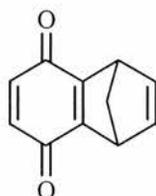


- h** Attempted preparation of 8-(4',5'-bis(ethoxycarbonyl)-1',3'-dithiol-2'-ylidene)-7,9-dithiahexacyclo[13.2.1.1<sup>5,11</sup>.0<sup>2,14</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>]nonadeca-2(14),4(12),16-triene-3,13-dione **146** 87

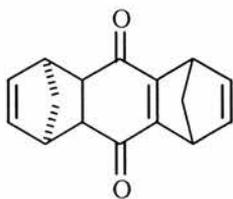


### **3 Formation of an unsaturated quinone adduct using another alternative route**

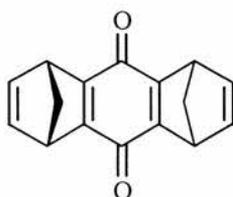
- a** Preparation of tricyclo[6.2.1.0<sup>2,7</sup>]undeca-2(7),4,9-triene-3,6-dione **158** 88



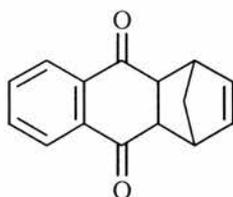
- b** Preparation of pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]hexadeca-2(11),6,13-triene-3,10-dione  
159 88



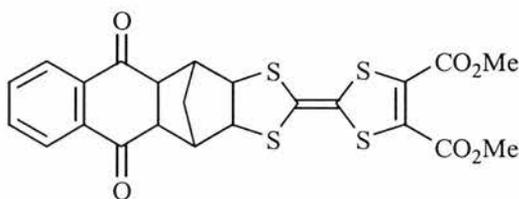
- c** Attempted preparation of pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>4,11</sup>.0<sup>4,9</sup>]hexadeca-2(11),4(9),6,13-tetraene-3,10-dione **160** 89



- d** Preparation of tetracyclo[10.2.1.0<sup>2,11</sup>.0<sup>4,9</sup>]pentadeca-4(9),5,7,13-tetraene-3,10-dione  
162 89



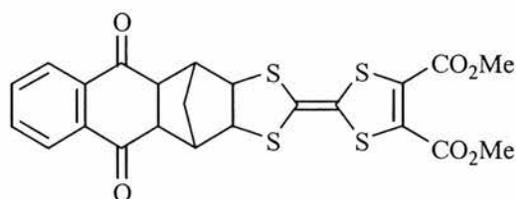
- e** Attempted preparation of 15-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-14,16-dithiapentacyclo[10.5.1.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]octadeca-4(9),5,7-triene-3,10-dione  
163 90



- f** Attempted preparation of 15-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-14,16-dithiapentacyclo[10.5.1.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]octadeca-4(9),5,7-triene-3,10-dione

163

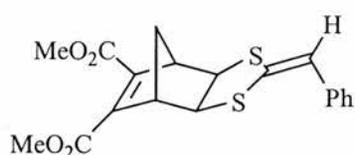
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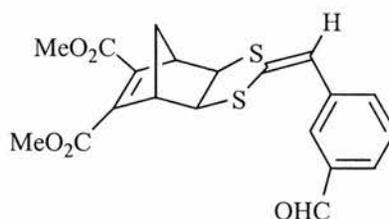
**G Convenient two-step conversion of aldehydes into 2-arylmethylene-1,3-dithioles**

**1 Synthesis of 1,3-dithiolanes via a Wittig reaction**

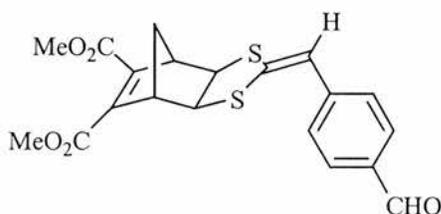
- a** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-phenylmethylene-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **173** 91



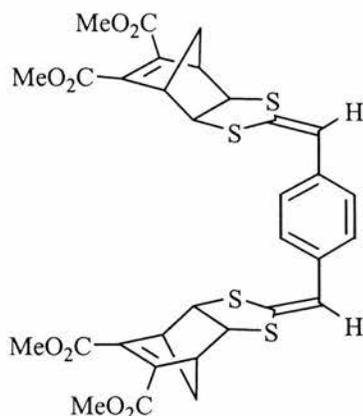
- b** Preparation of 2,6-*exo*-(8,9-bis(methoxycarbonyl)-4-(3'-formylphenylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **175** 92



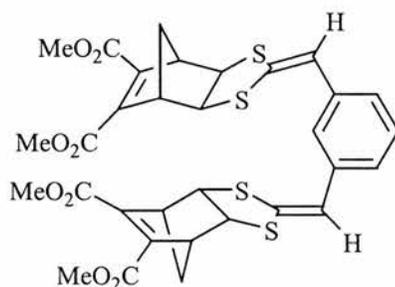
- c** Preparation of 2,6-*exo*-(8,9-bis(methoxycarbonyl)-4-(4'-formylphenylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **174** 92



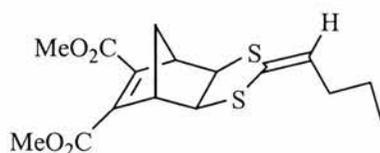
- d** Preparation of 1',4'-phenylenebis(4-methylenyl-8,9-bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene) **176** 93



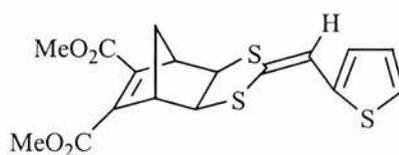
- e** Preparation of 1',3'-phenylenebis(4-methylenyl-8,9-bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene) **177** 94



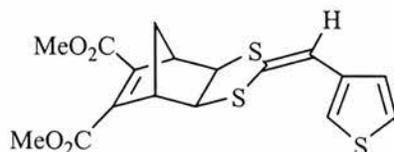
- f** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(1'-butylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **178** 94



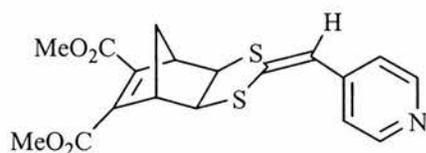
- g** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(2'-thienylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **179** 95



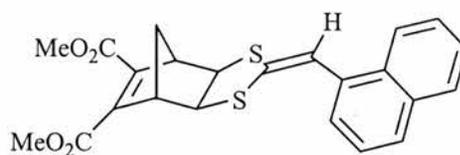
- h** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(3'-thienylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **180** 96



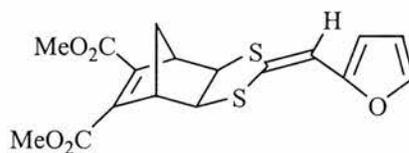
- i** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(4'-pyridylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **181** 97



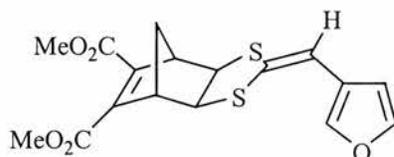
- j** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(1'-naphthylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **182** 98



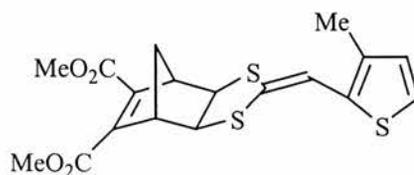
- k** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(2'-furylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **183** 98



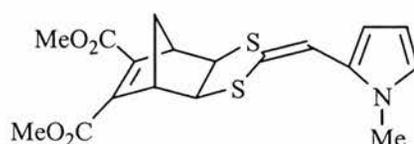
- l** Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(3'-furylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **184** 99



- m** Preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(3'-methyl-2'-thienylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **185** 100

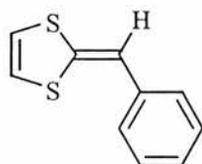


- n** Attempted preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(1'-methyl-2'-pyrrylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **186** 101

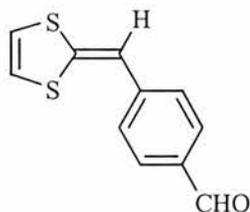


## 2 Synthesis of 2-substituted-1,3-dithioles via Flash Vacuum Pyrolysis of Wittig Products

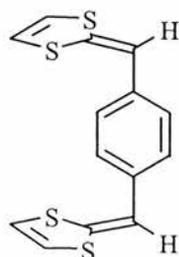
- a** Preparation of 2-benzylidene-1,3-dithiole **171** 101



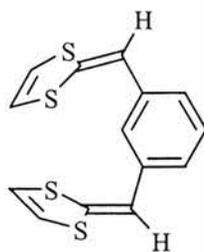
- b** Preparation of 2-(4'-formylbenzylidene)-1,3-dithiole **187** 102



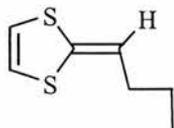
- c** Attempted preparation of 1',4'-phenylenebis(2-methylenyl-1,3-dithiole) **189** 102



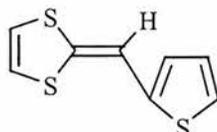
**d** Attempted preparation of 1',3'-phenylenebis(2-methylenyl-1,3-dithiole) **190** 103



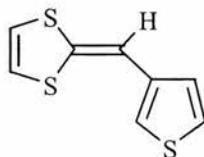
**e** Attempted preparation of 2-butylidene-1,3-dithiole **191** 103



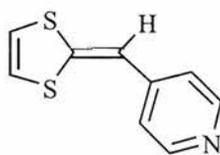
**f** Preparation of 2-(2'-thienylmethylene)-1,3-dithiole **192** 103



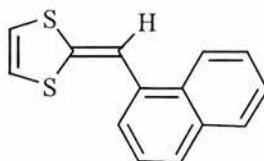
**g** Preparation of 2-(3'-thienylmethylene)-1,3-dithiole **193** 103



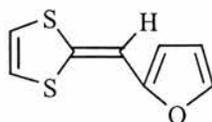
**h** Preparation of 2-(4'-pyridylmethylene)-1,3-dithiole **194** 104



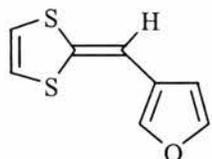
**i** Preparation of 2-(1'-naphthylmethylene)-1,3-dithiole **195** 104



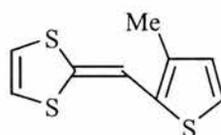
<b>j</b>	Preparation of 2-(2'-furylmethylene)-1,3-dithiole <b>196</b>	105
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<b>k</b>	Preparation of 2-(3'-furylmethylene)-1,3-dithiole <b>197</b>	105
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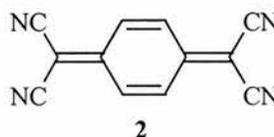
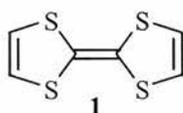
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# **INTRODUCTION**

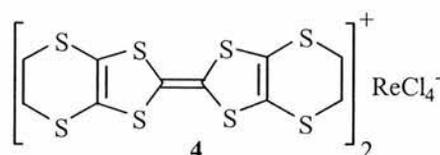
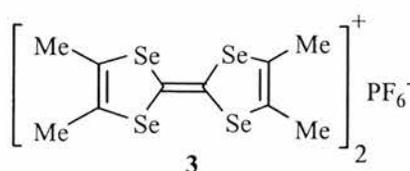
## A Tetrathiafulvalenes and dihydrotetrathiafulvalenes

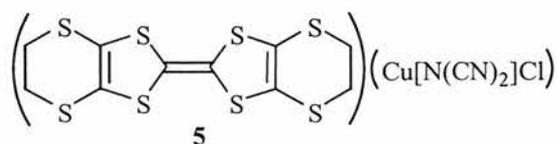
### 1 Historical background

Tetrathiafulvalene (TTF **1**) is a 14- $\pi$  electron non-aromatic system which can be oxidised to the cation and dication states relatively easily.<sup>1</sup> This results in a change in the symmetry of the molecule from a boat-like conformation to a planar conformation. The cation and dication states become aromatic due to the heteroaromaticity of the 1,3-dithiolium cation in contrast to the neutral TTF donor molecule.



In 1960 scientists at the Du Pont de Nemours Research Centre made the first ion radical salts using TCNQ **2** as an acceptor.<sup>2</sup> In 1970 Wudl reported the synthesis of tetrathiafulvalene **1** which could act as an electron donor forming a stable cation and dication.<sup>3,4</sup> In 1973 Cowan and Ferraris at Johns Hopkins University and Heeger and Garito at the University of Pennsylvania both discovered that TTF and TCNQ formed a 1:1 charge transfer complex which consisted of separate layers of donors and acceptors which were only stable to a narrow range of temperatures.<sup>5,6</sup> In 1979 Bechgaard and Jérôme observed superconductivity in  $(\text{TMTSF})_2\text{PF}_6$  **3** under applied hydrostatic pressure.<sup>7</sup> In 1983 superconductivity was observed in  $(\text{BEDT-TTF})_2\text{ReO}_4$  **4**.<sup>8,9</sup> Since 1990,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl **5** remains the highest  $T_c$  superconducting material based on organic molecules  $\{T_c = 12.8 \text{ K}, P = 0.3 \text{ kbar}\}$ .<sup>10</sup>





## 2 Mechanism of conduction

A mechanism for the metallic delocalisation of electrons is provided if a supermolecular orbital extends throughout the crystal lattice.<sup>11</sup> The width of the conduction band is dependent on the interactions between the molecular orbitals of neighbouring molecules. A partially filled energy band is needed for high conductivity. Planarity is a prerequisite for high chemical stability of the radical ion and for the efficient intermolecular delocalisation of charge carriers. These planar ions form stacks with short interplanar distances which means that most organic conductors are highly anisotropic materials and are termed one-dimensional materials. More recently there has been a growing interest in increasing the dimensionality of these materials. Close interstack chalcogen-chalcogen interactions stabilise the metallic state by suppressing the Peierls distortion which results in a charge density wave (CDW) or a spin density wave (SDW), which causes a charge localisation and inhibits electrical transport in the one-dimensional conductor.

According to the BCS (Bardeen, Cooper and Schrieffer) mechanism for superconductivity, Cooper pairs of electrons interact with phonons (lattice vibrations) such that the electrons are not scattered but rather flow freely in a highly coordinated manner allowing superconductivity to occur.<sup>12</sup>

The organic conductors are usually quasi-one dimensional and are arranged in linear columns of flat, symmetrical molecules. Most of the important interactions take place parallel to the columnar axis. These compounds have very high conductivities unlike most organic solids. They also have metallic states and metal-insulator (M-I) phase transitions. These types of compounds may also have a superconducting phase transition.

Electrical charge transfer can only occur along one path between two specific points. If this path is broken then no electron transport will arise. This could happen as a result of a disorder which would result in electron localisation which would impede the conduction path. Thermally induced chain defects occur in paths in a quasi-one-dimensional system when the temperature is greater than absolute zero. In the absence of long-range interactions no phase transitions would be able to occur. A lattice distortion causes a change in the molecular distribution and in the phase transition which causes the 1-D organic molecules to become unstable.

In two or three dimensional systems there is always more than one path between two points which means that lattice defects cannot cause electron localisation and therefore phase transitions may occur at temperatures greater than absolute zero. By suppressing a phase transition via a CDW or SDW to an insulating state, the organic metal may become a superconductor. Increasing the system's dimensionality should result in a change in its physical properties. Because the one and two dimensional systems are different to each other they may be subject to slightly different rules.

In a one-dimensional system the distribution of charge is homogeneous. A change in the voltage will result in a periodic electrostatic field which will change the charge density function. Electrons will be concentrated in areas where the attractive forces prevail. These waves are called CDWs. The transition to the semiconducting state occurs with SDWs if the Coulombic interactions are greater than those between the electrons and the lattice. This state is characterised by the alternate arrangements of electron spins along the chain. The CDWs and SDWs do not couple because they are harmonic phenomena of a different nature. A solitary wave or soliton is produced, if a wave scattering backwards couples with a wave scattering forwards. Because classical solitons preserve their shape after diffusion they are a model of fundamental particles. The character of soliton excitations in one-dimensional

systems depends on the value of electron correlations. A soliton appears as a SDW excitation if the energy of interaction between the electrons on the same site is greater than zero. Soliton state excitations are either connected with specific spin-charge relationships or with incomplete charge transfer. Each disturbance in the sequence of molecular arrangements signifies the presence of two areas separated by a defect, with soliton properties. Charge localisation may occur due to electron-phonon couplings. This causes an energy level to be situated between the conduction and valence bands. If an additional electron is located on the domain wall then a Peierls distortion will occur.

### **3 Some important concepts**

A phase transition results in an abrupt change in the physical properties of a system during a continuous change of external factors. The metal-insulator phase transition can be caused by a Peierls transition (lattice reconstruction), a Mott transition (inter-electron correlation) or an Anderson transition (electron localisation in disordered systems). These types of transitions occur in quasi-one dimensional systems.

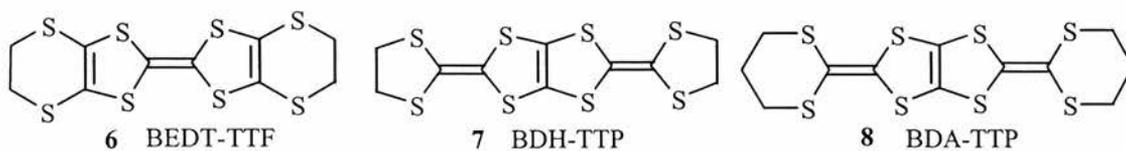
High temperature superconductivity was discovered in ceramics which represented a huge breakthrough in superconductivity.<sup>13</sup> It was assumed that the superconductivity was due to the participation of electron pairs in the electric transport. The mechanism responsible for the creation of these pairs is not fully understood.<sup>14</sup> A phonon is formed due to a lattice excitation quantum which is caused by an electron exciting the ionic lattice in the crystal. In a metal, electrons obey the Fermi-Dirac statistics and the Pauli Exclusion Principle. This implies that they cannot condense in an energy state with a momentum equal to zero. According to Cooper if there is a slight attraction between two electrons they can form a combined state whose total energy allows them to lie under the Fermi surface. This “Cooper pair” does not obey the Pauli Exclusion Principle. In 1957 Bardeen, Cooper and Schrieffer

formulated the microscopic theory of superconductivity, the BCS theory.<sup>15</sup> This theory explains that a ground state of the whole electronic system may be brought about due to attractive interactions between the electrons and would be separated from the excited state by an energy gap. The gap would be a direct consequence of the attractive electron-lattice-electron interactions which would overcome the Coulombic repulsion. The more polarizable the lattice is, the higher the superconducting transition temperature ( $T_c$ ) should be.<sup>12</sup>

#### 4 Superconductivity in partially saturated TTFs

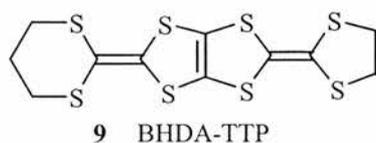
Having the six  $\pi$ -electrons on each ring is not critically important for electron donation as shown by the recent work of Yamada. The most important thing is having a carbon-carbon double bond surrounded by four sulfur atoms. The difference between saturated and fully unsaturated TTFs is shown by the difference in energy between the two oxidation potentials, the second of which is higher for the saturated TTFs.

Yamada and co-workers wanted to explore the possibility that tetrachalcogenafulvalene  $\pi$ -donors are not essential to the production of organic superconductors.<sup>16</sup> BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene] **6** has flexible six membered rings which allow it to have a variety of different conformations. This flexibility is believed to be responsible for the superconductivity found in its salts. BDH-TTF is composed of five-membered rings, which make it more rigid. The compound BDH-TTF [2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene] **7** is a structural isomer of BEDT-TTF but not a TTF containing donor. Its salts remain metallic down to very low temperatures but do not display superconductivity. The synthesis of BDA-TTF [2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene] **8**, the dithiane analogue of **7** was attempted because it had greater structural flexibility and therefore should be more likely to form superconducting salts.

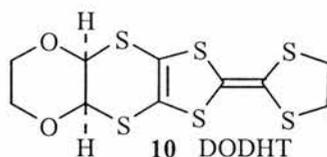


The group produced some superconducting salts  $\beta$ -(BDA-TTP)<sub>2</sub>X (X=SbF<sub>6</sub>, AsF<sub>6</sub>, PF<sub>6</sub>) which were the first superconductors which did not have a tetrachalcogenafulvalene molecule in the donor portion which was capable of taking part in the superconductivity. CV (cyclic voltammetry) data showed that the first oxidation potential of BDA-TTP **8** had shifted to a higher value than that of BDH-TTP **7** making it harder to oxidise. The difference between the first and second oxidation potentials ( $\Delta E$ ) is also smaller when compared with **7** suggesting that the electron donating ability is decreased but the dicationic state is easier to generate. This may be due to the fact that the dithiane ring is less planar than the dithiolane and does not go into a different conformation as easily to generate the cation radical species. However once the cation species is formed the trimethylene group in BDA-TTP acts as a stronger electron donor than the ethylene group in BDH-TTP **7** and forms the dication species more easily.

The group then chose to make the unsymmetrical donor DHDA-TTP [2-(1,3-dithiolan-2-ylidene)-5-(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene] **9** to see if it exhibited metallic or superconducting properties.<sup>17</sup> The CT salts  $(\beta$ -DHDA-TTP)<sub>2</sub>X (X=PF<sub>6</sub>, AsF<sub>6</sub>, SbF<sub>6</sub>) had a similar packing arrangement to the symmetrical analogue, but did not appear to have any short S...S contacts within the stack. However the metallic salts only displayed MI transitions instead of superconductivity.

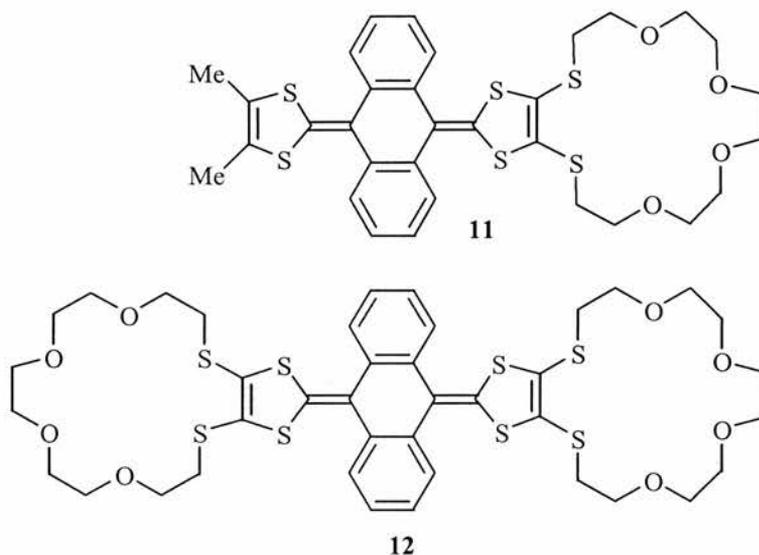


The group then asked the question whether or not it would be possible to synthesise donors with a less extended  $\pi$ -system which could produce superconductors.<sup>18</sup> The molecule DODHT [1,4-dioxane-2,3-diyl(dithio)dihydrotetrathiafulvalene] **10** was synthesised. Using electrocrystallisation they prepared two salts ( $\beta''$ -DODHT)<sub>2</sub>X (X= AsF<sub>6</sub> and PF<sub>6</sub>). Analysis of the crystal structure revealed the  $\beta''$ -phase in which the stacks had the same parallel inclination and showed that there were only intermolecular S $\cdots$ S contacts between the stacks and no contacts within the stacks. Under applied pressure the system showed a superconducting transition. This compound demonstrates that a superconductor can be obtained from a donor with a reduced  $\pi$ -system and bulky substituents.

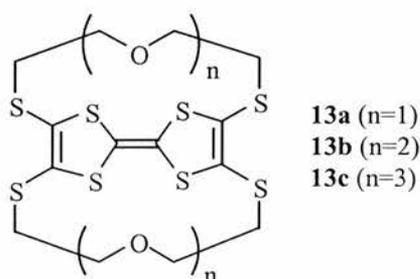


## 5 Recent developments in TTF chemistry

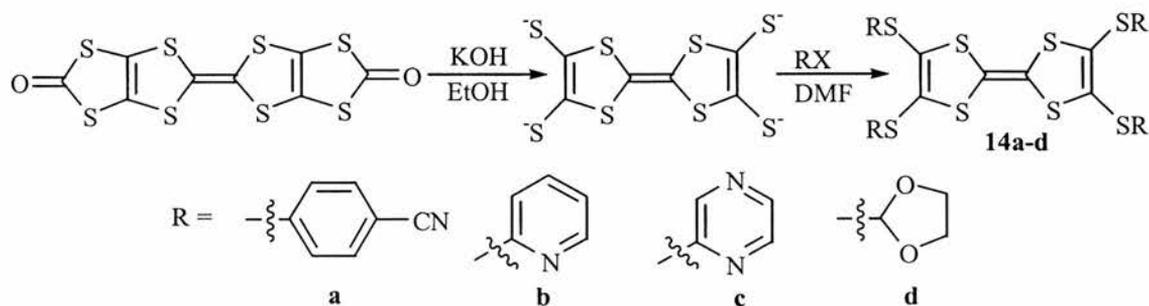
A series of crown annelated derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**11,12**) have been prepared for use as cation sensors.<sup>19</sup> When complexation occurs a change can be observed, both spectrophotometrically and voltammetrically. This has worked well for Na<sup>+</sup> and Ag<sup>+</sup>, but smaller oxidation potential shifts were observed when Li<sup>+</sup>, K<sup>+</sup> and Ba<sup>2+</sup> were complexed with **11** or **12**.



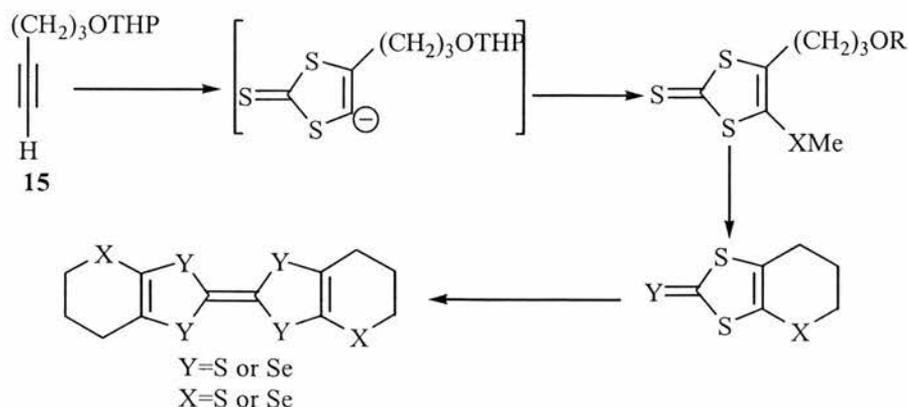
Some other TTF crown ethers **13a-c**, have been synthesised and have a high coordination ability to form complexes with metals such as Pb<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>.<sup>20</sup> This has been verified experimentally using UV/Vis spectroscopy and cyclic voltammetry.

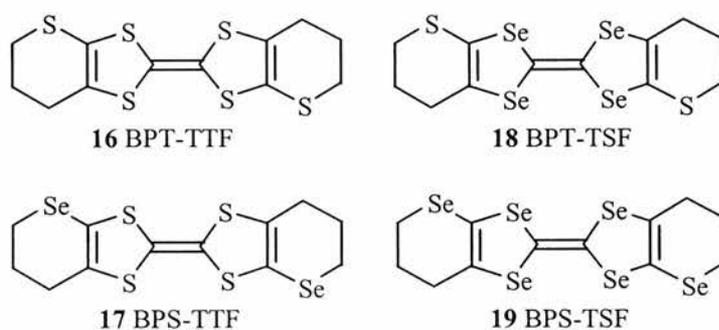


There is a lot of research currently focused on BEDT-TTF and its derivatives because it forms two dimensional salts which are believed to be more likely to form organic superconductors.<sup>21</sup> A new route for the synthesis of BEDT-TTF derivatives **14a-d** has been developed which is high yielding and allows the attachment of many functional groups to the core of the donor framework.

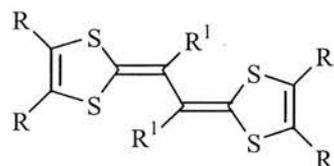


A series of novel heterocyclic-fused TTF-type electron donors **16-19** [16 bis(propylenethio)tetrathiafulvalene, **17** bis(propyleneseleno)tetrathiafulvalene, **18** bis(propylenethio)tetraselenafulvalene, **19** bis(propyleneseleno)tetraselenafulvalene] have been synthesised from readily available THP-protected pent-4-yn-1-ol **15**.<sup>22</sup> They all have good electron donating properties but only **18** and **19** give conductive radical cation salts {e.g. (**18**)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>, (**18**)<sub>2</sub>PF<sub>6</sub>, (**19**)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub> and (**19**)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>}.





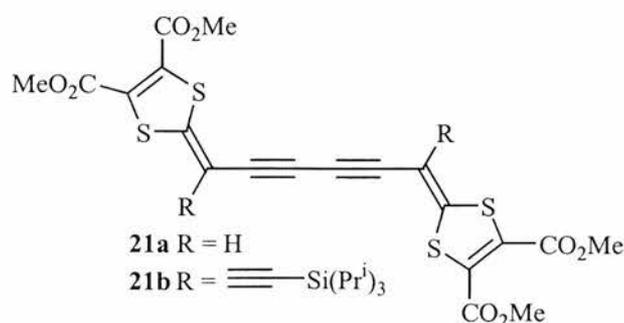
By extending the  $\pi$ -conjugation as shown in **20** the Coulombic repulsion between the two rings is reduced.<sup>23</sup> This is shown by the small  $\Delta E$  gap. The oxidation potentials are lower than BEDT-TTF indicating that they are stronger electron donors than BEDT-TTF. Having hydroxyphenyl groups attached to the donor helped the donors to form cation radical salts with unusual crystal structures where hydrogen bonding exists between the OH groups and their counter ions such as  $\text{PF}_6^-$  and  $\text{Au}(\text{CN})_2^-$ .

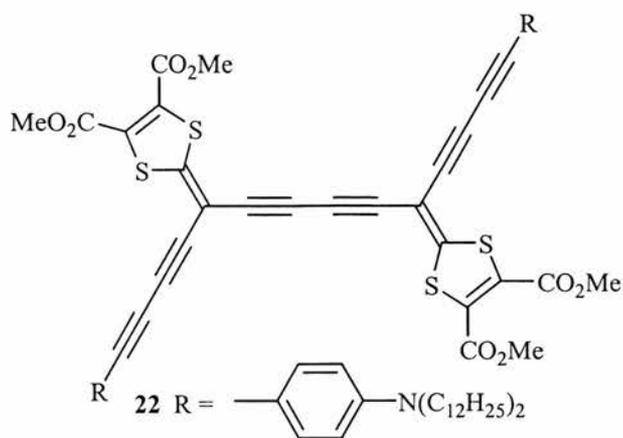


**20a**  $R, R = (\text{CH}=\text{CH})_2$ ,  $R^1 = \text{p-HOC}_6\text{H}_4$

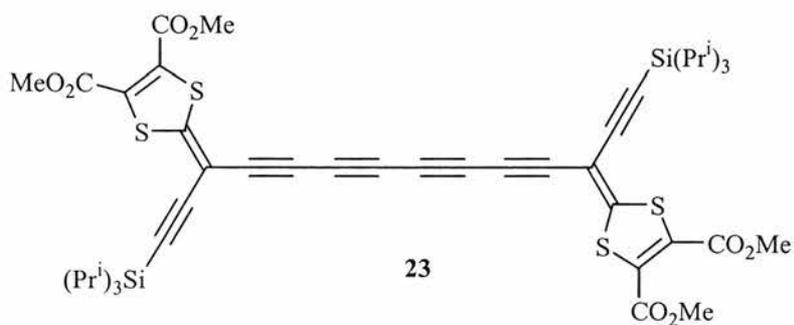
**20b**  $R, R = \text{SCH}_2\text{CH}_2\text{S}$ ,  $R^1 = \text{p-HOC}_6\text{H}_4$

Extended TTFs with hexa-2,4-diyne-1,6-diylidene spacers were synthesised to see if using acetylenic spacers for extended TTFs could enhance their properties.<sup>24</sup> Both **21a** and **22** experienced irreversible oxidation steps but **21b** was oxidised in two reversible 1 electron steps.

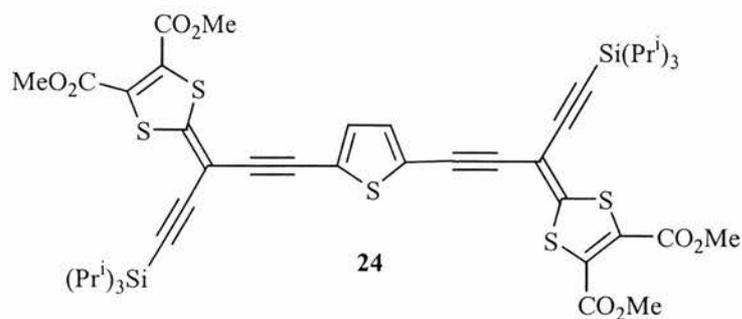




Further research on extended TTFs using acetylenic spacers has been carried out.<sup>25</sup> By increasing the length of conjugation in **21b** the coulombic interaction between the two oxidised dithioles is reduced and **23** is oxidised in one 2 electron step as compared to two 1 electron steps for **21b**.

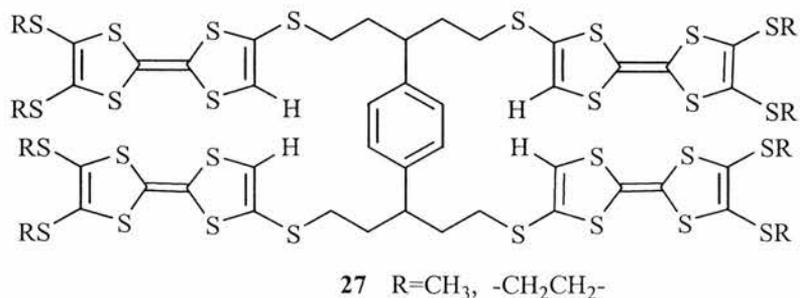
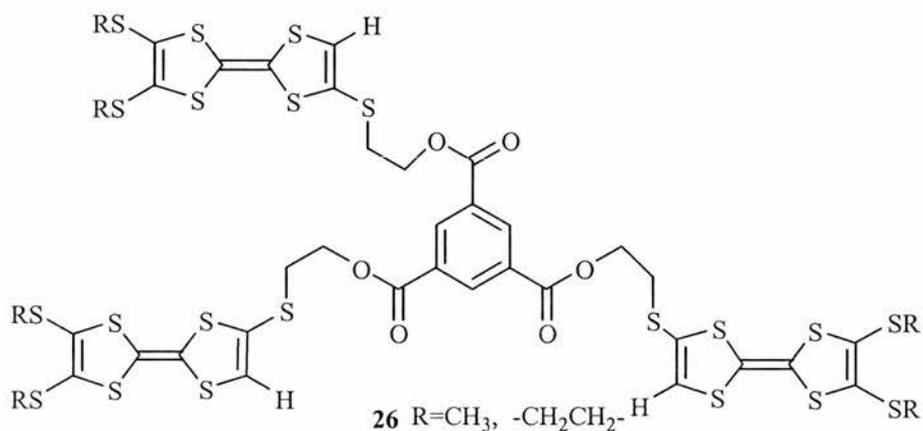
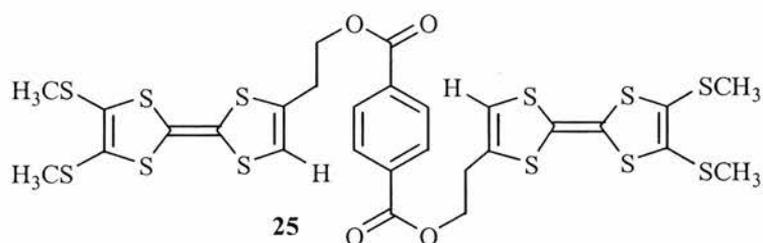


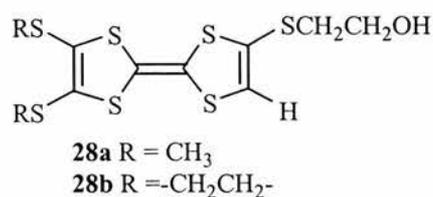
Inserting a thiophene ring in the acetylenic spacer caused a much greater decrease in the reduction potential than the oxidation potential in **24**.



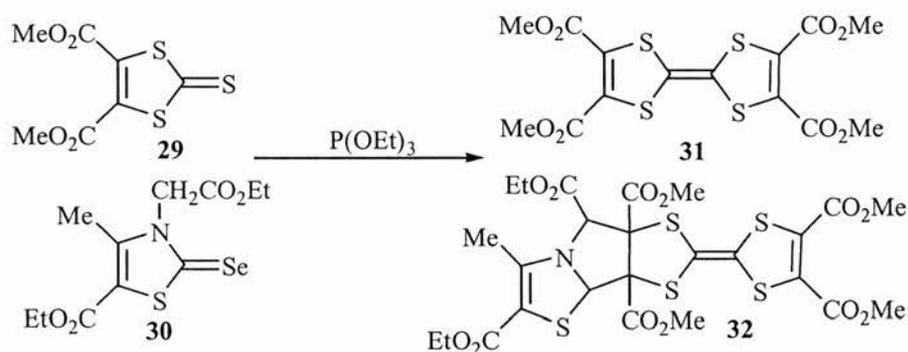
The acetylenic spacer units offer sites for the complexation of cobalt carbonyl clusters which would result in a change in the spectroscopic and electrochemical properties. Increasing the number of acetylenic units as in **23** results in a decrease in the HOMO-LUMO gap whereas increasing the linear conjugation has little effect. The compounds display good third order non-linear optical properties.

New multi-TTF electron donor derivatives **25-27** containing two to four TTF nuclei were synthesised.<sup>26</sup> The oxidation potentials are very similar for each of the donors and close to that of BEDT-TTF. The key intermediates **28a,b** possess a reactive alcohol function and are available in synthetically useful quantities and could be used for other synthetic transformations for the incorporation of TTF units into new compounds.

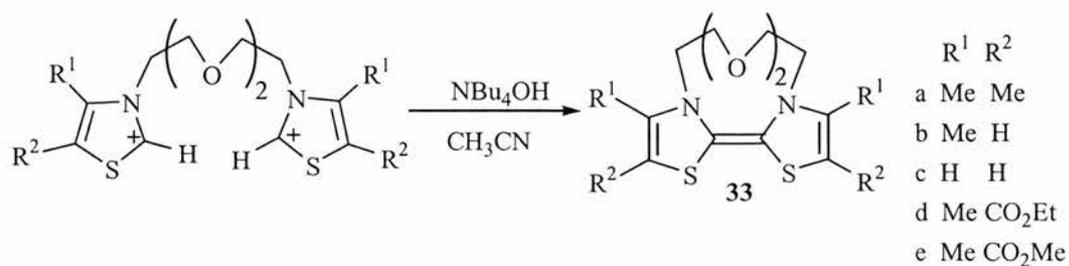




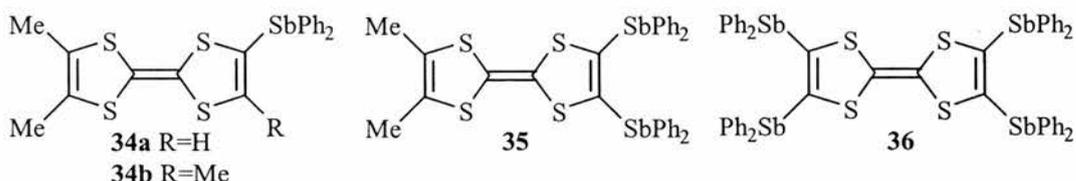
The synthesis of a trithiaazafulvalene (TTAF) was attempted but failed and instead resulted in the formation of TMTTF **31** and a novel product **32**.<sup>27</sup> This product is believed to have resulted from the unexpected 1,3-dipolar cycloaddition of an ylide generated from **30** and **31** which acts as the dipolarophile.



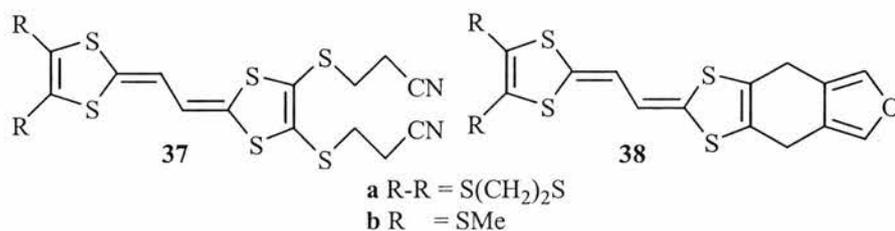
A series of crown-ether annelated dithiadiazafulvalenes **33** (DTDAF) were formed from an intermolecular coupling of the bisthiaazolium salt in basic media.<sup>28</sup> The compound series is unusual in that they are almost planar in the neutral state and adopt twisted conformations in the oxidised state. For **33e** the second electron is easier to remove due to the reduced Coulombic interactions.



A synthesis of TTFs which incorporate antimony onto the TTF core has been developed and has produced TTF stibines **34-36**.<sup>29</sup> Only the crystal structure of **34a** showed intermolecular Sb····S contacts and **34b** was able to form a CTC of formula  $(\mathbf{34b})_2[\text{Mo}_6\text{O}_{19}]$ .

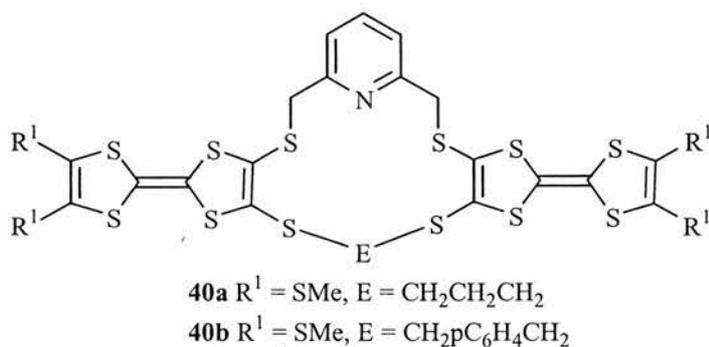
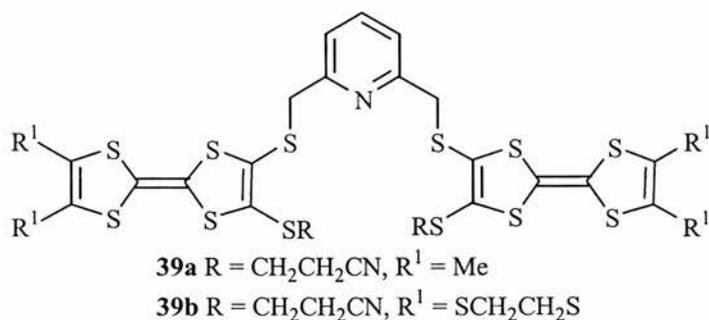


Some new extended TTFs such as **37a,b** and **38a,b** containing cyanoethylsulfanyl or furan groups were synthesised by reacting a 1,3-dithiole-2-thione and an aldehyde in  $\text{P}(\text{OEt})_3$ .<sup>30</sup> These TTFs cannot be obtained using a Wittig or a Wittig-Horner reaction. CV data for the compounds showed two reversible 1 electron oxidation waves. The  $\pi$ -electron donor ability is enhanced by delocalisation of the charge along the conjugated chain which stabilises the cation radical. The coulombic repulsion is reduced which causes a reduction in  $\Delta E$ .

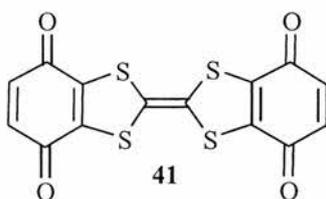


A synthesis for singly-bridged (**39a,b**) and doubly-bridged (**40a,b**) bis-TTFs containing 2,6-bis(thiomethyl)pyridine as a linker has been developed.<sup>31</sup> A two-step procedure was used for the synthesis of **40a,b** which avoided the awkward high dilution technique generally used to prevent polymerisation. CV data indicated two 1 electron

processes and one 2 electron process for **39**, but only two 2 electron processes for **40**.<sup>32</sup> This may be due to the partial rigidity of the doubly bonded bridged bis-TTF.



A new completely organic mixed valence compound **41** has been synthesised.<sup>33</sup> It was shown to have temperature-dependent intramolecular electron transfer (IET) and the rate constant for the thermally activated IET process was determined. This is also the first time a bridge exhibiting a strong electron-donating character, such as TTF has been used in a mixed valence system.

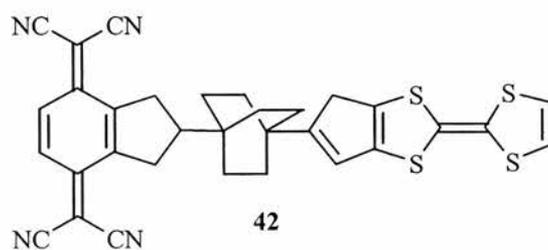


The theme of compounds containing both organic donor and acceptor functions is continued in the following section.

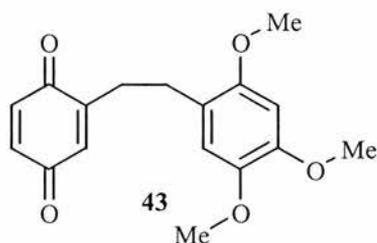
## B Donor-spacer-Acceptor Compounds

### 1 Background

A theoretical molecular rectifier **42** was proposed by Aviram and Ratner in 1974 based on using a single organic molecule.<sup>34</sup> It consisted of a donor  $\pi$ -system and an acceptor  $\pi$ -system separated by a sigma bonded tunnelling bridge.

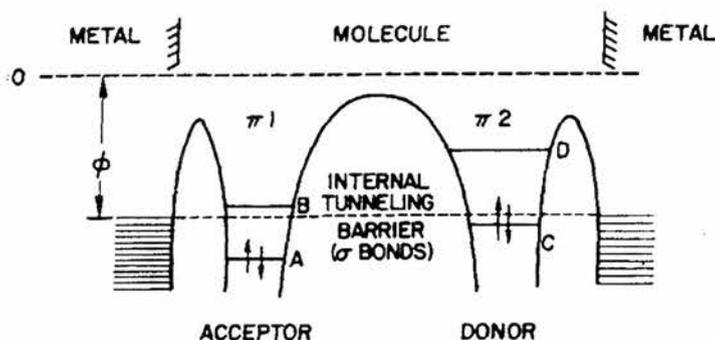


A conventional semiconductor rectifier consists of a p-n junction. This could be mimicked organically using substituent groups on aromatic systems as shown for example in **43**.<sup>35</sup> The quinone portion of the molecule **43** is in the oxidised form which means that the  $\pi$  electron density is reduced which increases the electron affinity. This portion of the molecule is classified as the acceptor or p-type because it can accept electrons. By using methoxy groups as the substituent groups on the benzene ring as in **43** the  $\pi$  electron density is increased because the methoxy groups are electron donating which lowers the ionisation potential thus making this portion of the molecule a donor or n-type.



It had previously been reported that charge transfer complexes have high electron conductivity and spin susceptibility due to the transfer of electrons to the acceptor from the donor.<sup>36</sup> This electron motion would in theory suggest that a rectifier could be built where electrons would pass only from a cathode to an acceptor or from a donor to an anode. The donor and acceptor  $\pi$  subunits could be insulated from each other using a sigma electron system. This type of molecule might then be expected to show rectifier properties in which current would pass from:

cathode  $\rightarrow$  acceptor  $\rightarrow$  donor  $\rightarrow$  anode

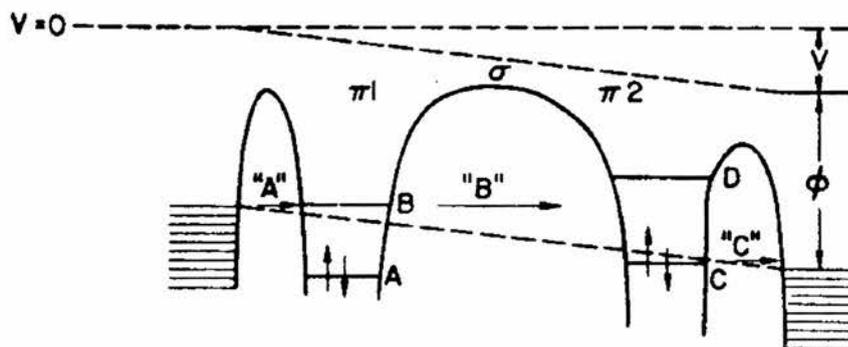


**Figure 1** schematic diagram of energy versus distance of the device. B and D are the affinity levels and A and C are the highest occupied levels of the acceptor and donor respectively.<sup>34</sup>

In Figure 1 the empty orbital which accepts electrons from the cathode is called the affinity state (B). In order to have proper rectification behaviour the affinity level of the acceptor must be totally or partially empty and lie at or above the Fermi level which is represented by the dotted line under B in the Figure 1.

When the applied field becomes large enough for the cathode levels to overlap with the acceptor levels then electron transfer onto the acceptor (B) becomes possible. This threshold depends primarily on the work function of the metal ( $\phi$ ) and the affinity perturbed level energy ( $E_B$ ).

When the applied voltage ( $V$ ) is greater than the difference between the donor ionisation potential (IP) and the work function of the metal ( $\phi$ ) then electron transfer from the donor orbital (C) to the anode becomes possible on the donor portion of the molecule as shown in Figure 2.

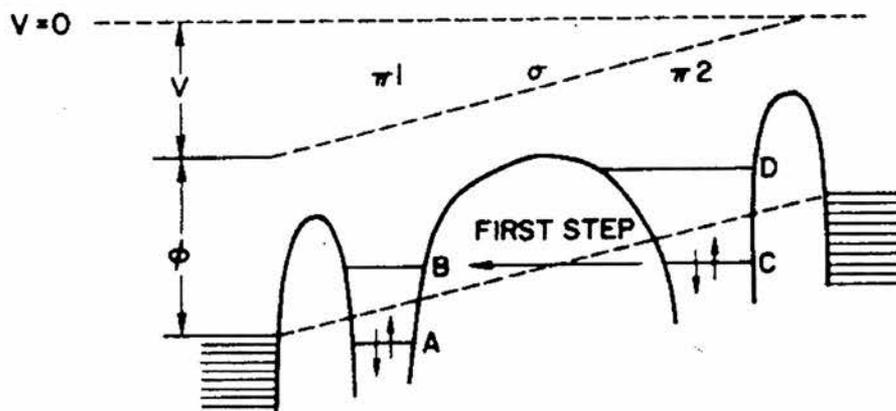


**Figure 2** Energy levels shift with applied voltage. “A”, “B” and “C” are three tunnelling processes.<sup>34</sup>

Motion of electrons from the acceptor to the donor will occur under the action of the field. The affinity level and hole left by the ionised donor are close enough in energy for an electron tunnelling process to occur. This process is generally inelastic. The passage of current through the rectifier molecule occurs as a three step process. Under forward bias as shown in Figure 2, the first step proceeds from the cathode to the acceptor, the second from the acceptor to the donor and the third from the donor to the anode.

If one considered the reverse applied voltage as shown in Figure 3, then the affinity level of the donor (D) would need to be reduced to the Fermi level of the anode on the right. The Fermi level of the cathode on the left would need to be reduced below the HOMO (highest occupied molecular orbital) of the acceptor (A) in order for tunnelling to occur. The

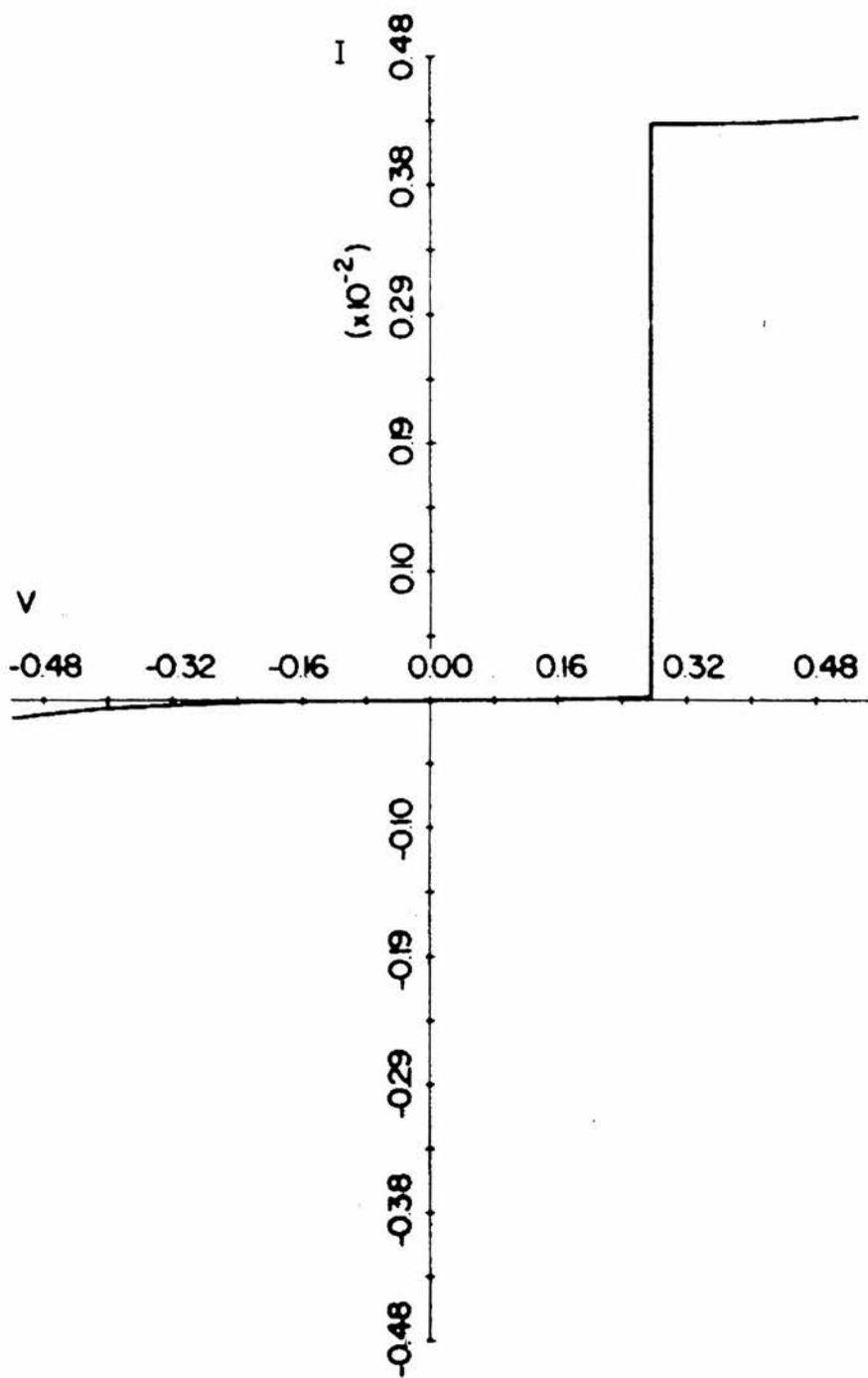
threshold voltage needed to allow this process to occur would be relatively high and therefore conduction is less favourable than with the forward bias voltage.



**Figure 3** Reverse applied voltage.<sup>34</sup>

An alternative mechanism for conduction would be internal tunnelling from level C of the donor to level B of the acceptor which would produce a hole on the right hand side and an electron on the left hand side as shown in Figure 3. After this initial step tunnelling from the charged  $\pi$  levels to and from the metals could occur. The donor HOMO of level C must be energetically greater than or equal to the acceptor  $\pi$  affinity orbital B in order for tunnelling to occur.

It is the non reversibility of internal tunnelling that yields the rectification properties of the molecules. Thus it should be possible to design materials that have a large threshold voltage for conduction in one direction over the other.



**Figure 4** Predicted I-V characteristics of a molecular rectifier including direct electrode to electrode tunnelling. I in A/cm<sup>2</sup>, V in volt, EA acceptor = 0.5 eV, IP donor = 5.3 eV,  $\phi = 5.1$  eV.<sup>34</sup>

Aviram and Ratner noticed that rectification was evident in which current passed to the right as shown in Figure 4.<sup>34</sup> The threshold potential for the passage of current was determined essentially by the voltage at which meaningful overlap of the broadened states (B & C) and respective metallic states occurred. The broadening was found to be negligible due to the large distance from the electrode so that the current potential curve is nearly discontinuous near the threshold.

## 2 Synthesis and properties of donor- $\sigma$ -acceptor compounds

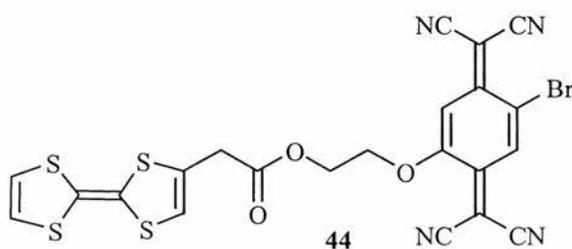
The prototype molecule suggested by Aviram and Ratner was chosen because of the excellent donor and acceptor properties of TTF and TCNQ, respectively.<sup>1</sup> The molecule should exhibit anisotropic electrical properties in order for rectification to occur. The materials must be aligned uniformly between two metal electrodes,  $M_1$  and  $M_2$ . The device will be asymmetric because the HOMO of the donor is relatively low and the LUMO of the acceptor is relatively high. The device will work if inelastic through bond tunnelling is more likely than elastic through space tunnelling, which is unaffected by molecular orbitals. Panetta and Metzger have put a lot of effort into making this theory a reality. Metzger has made the first confirmed unimolecular rectifier.<sup>37</sup>

The formation of stable and usually insoluble intermolecular charge transfer complexes prior to covalent coupling of TTF and the acceptor prevents the synthesis of many TTF-spacer-acceptor compounds.<sup>38</sup> A number of different routes have been employed to overcome this problem:

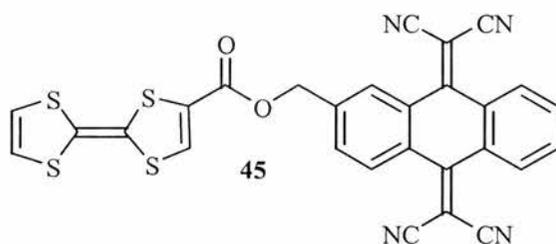
1. A TTF derivative can be linked to a weak acceptor which subsequently could then be converted to a stronger acceptor. The conversion of TTF-quinone into TTF-TCNQ would be an important step. Unfortunately this does not appear to have been reported in the literature.

2. A lithiated TTF could be substituted by an electrophilic reagent which after covalent bond formation would be transformed into an acceptor group.
3. Steric hindrance on the TTF or the acceptor unit could be exploited to prevent close  $\pi$ - $\pi$  associations.

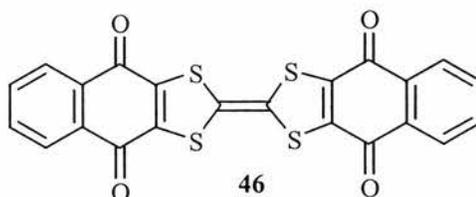
The first donor- $\sigma$ -acceptor compound prepared **44** was amorphous, difficult to purify and readily decomposed.<sup>39</sup> Proton NMR and ESR spectra contained broad signals which may indicate the presence of a charge transfer complex.



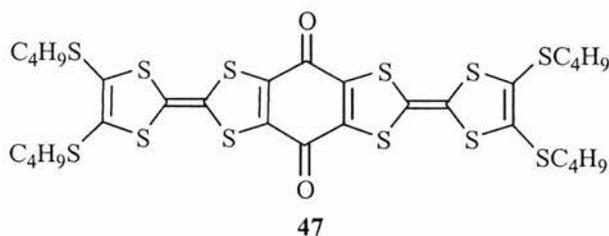
Due to the difficulty of synthesizing a TTF- $\sigma$ -TCNQ diad, Bryce and co-workers synthesised a TTF- $\sigma$ -TCAQ diad **45** instead.<sup>40</sup> They believed that the non-planarity of the TCAQ suppressed the intermolecular CT formation thereby allowing the covalent linkage of acceptor and TTF units. This was one of the first examples of a pure and stable TTF-spacer-TCNQ derivative.



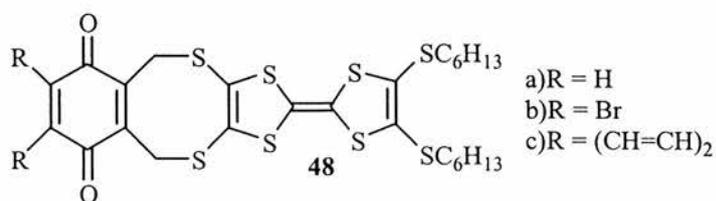
Using a quinone unit instead of a TCNQ unit should make donor-spacer-acceptor molecules easier to form because quinone is a weaker acceptor.<sup>41</sup> Watson and coworkers synthesised a triad **46** consisting of two naphthoquinone units separated by a TTF unit. Insolubility of the compound prevented full characterisation and cyclic voltammetry showed irreversible redox behaviour.



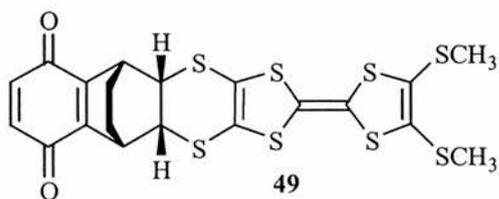
Frenzel and Müllen synthesised a triad **47** consisting of two TTF units separated by a quinone unit.<sup>42</sup> CV measurements showed that there was one reduction and two oxidation potentials. The two oxidation potentials were 2 electron suggesting that the two units functioned independently of each other. The UV-vis spectra showed a charge transfer band.



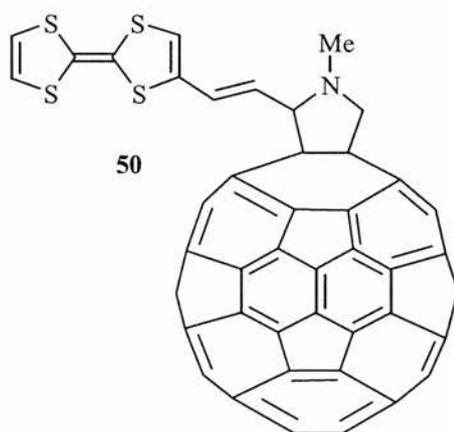
Martín and Segura reported the synthesis of three donor acceptor-compounds **48a-c** based on p-benzoquinone and TTF units.<sup>43,44</sup> The presence of long alkyl chains attached to the TTF moiety led to compounds that were highly soluble in common organic solvents. However cyclic voltammetry measurements showed that both parts behaved independently of each other and no ICT band was observed.



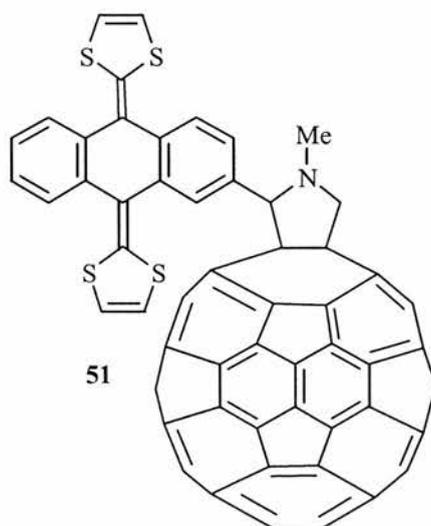
Khodorkovsky and co-workers synthesised a similar molecule **49** but this was found to have a bent conformation, which led unfortunately to inherent intramolecular through-space charge-transfer properties.<sup>45</sup>



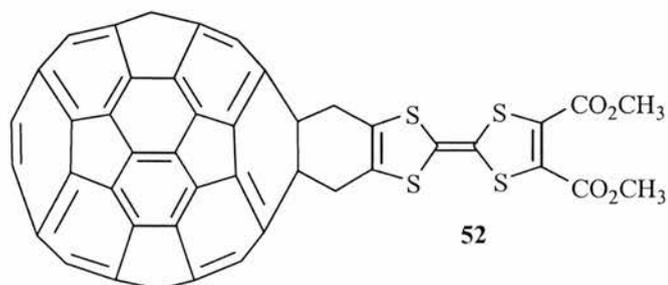
Linking TTF to C<sub>60</sub> covalently to form a diad has attracted much interest.<sup>46,47</sup> Two groups simultaneously synthesised **50** however no electron transfer process was observed from CV or UV-vis data although theoretical calculations had suggested that an intramolecular charge transfer (ICT) should have been possible.



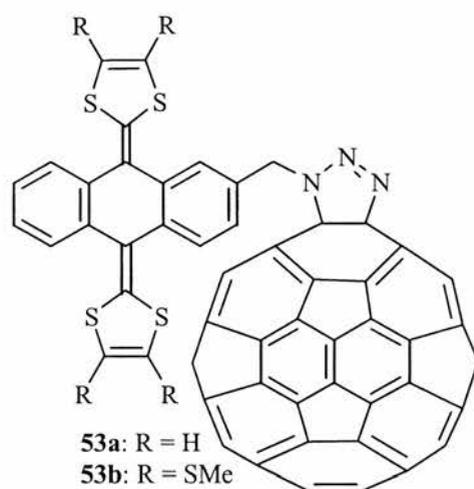
Martín and co-workers have carried out further work in this area and have prepared **51**.<sup>48</sup> CV data indicated that the two units functioned independently of each other. No charge transfer band was observed in the UV-vis spectra. However in the solid state the compound displayed paramagnetic behaviour.



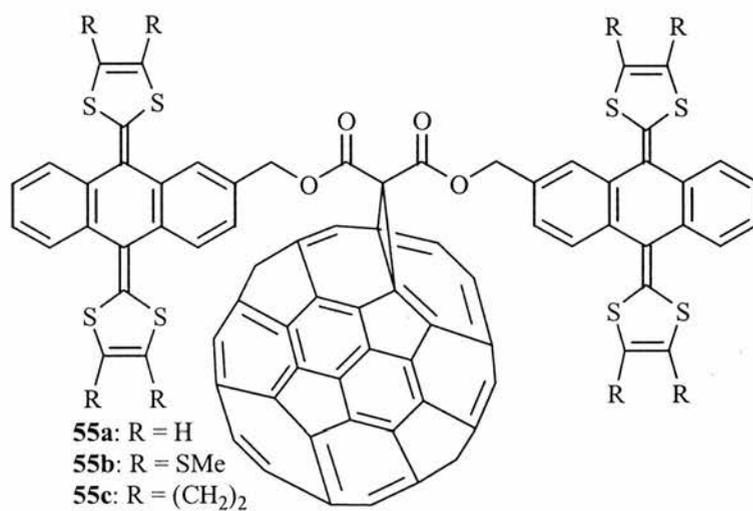
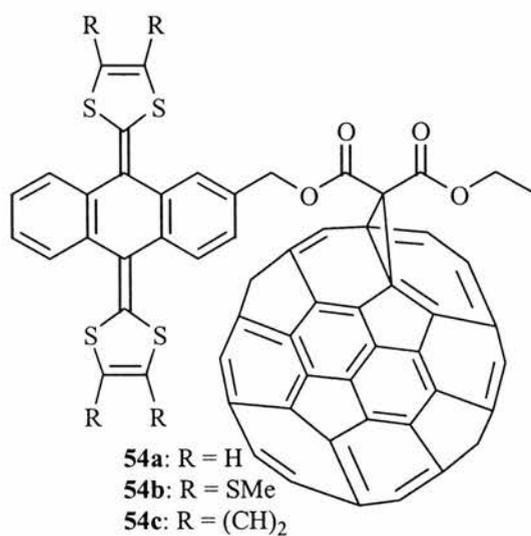
$C_{60}$  undergoes reactions with poorly conjugated electron deficient alkenes and a large number of products may arise due to the high number of reactive double bonds it has.<sup>49</sup> Rovira and co-workers synthesised a group of triads **52** consisting of TTF derivatives linked to a fullerene moiety which had a long life time. EPR studies were carried out on the radical ion systems obtained from the oxidation and reduction of the triads. No differences were observed for the derived radical cations from oxidation of the donor addends. However the hyperfine structure of the EPR shows notable differences for corresponding radical anions.



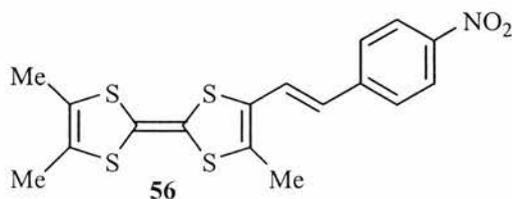
Martín and co-workers have synthesised azafulleroid dyads **53a,b** which behave as amphoteric redox systems.<sup>50</sup> CV (cyclic voltammetry) data shows two quasireversible 2 electron oxidation waves corresponding to the formation of the dication and three quasireversible 1 electron reduction waves corresponding to the first three reduction processes of C<sub>60</sub>. Experimental work showed that the radical pair had a longer lifetime than those previously reported.

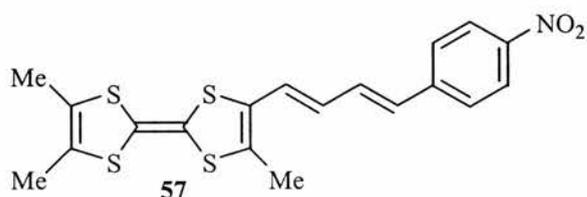


Diads **54a-c** and triads **55a-c** have also been synthesised.<sup>51</sup> CV data showed that the two donors in the triad functioned independently of each other. Both types of compounds have one 2 electron quasireversible oxidation wave and three 1 electron quasireversible reduction waves. Fluorescent spectra shows the formation of a meta-stable charge separated radical pair C<sub>60</sub><sup>-</sup>-(exTTF)<sup>+</sup>.

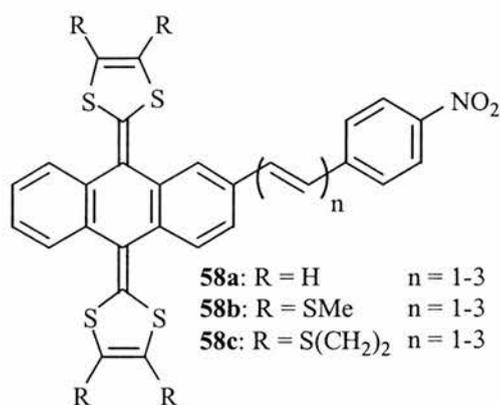


Bryce, Martín and co-workers have synthesised a range of donor- $\pi$ -acceptor compounds including **56** and **57** which display intramolecular charge transfer properties.<sup>52</sup> They also displayed second order NLO responses. They found that by introducing methyl substituents on the TTF core as in **56** resulted in an increase in the NLO response. Increasing the length of the conjugated spacer as shown in **57** does not result in a marked increase in the bathochromic shift.

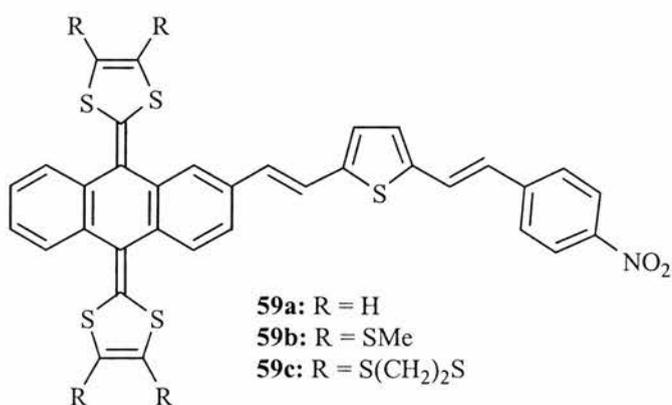




Martín and coworkers have synthesised a number of different families of compounds.<sup>53</sup> The first group, **58a-c**, **a** showed an ICT band which did not change with a corresponding change in the R group. The CV data shows that **a-c** have two 1 electron reduction waves and two 1 electron oxidation waves.



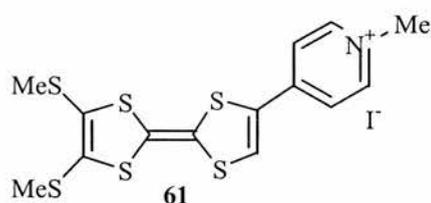
In the second group, **59a-c**, the length of the spacer was increased. All of the compounds showed ICT bands. CV data indicated that the dications were stable. By increasing the spacer length resulted in a corresponding increase in their second order NLO responses.



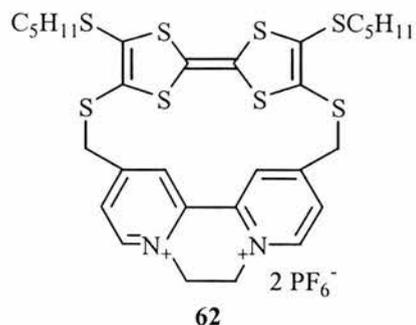
The last group compounds, **60a-c**, showed an ICT band occurring in their visible regions. The CV data indicates that they are poorer electron donors when compared with **58a-c** and **59a-c**.



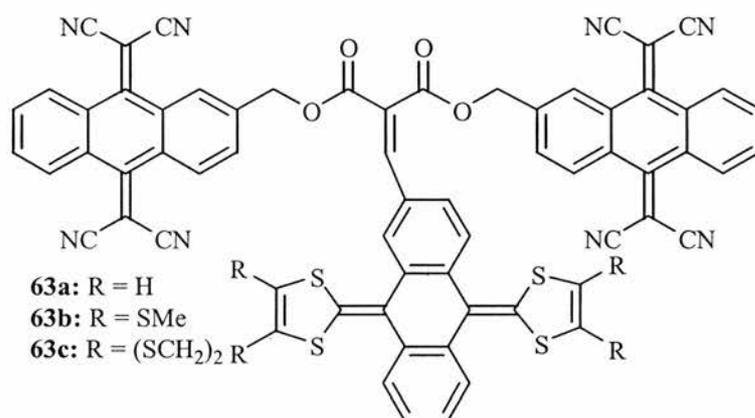
Becker and Khodorkovsky found a way of linking a strong donor and a strong acceptor together giving the TTF- $\sigma$ -Py<sup>+</sup> system **61**.<sup>54</sup> The molecule displays an ICT absorption band and has two reversible oxidation potentials.



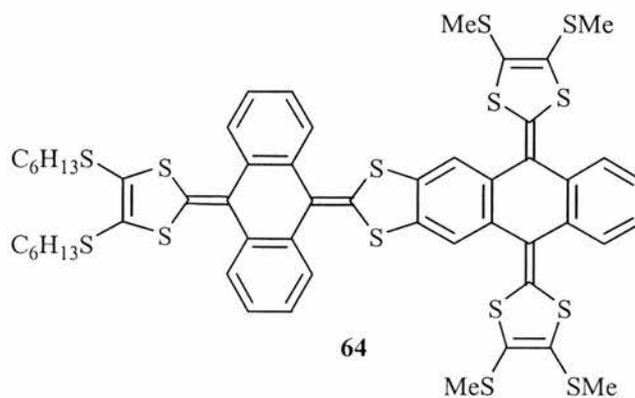
Becher and co-workers prepared a new donor-acceptor cyclophane, **62**, which showed strong electrostatic and CT interactions<sup>55</sup>.



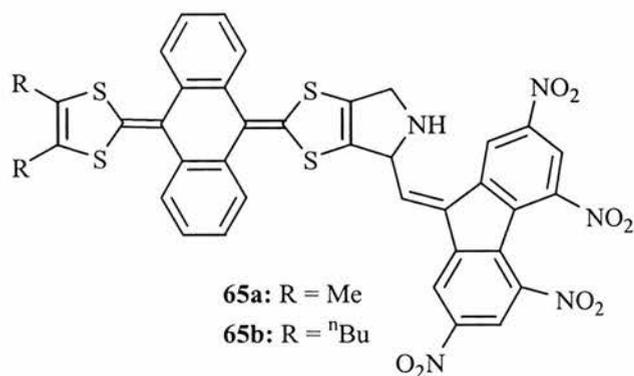
Martín and co-workers synthesised some electroactive triads **63a-c** using a Knoevenagel condensation.<sup>56</sup> These compounds displayed ICT bands which were believed to be due to a through space intramolecular interaction or through a  $\pi$ -bond charge transfer process. CV data shows two reduction potentials corresponding to two 2 electron processes and one reduction process corresponding to two 1 electron processes and also shows the stability of the dication and dianion species. These compounds could be used in the study of long lived charge separated states.



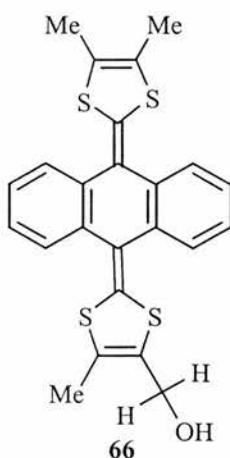
The first compound **64** has two 2 electron oxidation potentials corresponding to the dication and tetracation state which is probably due to an intramolecular interaction.<sup>57</sup> UV-vis spectral measurements supported this claim and were reversible indicating that the CT band was not due to decomposition products.



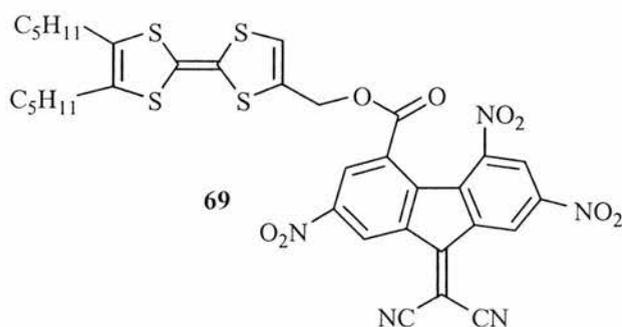
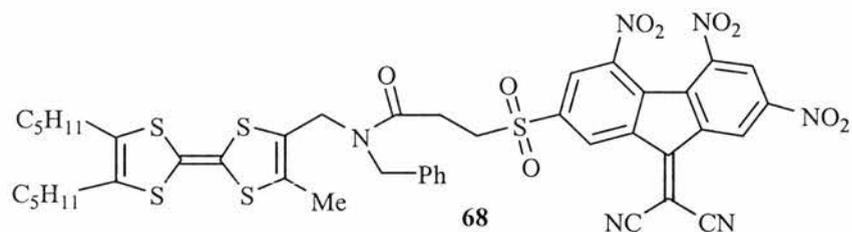
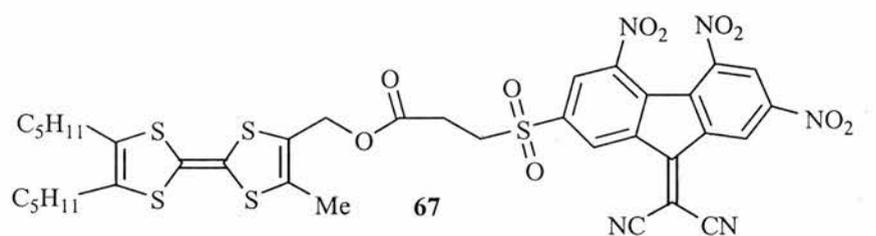
The two compounds, **65a,b**, had a low energy band present in the UV-vis spectrum which was independent of concentration indicating that the band was due to an intramolecular charge transfer.<sup>55</sup> The CV data showed that both compounds have two oxidation potentials and one reduction potential.



Bryce and co-workers have extended the chemistry of dihydroanthracene derivatives making a new compound **66** which can be easily esterfied, dimerised and trimerised.<sup>58</sup> The ease of esterification means that this  $\pi$ -system could be incorporated into organic dendrimer systems which possess well defined redox behaviour. The anthracenediylidene rings in the donor portion of the molecule have been shown to become planar and aromatic and the 1,3-dithiolium cations become orthogonal to the plane upon oxidation to the dication.



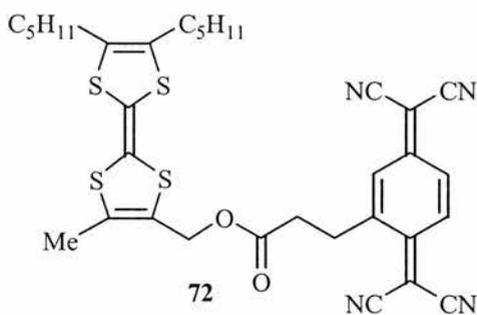
Bryce and co-workers have devised a route to link strong acceptors to give three novel  $R_3$ TTF- $\sigma$ -A compounds.<sup>59</sup> The major difficulty in converting TTF-benzoquinone diad to the TTF-TCNQ diad is due to the adverse effects of using acidic conditions. Condensation of polynitrofluoren-9-ones with malononitrile takes place under mild conditions and the dicyanomethylene derivatives, **67-69**, have a similar electron affinity to TCNQ. Using IR data on the CN groups they were able to show that charge transfer had occurred in the solid state. EPR indicated that a radical cation had been formed. CV data shows two reversible 1 electron oxidation waves due to the TTF unit and three reversible 1 electron reduction waves due to the fluorine fragment. These compounds had the smallest solution HOMO-LUMO gap ever recorded for closed shell organic compounds.



A new type of spacer was used in a D-A compound to give the following molecules **70** and **71**.<sup>60</sup> It was found that the  $\pi$ -chromophores of the donor and acceptor were aligned in different orientations.



A new TTF-TCNQ diad **72** has very recently been synthesised by Bryce and co-workers.<sup>61</sup> The molecule had two reversible 1 electron oxidation waves and two reversible 1 electron reduction waves. The EPR spectrum showed two signals suggesting a low concentration of the TTF radical cation and TCNQ radical anion being generated by thermally induced intramolecular charge-transfer at RT.

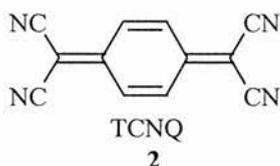


## C Charge Transfer Complexes

### 1 Background

Strong  $\pi$ -molecular donor and acceptor molecules often react together to form radical ion salts (RISs,  $X^+A^-$  and  $D^+X^-$ ) and charge transfer complexes (CTCs, DA and  $D^+A^-$ ) which have high conductivities. These are called organic conductors.<sup>62</sup>

TCNQ (tetracyano-p-quinodimethane) is a strong  $\pi$ -molecular acceptor.<sup>2</sup> The high conductivity of TCNQ was associated with crystal structures in which planar molecules were packed face to face like a deck of playing cards into segregated stacks of cations and TCNQs. The  $\pi$ -overlap and CT interaction between adjacent molecules in the stacking direction was strong, causing unpaired electrons to be partially delocalised along the one-dimensional molecular stacks and allowed conduction to occur in that direction. As explained previously in section A it was found that the 1:1 TTF:TCNQ CTC had a conductivity which increased dramatically below room temperature.<sup>5,6</sup> This was high enough to be considered an organic metal. Below this temperature a phase transition from a metal to a superconductor state occurs.



Charge Transfer Complexes are stable complex associations which are obtained as a result of an electron transfer between an electron donor and an acceptor. Mulliken proposed the intermolecular charge transfer resonance theory to show that the colour change was the first experimental sign that a CT salt had been formed.<sup>63</sup> The charge transfer (CT)

interactions in compounds arise from  $\pi$ -type orbitals and involve the formation of homomolecular stacks. These systems are divided into two series: charge transfer complexes (CTCs) and radical ion salts (RISs).

- CTCs: Neutral molecules undergo partial charge transfer from the donor to the acceptor to give stable complexes. The amount of charge transfer ( $\rho$ ) depends on the electron affinity of the acceptor and the ionisation potential of the donor.
- RISs: The donors and acceptors are transformed chemically into ions by an oxidation or a reduction process, which are then spatially organised and a molecular association can occur between the radical ion and counter ion and may form a closed shell system. Mixed valence systems arise from reactions of donors and acceptors with moderate redox potentials or with a weak/strong acceptor and a strong/weak donor. The reaction of a strong donor and acceptor gives an ionic (single valence) complex. Alternatively the neutral complex arises from the reaction of a weak donor and acceptor in which no charge transfer occurs.

Tetrachalcogenafulvalenes such as tetrathiafulvalene give radical cation salts (RCSs) with diamagnetic anions such as  $\text{Cl}^-$ ,  $\text{PF}_6^-$  and  $\text{AuBr}_2^-$  and CTCs with  $\pi$ -systems such as TCNQ.<sup>10</sup>

Theoretically it was hoped that the complexes would form heteromolecular (AD) blocks. However experimentally it was shown that the donors and acceptors form homomolecular blocks as dimers, trimers and tetramers.<sup>64</sup> The degree of charge transfer in the CTC or of ionicity of the radical ion in the RIS is a crucial parameter and is controlled by the redox potentials in solution or through the compound stoichiometry respectively. If  $\pi$ -molecular orbitals are occupied by radical electrons then these can overlap to form a continuous path in one direction giving stacked or planar sheets, or in two-dimensional sheets.<sup>65</sup> The inert counterion plays a crucial role in the properties of RCSs.

The presence of a supermolecular orbital provides a mechanism for metallic delocalization of electrons in which the width of the conduction band depends on interactions between molecular orbitals on neighbouring atoms. The size of the energy gap between the valence and conduction bands determines whether the compound is an insulator or not. As the gap gets smaller the thermal excitation of electrons from the valence to the conduction band becomes more likely and the compound becomes a semiconductor. In order for metallic behaviour to occur large numbers of electrons need to be able to move easily from partially filled bands to higher energy states. In CTCs these states are represented by the HOMOs (highest occupied molecular orbitals) of the donor species and the LUMOs (lowest unoccupied molecular orbitals) of the acceptor species. The HOMO of the donor corresponds to the Fermi level and it is the electrons in energy states very near to this level that influence the physical properties. The conductivity in organic metals is temperature dependent and dominated by the scattering of electrons with the atomic lattice vibrations. A decrease in temperature has a corresponding decrease in the lattice vibrations which allows greater intermolecular overlap which increases conductivity. Conversely a semiconductor's conductivity decreases with decreasing temperature.

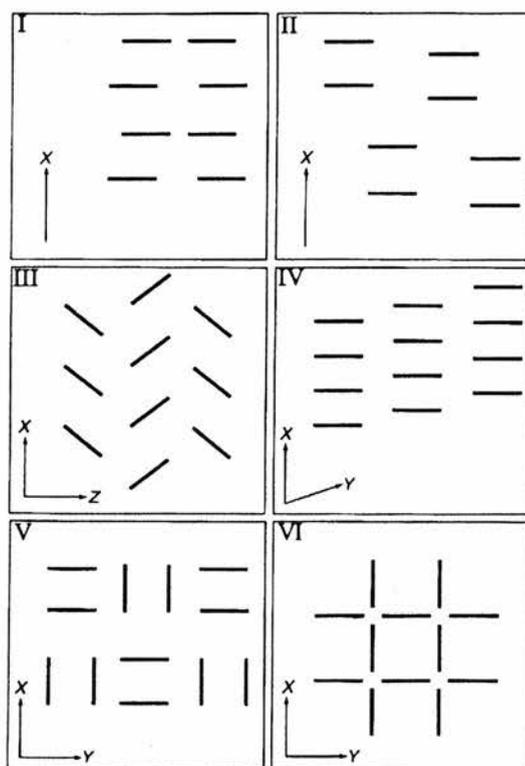
In metallic conduction individual electrons act as the charge carriers. However superconductivity is caused by the highly coordinated motion of electron pairs according to the BCS (Bardeen, Cooper, and Schrieffer) theory.<sup>66</sup> Electron pairing can be driven by phonons below a critical temperature ( $T_c$ ). Above  $T_c$  superconductivity is lost. A half filled band has no neutral molecules in the stack. Each molecule has an unpaired spin so there is a driving force for spin pairing. A Peierls distortion occurs when molecules dimerize and form an energy gap between the bonding and anti-bonding energy levels with a resulting loss in metallic conduction.



Organoselenium donors provided the first generation of organic superconductors [(TMTSF)<sub>2</sub>X] which were reported by Bechgaard.<sup>7</sup> This increase in dimensionality spurred interest in organotellurium systems but tetratellurafulvalene (TTeF) was much harder to access synthetically.<sup>74</sup> It was found that within the series TXF-TCNQ (X=S, Se, and Te) that the electrical conductivity increases as X varies from S to Te which is mainly due to conductivity enhancement within the donor stacks.<sup>75,76</sup>

Experimental data has shown that there are a number of different molecular arrangements rather than just a regular stack as shown in Figure 5.<sup>77</sup>

Bechgaard salts form (I) zig-zag stacking of centrosymmetric dimers or (II) strongly dimerized chains with deformed stacking axis or BEDT-TTF forms sheets of stacks in the  $\alpha$ -phases (III) and  $\beta$ -phases(IV) while sheets of interacting orthogonal dimers are called  $\kappa$ -phases (V) and polymeric like sheets are called  $\tau$ -phases (VI)



**Figure 5** Illustration of molecular arrangements in some tetrachalcogenofulvalene salts<sup>10</sup>

## 2 Crystal structures

For CTCs and RISs the structural properties depend on the nature of the donor, the acceptor and the counterion. Different phases can be obtained for the same compound. The shape of the crystal may indicate the internal structure of the complex or salt. Needle-like crystals usually have a columnar structure and plate-like crystals have a lamellar structure.

- Columnar structures usually occur in Bechgaard salts and other quasi-1-dimensional conductors. These consist of zig-zag columnar stacking which dimerises along the stacking axis and has intercolumn interactions of varying strength.
- Quasi-2-dimensional conductors usually have a lamellar structure. The crystal shape depends on the crystal phase. The crystals pack into layers of alternating sheets of donor molecules and anions with S-S interactions within the donor sheets. According to how the donor molecules pack gives rise to the different phases. The donors pack face to face (intrastacking) to form stacks and these stacks then pack side by side (interstacking) to form layers. Differences in the intrastack and interstack packing give rise to different packing patterns such as herringbone pattern ( $\alpha$ -phase), honeycomb pattern ( $\beta$ -phase) and orthogonal dimers- $\kappa$ -phase.<sup>76</sup>

The large difference in conductivity in insulators and conductors is due to:

- A difference between the complete and partial reduction of TCNQ molecules in the solid which is due to a complete or partial transfer of charge from the donor to the TCNQ molecules.
- The degree of charge transfer ( $\rho$ ) is determined mainly by the ionisation potential of the donor and then by the electrostatic Coulomb interactions which bind these ionic solids.

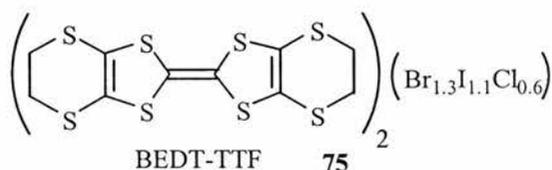
- For new donors those having a combination of intermediate size and ionisation potential are likely to occur in between fully ionic and neutral donors and therefore should have mixed-valence, highly conducting stacks

The salts are separated into classes based on the magnitude of conductivity which is caused by a difference in the amount of charge transfer. Class 1 salts are insulating due to their low conductivity and high activation energy for electrical conduction which makes them difficult to reduce. Class 2 salts are metallic due to their high conductivity making them easier to reduce, which makes partial transfer favourable and gives mixed valence stacks which are highly conducting. These two classes may also be distinguished using optical absorbance spectroscopy. The class 1 salts are insulating even if they have uniform stacks. This implies that stack distortions do not account for large differences in their conductivity. These salts may be insulating because of strong Coulomb interactions and spin-Peierls transitions. If the magnitude of the Coulomb interactions is not reduced then it will be larger than the bandwidth of the delocalising electrons. The unpaired electrons will then be localised on each TCNQ anion. This means the compound will then act as an insulator. Organic metals lie in a narrow range between neutral and fully ionic insulators.

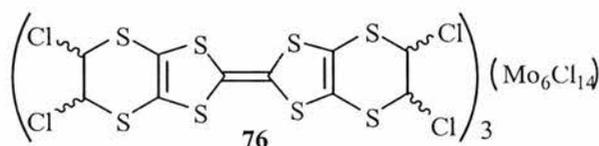
In conclusion there is a relationship between ionic binding and conductivity.<sup>62</sup> Donors of small size and low oxidation potential form strong ionic salts with TCNQ resulting in complete charge transfer. These salts are insulators. Very large donors with high ionisation potentials form neutral molecular solids. Donors that are intermediate in between these two ranges form weakly ionic salts with TCNQ with incomplete charge transfer. These salts are potentially highly conducting.

### 3 Recent Developments

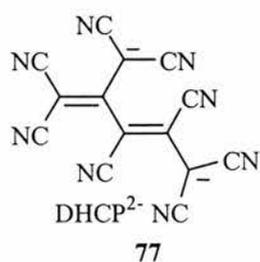
The organic conductor **75** (BEDT-TTF)<sub>2</sub>Br<sub>1.3</sub>I<sub>1.1</sub>Cl<sub>0.6</sub> was shown to exist in three crystalline polymorphic forms ( $\alpha'$ ,  $\alpha''$ ,  $\beta''$ ) which possess different transport properties such as superconductor and metal phase transitions.<sup>78</sup> This complex was able to adopt the same metal-like  $\beta''$ -phase at low and high temperatures. ESR spectroscopy and X-ray diffraction analysis have shown the existence of the reversible semiconductor to metal ( $\alpha'' \leftrightarrow \beta''$ ) phase transition. This had not been seen previously in molecular organic conductors.



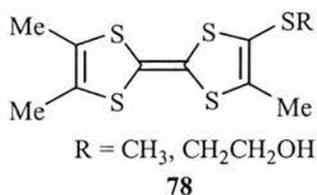
Incorporating halide atoms on the TTF donor as shown in complex **76** can be used to control the solid state organisation of molecular conductors.<sup>79</sup> Using electrocrystallisation of the halogenated TTF gave (tetrachloro-BEDT-TTF)<sub>3</sub>[Mo<sub>6</sub>Cl<sub>14</sub>] **76**.



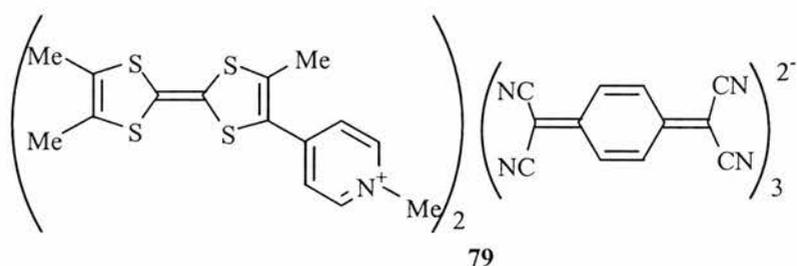
The dianion, DHCP (2-dicyanomethylene-1,1,3,4,5,5-hexacyanopentene) **77** was reacted with BEDT-TTF to give two CTCs.<sup>80</sup> One of the complexes showed a metal-insulator transition at 180 K and the other showed metallic behaviour down to 1.3 K. Both complexes have the same stoichiometry and the BEDT-TTF molecules have the same  $\beta''$ -type packing mode, but the conformation of DHCP<sup>2-</sup> was (Z) in the first complex and (E) in the second.



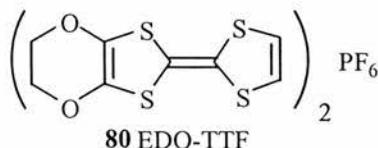
CTCs and RCSs have been prepared by reacting TCNQ or Br<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> with TTF derivatives **78** containing hydroxyl groups giving a 1:1 stoichiometry suggesting that the donor has been oxidised to the D<sup>+</sup> state.<sup>81</sup> The flexibility of the side chains containing the hydroxyl chains facilitates H bond formation but the steric effects may hinder the formation of molecular stacking regular enough to allow electronic delocalisation which would explain the compounds' low conductivity.



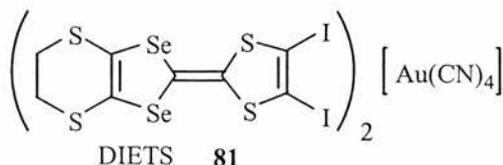
An iodine salt has been reacted with TCNQ to give a charge transfer salt **79** which acts as a semiconductor.<sup>82</sup> The iodide is responsible for reducing the TCNQ and not the TTF moiety. The TTF system displays both inter and intra-molecular charge transfer properties.



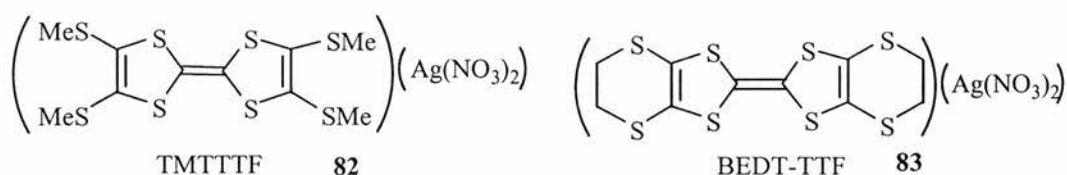
A novel metal-insulator phase transition was discovered in (EDO-TTF)<sub>2</sub>PF<sub>6</sub> **80** which is caused by a combination of the Peierls, charge ordering and anion ordering transitions.<sup>83</sup>



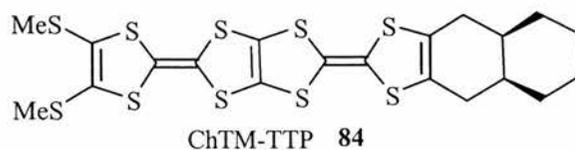
By placing the organic conductor  $\theta$ -(DIETS)<sub>2</sub>(Au(CN)<sub>4</sub>) **81** under uniaxial strain superconductivity was discovered which was due to the characteristic iodine bonds.<sup>84</sup> Superconductivity occurs as the temperature increases above 8 K under a uniaxial strain of 10 kbar which is the highest recorded temperature among known organic superconductors based on unsymmetrical TTF derivatives. Uniaxial stress was applied instead of hydrostatic pressure to improve the anisotropic character of the complex. The selectivity of the intermolecular interaction is enhanced and the conducting behaviour changes. Halogen bonds are used for any halogen based intermolecular interaction. The electronegativity of iodine is smaller than that of carbon. According to MO calculations the  $\sigma$ -type LUMO should be highly localized on the carbon of the carbon-halogen bond. This is therefore called an iodine bond. The crystal structure shows that the donor molecules pack in a herring bone type fashion with each iodine atom bonded to one CN atom on the Au(CN)<sub>4</sub>. The supramolecular network is constructed through these unique iodine bonds.



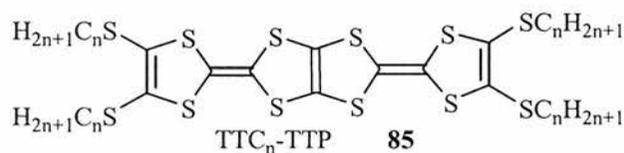
Two CT silver complexes were prepared, (TMTTTF)(Ag(NO<sub>3</sub>)<sub>2</sub>) **82** and (BEDT-TTF)(Ag(NO<sub>3</sub>)<sub>2</sub>) **83**.<sup>85</sup> It was found for the first compound that the central C=C bond lengths in the donor and the complex were similar. The IR data for the C=C stretching frequency was also similar suggesting that the complex is an insulator. This donor has higher oxidation potentials than BEDT-TTF and would therefore be harder to oxidise. In the second complex the central C=C bond length and stretching frequency had changed. The colour of the compound had changed to black in the complex. The conductivity was shown to increase as the temperature was reduced below 150 K indicating that the complex is a semiconductor.



Bis-fused TTF donors or TTPs (tetrathiapentalene) have produced a large number of radical cation salts which show metallic behaviour down to liquid He temperatures.<sup>86</sup> The series has a strong tendency to construct uniform stacks and quasi-two-dimensional electronic structures. This uniform stacking pattern is unfavourable to the appearance of magnetic or superconducting phase transitions. A cyclohexane ring was attached to the TTP molecule in an attempt to introduce dimerization. The newly synthesised ChTM-TTP molecule **84** becomes a quasi-one dimensional conductor which shows metallic behaviour until 120 K and undergoes a magnetic phase transition at 40 K. Using electrocrystallisation the following conductors were prepared: (ChTM-TTP)<sub>2</sub>AuBr<sub>2</sub>, (ChTM-TTP)<sub>2</sub>GaCl<sub>4</sub>, (ChTM-TTP)ReO<sub>4</sub>. The first two salts are antiferromagnetic insulators. These are the first salts to show an antiferromagnetic state among the TTP series. The third salt has a 1:1 Donor:Acceptor ratio which would suggest that it is a semiconductor.

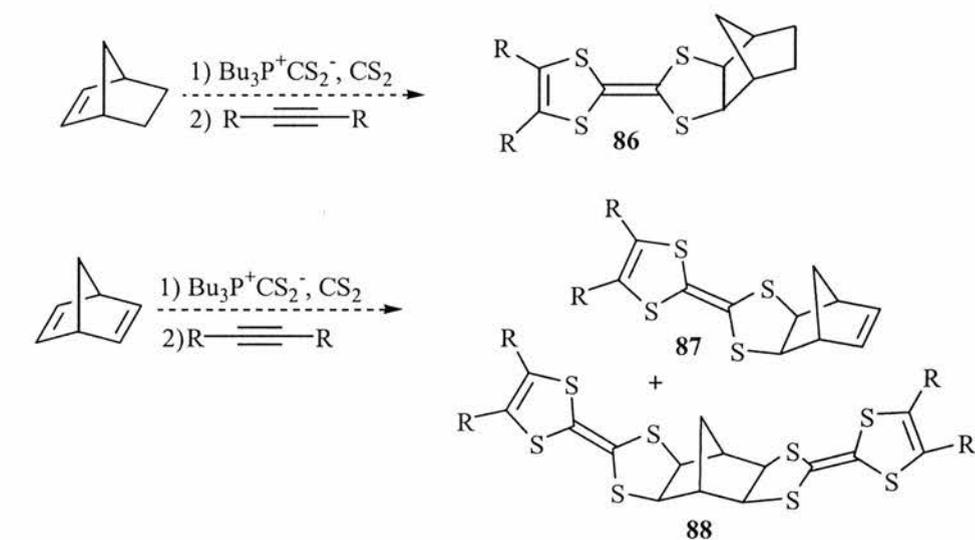


TTC<sub>n</sub>-TTP **85** consists of TTF with long alkylthio chains attached to the peripheral parts of the TTF molecule.<sup>87</sup> X-ray analysis showed that the molecules stack dimerically due to aggregation of the alkylthio chains which is known as the fastner effect. The neutral donors have been found to act as single component conductors and have low resistivities. CTCs were formed using electrochemical oxidation using BF<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> as counter ions. Only the (TTC<sub>n</sub>-TTP)<sub>2</sub>ClO<sub>4</sub> complex could be analysed fully and its β"-structure is very rare in CTCs of TTP. It had low resistivity and the conductivity showed flat temperature dependence until 250 K which then gradually decreased below this temperature.

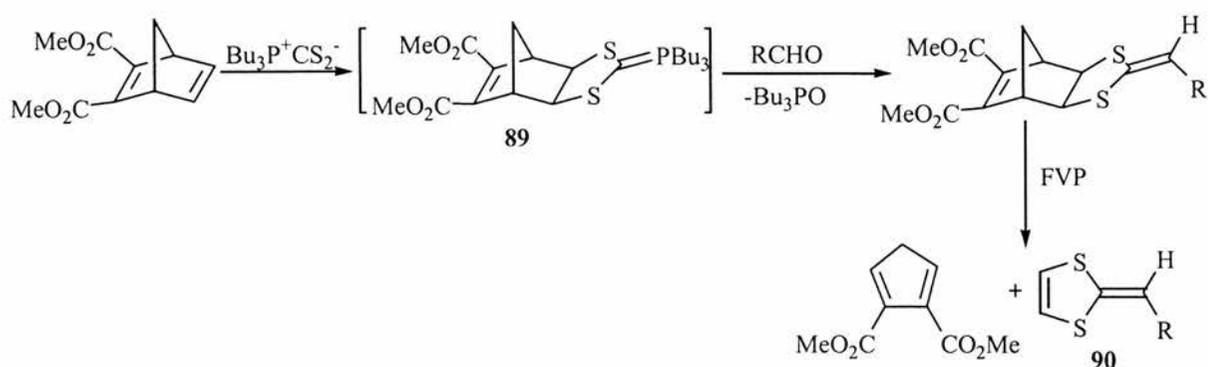


#### D. Programme of Research

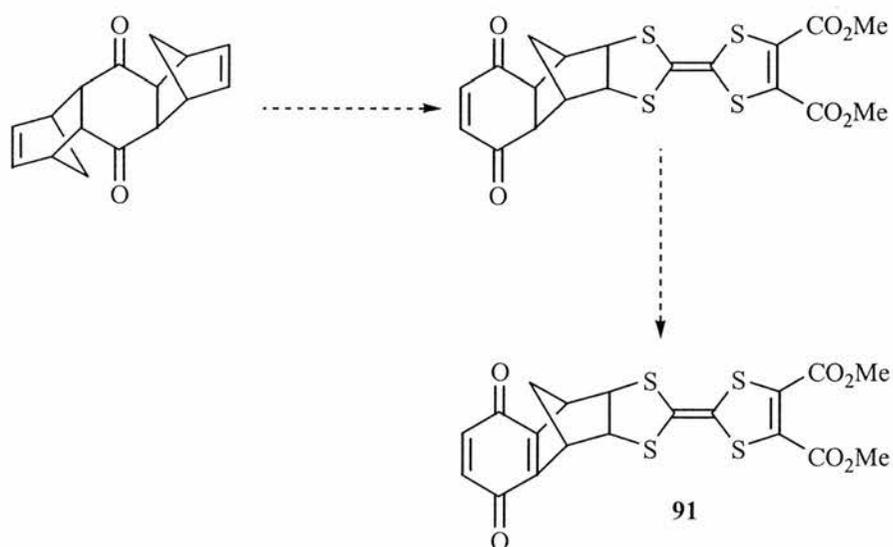
As mentioned in section A there is considerable interest in tetrathiafulvalenes. Yamada's group has shown that dihydrotetrathiafulvalenes can also be used to make CTCs which also behave as organic conductors. The first aim of this project was to synthesise a range of norbornane-fused dihydrotetrathiafulvalenes such as **86-88** and measure their oxidation potentials using cyclic voltammetry. On the basis of these results it was hoped to pick suitable acceptors such as halogens or TCNQ to form CTCs which may act as organic conductors. Removal of the ester groups usually present in these compounds might well result in more powerful donors and this would be investigated.



An attempt would also be made to develop a new synthesis of 2-alkylidene-1,3-dithioles **90** using a two step procedure starting from an aldehyde and the intermediate **89** using the Wittig-retro Diels Alder approach as shown.



There is huge interest in molecular electronics as outlined earlier. A further aim was to see whether the synthetic methods for dihydroTTFs developed previously in this laboratory could be applied to produce the donor- $\sigma$ -acceptor compound **91**. Some of the steps in this synthesis had been completed by a previous worker,<sup>88</sup> but more work was required to reach the target compound.



Finally the extension of the  $\text{Bu}_3\text{P}/\text{CS}_2$  adduct cycloaddition chemistry to other heterocumulenes such as isothiocyanates, isocyanates and carbodiimides would be investigated.

## **EXPERIMENTAL**

## **A Instrumentation and General Techniques**

### **1 NMR Spectroscopy**

#### **<sup>1</sup>H-NMR**

Routine spectra were obtained at 300 MHz on a Bruker B-ACS60 Avance 300 or on a Varian Gemini 2000.

#### **<sup>13</sup>C-NMR**

Spectra were obtained at 75 MHz on a Bruker B-ACS60 Avance 300 or on a Varian Gemini 2000.

Both the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained from solutions in CDCl<sub>3</sub> unless otherwise stated. All spectra were referenced to internal tetramethylsilane and the chemical shifts for all NMR spectra are expressed in parts per million to high frequency of the reference.

#### **<sup>31</sup>P NMR**

All spectra were obtained at 121 MHz on a Bruker B-ACS60 Avance 300 or on a Varian Gemini 2000 and were referenced to 85% phosphoric acid as the external standard.

### **2 Infrared spectroscopy**

The IR spectra were obtained on a Perkin Elmer FT-IR Paragon 1000 spectrometer. Solids were run as nujol mulls and liquids were run as thin films on NaCl plates.

### **3 Mass Spectroscopy**

Mass spectra and accurate mass measurements were obtained on a VG Platform spectrometer operated by Mrs. Caroline Horsburgh. Unless otherwise stated the spectra were obtained using electron impact at 70 eV. Chemical ionisation spectra

were obtained using isobutane as the ionising gas and fast atom bombardment spectra were obtained using 3-nitrobenzyl alcohol as the matrix.

#### **4 Elemental Analysis**

Microanalysis was carried out for C, H and S using an EA 1110 CHNS CE instruments elemental analyser by Mrs. S. Williamson.

#### **5 Melting Points**

Routine melting points were carried out on a Gallenkamp melting point apparatus. Melting points for new compounds were determined on a Reichert hot-stage microscope. All melting points are uncorrected.

#### **6 Thin Layer Chromatography**

Thin layer chromatography was performed using 0.2 mm layers of silica supported on aluminium sheets (Merck, Silica Gel 60F<sub>254</sub>). The components were observed under ultraviolet light and/or stained with iodine.

#### **7 Preparative Thin Layer Chromatography**

This was carried out using 1.0 mm layers of silica (Merck, Kieselgel), containing 0.5% Woelm fluorescent green indicator, on glass plates. After locating the components with ultraviolet light, the bands were scraped off and the products removed from the support by soaking in dichloromethane or methanol for 30 min-3h.

#### **8 Column Chromatography**

For column chromatography BDH flash grade silica gel was used.

#### **9 Dry Solvents**

Diethyl ether was freshly distilled from sodium benzophenone ketyl and THF was distilled from potassium benzophenone ketyl. Other solvents were used as received, without further drying.

## 10 Drying and Evaporation of Organic Solutions

Organic solutions were dried by standing over anhydrous magnesium sulfate and evaporated under reduced pressure on a rotary evaporator.

## 11 Flash Vacuum Pyrolysis

The apparatus used was based on the design of W. D. Crow, Australian National University. A similar set up is illustrated in a recent book written by Brown.<sup>89</sup> The essential features of the apparatus are illustrated in Figure 6. The sample was volatilised from a horizontal inlet tube, heated via an external heat source, through a  $30 \times 2.5 \text{ cm}^2$  silica tube. This was heated at temperatures in the range of 500-600 °C by a Carbolite Eurotherm Tube Furnace MTF-12/38A, the temperature being measured by a Pt/Pt-13% Rh thermocouple situated in the centre of the furnace. The non-volatile products were collected at the furnace exit and the volatile products collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of  $10^{-2}$  to  $10^{-3}$  Torr by an Edwards Model E2M5 high

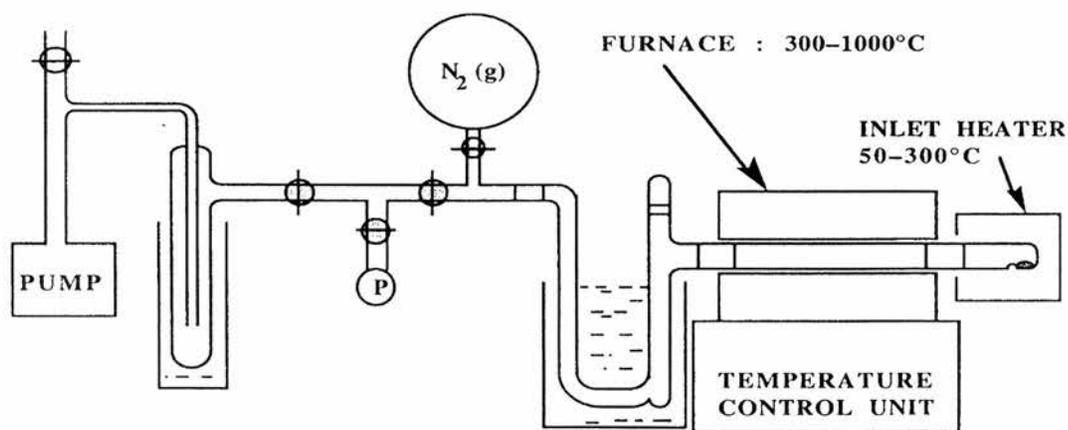


Figure 6 FVP apparatus.<sup>89</sup>

capacity rotary oil pump, the pressure being measured on a Pirani gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1-10 ms. After the pyrolysis the system was isolated from the pump. The products were then dissolved in  $\text{CDCl}_3$  and analysed directly using NMR.

## 12 Cyclic Voltammetry

Cyclic voltammetry was performed using an EG & G 273 A potentiostat under PC control with m270 software using a scan rate of  $20 \text{ mVs}^{-1}$ . The working electrode was a Pt bead (0.5 mm diameter), the auxiliary electrode was a platinum wire and the reference electrode was  $\text{Ag/Ag}^+$  (0.01 M  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$ ). The supporting electrolyte was recrystallised  $\text{Bu}_4\text{NPF}_6$  and the acetonitrile was HPLC grade. The compounds (5mg) were accurately weighed out on a Mettler H10W balance.

## 13 X-Ray Crystallography

Data were collected on a Bruker SMART diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods and refined using full-matrix least squares methods. Atomic coordinates and bond lengths and angles are listed in the Appendix and the X-ray structures are shown in the Discussion.

## 14 EPR Spectroscopy

EPR spectra were recorded with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Samples of the substrate and solvent in 4mm quartz tubes were deaerated by bubbling nitrogen through for 20 min. 1 mM solutions

of compound **91** were made up in t-butylbenzene and in acetonitrile. The measurements were carried out at  $T = 300, 320$  and  $335$  K. Signals were doubly integrated using the Bruker WinEPR software and radical concentrations were calculated by reference to a 1mM solution of DPPH in acetonitrile which was measured using identical conditions.

## **B Formation of Norbornane and Norbornene-Fused Dihydratetrathiafulvalenes**

### **1 Preparation of Starting Materials**

#### **a Preparation of tri-n-butylphosphoniodithioformate **92**<sup>90</sup>**

Carbon disulfide (25.50 g, 14 cm<sup>3</sup>, 0.34 mol) was dissolved in pet. ether (200 cm<sup>3</sup>) and cooled to 0 °C. Tri-n-butylphosphine (47.1 g, 58 cm<sup>3</sup>, 0.23 mol) was dissolved in pet. ether (100 cm<sup>3</sup>) and the resulting solution was added dropwise to the carbon disulfide solution with constant stirring for 0.5 h. A brick red solid began to form after this stage. The red solid was filtered off and washed with pet. ether leaving the product **92** (55.06 g, 85%) as a red solid, mp 65–66 °C (lit.,<sup>91</sup> 65 °C);  $\delta_{\text{H}}$  2.35 (6 H, m, 1-H), 1.53 (12 H, m, 2,3-H) and 0.95 (9 H, m, 4-H).

#### **b Preparation of 2,6-exo-4-dithiocarboxylato-4-tri-n-butylphosphonio-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **94****

Tri-n-butylphosphoniodithioformate **92** (22.95 g, 0.08 mol) was dissolved in dry diethyl ether giving a dark red solution. To this solution carbon disulfide (6.27 g, 0.08 mol) and norbornene (7.76 g, 0.08 mol) were added and after 4 h of stirring a pink solid had precipitated out of solution. The solid was filtered off and washed with dry ether until the filtrate was colourless leaving the product **94** (18.57 g, 50%) as a pink solid, mp 95–97 °C (lit.,<sup>92</sup> 106–108 °C);  $\delta_{\text{H}}$  3.65 (2 H, s, 2,6-H), 2.80–2.54 (6 H, m), 2.33 (2 H, s, 1,7-H) and 2.02–0.73 (27 H, m).

#### **c Preparation of 4,10-bis(dithiocarboxylato)-4,10-bis(tri-n-butylphosphonio)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane **98****

Tri-n-butylphosphoniodithioformate **92** (27.87 g 100.10 mmol) was dissolved in dry diethyl ether (100 cm<sup>3</sup>). To this solution norbornadiene (4.69 g, 51.00 mmol) and carbon

disulfide (7.62 g, 100.10 mmol) were added. The mixture was stirred at RT for 5 h during which time a pink precipitate formed in solution. The solid was filtered off and washed with ether until the filtrate was colourless leaving the product **98** (37.63 g, 92%) as a pink solid. The product was insoluble in common organic solvents and no NMR spectra could be obtained, mp 69–70 °C (lit.,<sup>92</sup> 86–88 °C).

**d Preparation of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate 109<sup>93</sup>**

Dicyclopentadiene was cracked using fraction distillation and the monomer was collected in an ice cooled receiving flask. Dimethyl acetylenedicarboxylate (DMAD) (27.00 g, 0.20 mol) was added dropwise to a stirred sample of the freshly distilled cyclopentadiene (17.00 g, 0.26 mol) over 0.5 h. The flask was cooled in an ice water bath whenever the reaction mixture began to heat up. After stirring overnight the solution was evaporated and the residue was purified using kugelrohr distillation to give the pure product **109** (25.20 g, 61 %) as a colourless oil, bp 150 °C/15 Torr (lit.,<sup>94</sup> 134–135 °C/10–11 Torr);  $\nu_{\max}/\text{cm}^{-1}$  1717, 1627, 1291, 1151, 1101 and 715;  $\delta_{\text{H}}$  6.92 (2 H, t,  $J$  2, HC=CH), 3.94 (2 H, m, 1,4-H), 3.78 (6 H, s, 2 × OMe), 2.28 (1 H, half AB pattern of t,  $J$  7, 2, 7-H *syn*) and 2.10 (1 H, half AB pattern,  $J$  7, 7-H *anti*);  $\delta_{\text{C}}$  165.4 (C=O), 152.4 (C-2, C-3), 142.3 (HC=CH), 72.9 (C-1, C-4), 53.4 (2 × OMe) and 51.9 (C-7).

**e Preparation of methyl phenylpropiolate in two steps**

**(i) Preparation of phenylpropionic acid**

Phenylacetylene (8.61 g, 0.08 mol) and dry THF (10 cm<sup>3</sup>) were poured into a clean dry 3-necked flask. The flask was put under vacuum to remove any air and then filled with nitrogen gas. This procedure was repeated 3 times. n-Butyllithium in hexane (2.5 M, 34 cm<sup>3</sup>, 0.08 mol) was added to the solution via a syringe. The solution turned to a dark red colour

indicating that deprotonation had occurred. Carbon dioxide was bubbled through the solution via an inlet tube for 1 hour. The solution became cloudy and solid precipitated out of solution. The solution was poured into a separating funnel containing water. The mixture was extracted with diethyl ether to remove any starting material. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with diethyl ether. The extract was dried and evaporated leaving the product (5.92 g, 49%) as an oil from which crystals later formed; mp 104–106 °C (lit.,<sup>95</sup> 135–137 °C);  $\delta_{\text{H}}$  9.98 (1 H, br s, OH), 7.62 (2 H, dd,  $J$  7,1, 2',6'-H), 7.54 (1 H, dd,  $J$  7,1, 4'-H) and 7.40 (2 H, t,  $J$  7, 3', 5'-H).

**(ii) Conversion of phenylpropionic acid into methyl phenylpropiolate**

Phenylpropionic acid (5.92 g, 0.04 mol) was heated under reflux for 1 h in excess thionyl chloride (14.00 g, 10 cm<sup>3</sup>, 0.12 mol). Excess solvent was removed under reduced pressure. Methanol (40 cm<sup>3</sup>, 31.60 g, 0.99 mol) was added carefully and after the initial vigorous reaction had subsided the mixture was heated under reflux for 1.5 h. Excess methanol was removed under reduced pressure. Kugelrohr distillation was used to obtain the product **89** (2.16 g, 34%) as a yellow liquid;  $\delta_{\text{H}}$  7.60 (2 H, d, Ar-H), 7.40 (3 H, m, Ar-H) and 3.85 (3 H, s, OMe),  $\delta_{\text{C}}$  154.1 (C=O), 132.7 (Ar-C-2, Ar-C-6), 130.4 (Ar-C-4), 128.3 (Ar-C-3, Ar-C-5), 119.2 (Ar-C-1), 86.1 (C-1 or C-2), 80.1 (C-1 or C-2) and 52.4 (OMe).

**f Alternative preparation of methyl phenylpropiolate<sup>96</sup>**

Phenylacetylene (1.02 g, 10.00 mmol) in dry ether was cooled to –30 °C in a round bottomed flask under N<sub>2</sub>(g). n-Butyl-lithium in hexane (2.50 M, 4 cm<sup>3</sup>, 10.00 mmol) was added dropwise via a syringe and the reaction mixture was stirred for 30 minutes at –30 °C. Methyl chloroformate (0.95 g, 0.77 cm<sup>3</sup>, 10.01 mmol) was added to the solution via a

syringe. The reaction was left stirring for 20 min at  $-30\text{ }^{\circ}\text{C}$  and then allowed to warm up to RT and was left stirring overnight. A cloudy solution had formed which was filtered and the solvent was removed in vacuo. NMR analysis of the crude product indicated that it contained the product and some starting material. Kugelrohr distillation (using a water pump vacuum) gave the product **89** (1.29 g, 81 %) as a colourless liquid,  $\delta_{\text{H}}$  and  $\delta_{\text{C}}$  as in e(ii).

## 2 Preparation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99**<sup>97</sup>

The norbornene adduct **94** (4.17 g, 9.29 mmol) was dissolved in acetonitrile (50 cm<sup>3</sup>) giving a pink coloured solution. DMAD (1.32 g, 9.29 mmol) was added to the mixture which turned colour from red to orange. The mixture was stirred for 3 days and had turned a red brown colour with some precipitate present. More DMAD (1.32 g, 9.29 mmol) was added and the precipitate disappeared. The solution was left stirring overnight and the solvent was then evaporated off under reduced pressure. The crude product was purified using flash chromatography (SiO<sub>2</sub>, dichloromethane/pet. ether, 1:1). Two fractions were obtained and both were recrystallised from hexane. Fraction A (0.65 g) contained the product and an unknown compound while B was the pure product **99** (0.71 g, 20%) as red crystalline platelets, mp 98–100 °C (lit.,<sup>97</sup> 110–111 °C),  $\nu_{\text{max}}/\text{cm}^{-1}$  1737, 1577, 1258, 1093, 1026, 977, 905 and 764;  $\delta_{\text{H}}$  3.86 (2 H, d,  $J$  1, 2,6-H), 3.83 (3 H, s, OMe), 3.82 (3 H, s, OMe), 2.38 (2 H, s, 1,7-H), 1.86 (1 H, d,  $J$  10, 10-H *syn*), 1.62 (1 H, d,  $J$  10, 10-H *anti*) and 0.94 (4 H, t,  $J$  9, 8, 9-H);  $\delta_{\text{C}}$  159.8 (2 × C=O), 131.2 (C-4', C-5'), 118.9 and 112.8 (C-4, C-2'), 62.5 (C-2, C-6), 52.9 (2×OMe), 44.8 (C-1, C-7), 32.1 (C-10) and 27.5 (C-8, C-9).

In a repeat of this reaction the unknown byproduct was found to have the following properties, mp 78–80 °C,  $\nu_{\text{max}}/\text{cm}^{-1}$  1731, 1668, 1639, 1296, 1184, 1054, 889, 769, 735 and

686;  $\delta_{\text{H}}$  4.43 (d,  $J$  2), 4.10 (d,  $J$  2), 3.80 (s), 2.49 (d,  $J$  5), 2.40 (d,  $J$  5), 2.31 (dd,  $J$  7), 2.26 (dd,  $J$  7), 1.88-1.68 (m), 1.66-1.31 (m) and 0.97 (t,  $J$  7);  $\delta_{\text{C}}$  67.5, 57.0, 44.7 (d,  $J$  11), 33.1, 32.2, 30.9, 30.2, 28.3, 27.8, 24.5, 24.4, 23.9 and 13.7;  $\delta_{\text{p}}$  49.7;  $m/z$  (CI) 277 (6%), 245 (9), 235 (61), 203 (100), 187 (71) and 93 (7).

### 3 Preparation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **101**<sup>88</sup>

The norbornadiene adduct **98** (0.52 g, 0.65 mmol) was suspended in dichloromethane (40 cm<sup>3</sup>) giving a pink coloured suspension. DMAD (0.09 g, 0.65 mmol) was added and the solution was stirred for 4 days changing colour from pink to orange to dark red. A second portion of DMAD (0.02 g, 0.14 mmol) was added and the solution was stirred overnight. The solution was left standing on the bench for 2 weeks and the solvent was then removed under reduced pressure. Flash column chromatography was used to purify the product (SiO<sub>2</sub>, dichloromethane/pet. ether, 1:1, gradient elution to dichloromethane). Five fractions were obtained and only one was kept. NMR analysis showed that the fraction contained the mono dihydrotetrathiafulvalene. The pure product **101** (0.01 g, 3%) was obtained as bright red platelets, mp 96–99 °C (lit.,<sup>98</sup> 103–104 °C);  $\nu_{\text{max}}/\text{cm}^{-1}$  1731, 1577, 1263, 1098, 1026 and 769;  $\delta_{\text{H}}$  6.19 (2 H, t,  $J$  2, 8,9-H), 3.92 (2 H, d,  $J$  2, 2,6-H), 3.83 (6 H, s, 2 × OMe), 2.95 (2 H, t,  $J$  2, 1,7-H), 1.92 (1 H, d,  $J$  10, 10-H *syn*) and 1.63 (1 H, d,  $J$  10, 10-H *anti*);  $\delta_{\text{C}}$  160.1 (2 × C=O), 138.0 (C-8, C-9), 60.1 (C-2, C-6), 53.2 (2 × OMe), 50.5 (C-1, C-7) and 42.5 (C-10).

#### 4 Preparation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane 102<sup>97</sup>

The norbornadiene adduct **98** (22.00 g, 27.50 mmol) was suspended in dichloromethane (40 cm<sup>3</sup>) and DMAD (7.40 g, 52.10 mmol) was added and the solution was stirred for 5 days. The solution was still cloudy after 5 days and another portion of DMAD (3.72 g, 26.20 mmol) was added and the solution was allowed to stir for a further 2 days by which time it had turned dark red. The solvent was removed under reduced pressure and the crude product was purified using flash column chromatography (SiO<sub>2</sub>, pet. ether/dichloromethane, 1:1, gradient elution to methanol-dichloromethane, 10:90) which gave 2 fractions. **A** contained the mono dihydrotetrathiafulvalene which was recrystallised from hexane giving the pure product **101** (0.21 g, 2.4%) as red crystals. **B** contained the bis-dihydrotetrathiafulvalene which was recrystallised from ethyl acetate giving the pure product **102** (2.47 g, 13%) as a dark red solid, mp 284–286 °C (lit.,<sup>97</sup> 284–286 °C);  $\nu_{\max}/\text{cm}^{-1}$  1732, 1577, 1263, 1098, 1026 and 769;  $\delta_{\text{H}}$  3.89 (4 H, s, 2,6,8,12-H), 3.83 (12 H, s, 4 × OMe), 2.55 (2 H, s, 1,7-H), 1.86 (2 H, s, 13-H);  $\delta_{\text{C}}$  159.8 (2 × C=O), 131.4 (C-4',C-5'), 117.0 and 116.9 (C-4, C-10, C-2'), 60.2 (C-2, C-6, C-8, C-12), 53.3 (4 × OMe), 53.1 (C-1, C-7) and 27.2 (C-13).

#### 5 Preparation of 2,6-exo-4-(4'-methoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane 103<sup>97</sup>

The norbornene adduct **94** (3.25 g, 7.24 mmol) was dissolved in dichloromethane (100 cm<sup>3</sup>). Methyl phenylpropiolate (1.16 g, 7.24 mmol) was added to the dark red solution, which was stirred for 2 days. The solvent was removed in vacuo. The crude product was purified using flash column chromatography (SiO<sub>2</sub>, dichloromethane/n-hexane 1:1, gradient elution to dichloromethane: methanol, 90:10) which gave 4 fractions. The product and

methyl phenylpropiolate were contained in one of the fractions. Kugelrohr distillation was used to remove the latter giving the pure product **103** (0.87 g, 30%), as a red coloured oil. Subsequent recrystallisation attempts failed and the solvent was removed under vacuum leaving a hard resinous solid; mp 48–50 °C (lit.,<sup>97</sup> 48–50 °C)(Found: C, 55.7; H, 4.6; S, 30.9. C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>S<sub>4</sub> requires C, 56.1; H, 4.5; S, 31.5%);  $\delta_{\text{H}}$  7.38 (5 H, m, Ar-H), 3.87 (2 H, t, *J* 2, 2,6-H), 3.64 (3 H, s, OMe), 2.40 (2 H, br s, 1,7-H), 1.94 (1 H, half AB pattern of t, *J* 11, 2, 10-H), 1.63 (1 H, m, 10-H) and 1.23 (4 H, m, 8,9-H);  $\nu_{\text{max}}/\text{cm}^{-1}$  1732, 1572, 1256, 1203, 1071 and 726;  $\delta_{\text{C}}$  159.5 (C=O), 147.7 (C-5'), 131.2 (Ar C-1), 129.3 (Ar C-4), 128.6 (Ar C-2, Ar C-6), 127.9 (Ar C-3, Ar C-5), 118.7 (C-4 or C-2'), 116.0 (C-4'), 114.0 (C-4 or C-2'), 62.5 and 62.4 (C-2, C-6), 52.0 (OMe), 44.7 (C-1, C-7), 32.1 (C-10) and 27.5 (C-8, C-9); *m/z* 406 (M<sup>+</sup>, 100%), 280 (26), 160 (39), 129 (22), 102 (15) and 66 (7).

## **6 Preparation of 2,6-exo-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **104****

The norbornene adduct **94** (8.26 g, 18.40 mmol) was dissolved in dichloromethane (100 cm<sup>3</sup>) and ethyl phenylpropiolate (3.21 g, 18.40 mmol) was added to the dark red solution. This solution was allowed to stir for 3 days. The solvent was removed under reduced pressure leaving red coloured oil. Flash column chromatography (SiO<sub>2</sub>, dichloromethane/pet. ether 1:1) was used to purify the oil. However the product still contained some starting ester and kugelrohr distillation was used to remove this. Recrystallisation was then attempted from ethyl acetate and from hexane but was unsuccessful. The product was rechromatographed (45:55 diethyl ether: n-hexane) giving three fractions one of which contained the product. This was recrystallised from ether to give the pure product **104** (0.48 g, 6%) as orange-red platelets; mp 108–110 °C (Found: C, 57.0;

H, 4.5. C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>S<sub>4</sub> requires C, 57.1, H, 4.8%);  $\nu_{\max}/\text{cm}^{-1}$  1697, 1572, 1290, 1070, 1004, 740 and 696;  $\delta_{\text{H}}$  7.37 (5 H, s, Ar-H), 4.07 (2 H, q,  $J$  7, CH<sub>2</sub>CH<sub>3</sub>), 3.86 (2 H, t,  $J$  2, 2,6-H), 2.39 (2 H, br s, 1,7-H), 1.94 (1 H, dd,  $J$  11, 2, 10-H *syn*), 1.62 (1 H, dt,  $J$  11, 2, 10-H *anti*), 1.22 (4 H, m, 8,9-H) and 1.11 (3 H, t,  $J$  7, CH<sub>2</sub>CH<sub>3</sub>);  $\delta_{\text{C}}$  159.4 (C=O), 147.4 (C-5'), 131.5 (Ar-C-1), 129.4 (Ar-C-4), 128.8 (Ar-C-2, Ar-C-6), 128.0 (Ar-C-3, Ar-C-5), 119.7 (C-4 or C-2'), 115.8 (C-4'), 114.7 (C-4 or C-2'), 62.6 and 62.5 (C-2, C-6), 61.3 (CH<sub>2</sub>CH<sub>3</sub>), 45.0 and 44.9 (C-1, C-7), 32.3 (C-10), 27.7 (C-8, C-9) and 13.8 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  420 (M<sup>+</sup>, 100%), 294 (22), 266 (11), 229 (9), 174 (21), 129 (22), 121 (10), 102 (42) and 69 (10).

## 7 Preparation of 2,6-exo-4-(4'-methoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 105<sup>98</sup>

Methyl phenylpropiolate (1.24 g, 7.74 mmol) was added to a suspension of the norbornadiene adduct **98** (6.16 g, 7.68 mmol) in dichloromethane (50 cm<sup>3</sup>) and stirred for 7 days. The solvent was removed under reduced pressure. The crude product was purified using flash column chromatography (SiO<sub>2</sub>, dichloromethane/n-hexane 1:1) which gave 2 fractions. The second fraction contained the product and some starting ester. The latter was removed using kugelrohr distillation to give the product **105** (0.42 g, 13%) as a red coloured oil,  $\delta_{\text{H}}$  7.30 (5 H, s, Ar-H), 6.19 (2 H, t,  $J$  2, 8,9-H), 3.87 (2 H, t,  $J$  2, 2,6-H), 3.63 (3 H, s, OMe), 2.95 (2 H, d,  $J$  1, 1,7-H), 1.97 (1 H, half AB pattern,  $J$  10, 10-H *syn*) and 1.62 (1 H, half AB pattern of t,  $J$  10, 2, 10-H *anti*);  $\delta_{\text{C}}$  159.9 (C=O), 148.1 (C-5'), 138.1 and 138.0 (C-8, C-9), 131.4 (Ar C-1), 129.6 (Ar C-4), 128.9 (Ar C-2, Ar C-6), 128.1 (Ar C-3, Ar C-5), 118.9 and 117.7 (C-4, C-2'), 115.1 (C-4'), 60.1 and 60.0 (C-2, C-6), 52.2 (OMe), 50.6 and 50.5 (C-1, C-7) and 42.6 (C-10).

## 8 Preparation of 2,6-exo-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 106

The norbornadiene adduct **98** (16.48 g, 21.00 mmol) was added to dichloromethane (150 cm<sup>3</sup>) forming a suspension. To this ethyl propiolate (7.32 g, 42.00 mmol) was added forming an orange-pink coloured suspension. The suspension was stirred for 6 days and changed colour to orange, then to brown and finally to dark red. The solvent was evaporated off under reduced pressure leaving a red coloured oil. This was subjected to flash column chromatography (SiO<sub>2</sub>, dichloromethane/pet. ether 40:60) which gave one fraction containing the crude product and three other fractions containing unknown byproducts. The starting ester was removed from the oil using kugelrohr distillation (T = 100–105 °C/0.5 Torr). Recrystallisation from ethyl acetate and hexane yielded the pure product **106** (0.33 g, 4%) as orange coloured needles, mp 154–156 °C (Found: C, 57.4; H, 4.1. C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>S<sub>4</sub> requires C, 57.4; H, 4.3%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1698, 1576, 1287, 1074, 1006 and 745;  $\delta_{\text{H}}$  7.37 (5 H, s, Ar-H), 6.20 (2 H, t, *J* 2, 8,9-H), 4.09 (2 H, q, *J* 7, CH<sub>2</sub>CH<sub>3</sub>), 3.92 (2 H, t, *J* 2, 2,6-H), 2.98 (2 H, s, 1,7-H), 2.02 and 1.65 (2 H, AB pattern of t, *J* 10, 2, 10-H) and 1.10 (3 H, t, *J* 7, CH<sub>2</sub>CH<sub>3</sub>);  $\delta_{\text{C}}$  162.2 (C=O), 147.5 (C-5'), 138.1 and 138.0 (C-8, C-9), 131.6 (Ar C-1), 129.5 (Ar-C-4), 128.9 (Ar-C-2, Ar-C-6), 128.1 (Ar-C-3, Ar-C-5), 119.8 and 117.4 (C-4, C-2'), 115.4 (C-4'), 61.5 (CH<sub>2</sub>CH<sub>3</sub>), 60.1 and 60.0 (C-2, C-6), 50.6 and 50.5 (C-1, C-7), 42.6 (C-10) and 13.9 (CH<sub>2</sub>CH<sub>3</sub>); *m/z* 418 (M<sup>+</sup>, 58%), 352 (100), 155 (79), 121 (28), 102 (31), 81 (25), 69 (54) and 57 (45).

## 9 Preparation of 2,6-exo-4-(4'-methoxycarbonyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 107

The norbornadiene adduct **98** (9.75 g, 12.18 mmol) was suspended in dichloromethane (50 cm<sup>3</sup>). Methyl propiolate (1.02 g, 12.13 mmol) was added and the

mixture was stirred for 7 days. The colour of the mixture changed from pink to orange-brown. The solvent was evaporated off leaving an orange-brown coloured oil. Flash column chromatography (SiO<sub>2</sub>, dichloromethane/pet. ether 1:1) gave 4 fractions the second of which contained the product and a by product. Recrystallisation from hexane gave the pure product **107** (0.11 g, 3%) as an orange solid, mp 132–134 °C (lit.,<sup>98</sup> 137–138 °C);  $\delta_{\text{H}}$  7.29 (1 H, s, =CH), 6.19 (2 H, t, *J* 2, HC=CH), 3.92 (2 H, m, 2,6-H), 3.80 (3 H, s, OMe), 2.96 (2 H, d, *J* 1, 1,7-H), 1.94 and 1.63 (2 H, AB pattern of t, *J* 10, 2, 10-H *syn* and *anti*);  $\delta_{\text{C}}$  159.9 (C=O), 138.0 and 137.9 (C-8, C-9), 131.9 and 127.3 (C-4', C-5'), 118.5 and 118.0 (C-4, C-2'), 60.1 and 59.9 (C-2, C-6), 52.6 (OMe), 50.5 (C-1, C-7) and 42.5 (C-10).

#### **10 Preparation of 2,6-exo-4-(4'-ethoxycarbonyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **108****

Tri-*n*-butylphosphoniodithioformate **92** (1.00 g, 3.60 mmol) was dissolved in dichloromethane. Carbon disulfide (0.27 g, 3.60 mmol) and norbornadiene (0.33 g, 3.60 mmol) were added to this solution. The solution was stirred for 3 days and then ethyl propiolate (0.35 g, 3.60 mmol) was added. The colour of the solution changed from orange to a dark red-brown colour. This solution was stirred for a further 3 days. The solvent was then evaporated off and the crude product was purified using flash chromatography (SiO<sub>2</sub>, dichloromethane/pet. ether, 1:1). Three fractions were obtained and then the solvent mixture was changed to 100% dichloromethane giving a further fraction. Only the first fraction was kept. The solvent was evaporated off under reduced pressure giving the pure product **108** (0.15 g, 13%) as a yellow solid, mp 119–121 °C (lit.,<sup>98</sup> 123–126 °C);  $\delta_{\text{H}}$  7.30 (1 H, s, CH=CO<sub>2</sub>Et), 6.20 (2 H, s, 8,9-H), 4.25 (2 H, q, *J* 7, CH<sub>2</sub>CH<sub>3</sub>), 3.92 (2 H, s, 2,6-H), 2.96 (2 H, br s, 1,7-H), 1.95 (1 H, d, *J* 8, 10-H *syn*), 1.62 (1 H, d, *J* 8, 10-H *anti*) and 1.33 (3 H, t, *J* 7, CH<sub>3</sub>);  $\delta_{\text{C}}$  159.3 (CO), 137.9 and 137.8 (C-8, C-9), 131.4 (C-5'), 127.7 (C-4'), 118.2 and

117.9 (C-4, C-2'), 61.7 (CH<sub>2</sub>CH<sub>3</sub>), 60.0 and 59.8 (C-2, C-6), 50.4 (C-1, C-7), 42.4 (C-10) and 14.1 (CH<sub>2</sub>CH<sub>3</sub>); *m/z* 342 (M<sup>+</sup>, 18%), 276 (36), 248 (17), 206 (9), 146 (7), 118 (5), 90 (9) and 66 (100).<sup>98</sup>

#### **11 Preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 110<sup>98</sup>**

Dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate **109** (1.49 g, 7.16 mmol) was added to a solution of Bu<sub>3</sub>P<sup>+</sup>.CS<sub>2</sub><sup>-</sup> **92** (2.00 g, 7.18 mmol) and carbon disulfide (0.54 g, 7.10 mmol) in dichloromethane (50 cm<sup>3</sup>) and was stirred at RT for 5 h. DMAD (1.16 g, 8.20 mmol) was added dropwise causing a slight colour change and temperature rise. The mixture was stirred for 18 h and monitored using TLC. DMAD (0.58 g, 4.10 mmol) was added again and the mixture was stirred for a further 24 h. The solvent was evaporated off and a red-brown oil remained. The oil was purified with flash chromatography (SiO<sub>2</sub>, dichloromethane 100%). TLC identified five fractions. Analysis of the fractions showed that only the last one contained the product. The solvent was removed and the product **110** (0.83 g, 23%) was obtained as an orange solid, mp 128–135 °C (lit.,<sup>98</sup> 146–147 °C); δ<sub>H</sub> 4.17 (2 H, d, *J* 1, 2,6-H), 3.86 (6 H, s, 2 × OMe), 3.82 (6 H, s, 2 × OMe), 3.35 (2 H, s, 1,7-H), 1.98 (1 H, d, *J* 10, 10-H) and 1.88 (1 H, d, *J* 10, 10-H).

#### **12 Attempted dehydrogenation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane 99 using sulfur<sup>99</sup>**

The dihydrotetrathiafulvalene **99** (0.10 g, 0.26 mmol) was mixed with sulfur (0.02 g, 0.50 mmol) using a mortar and pestle. The mixture was scraped into a round-bottomed flask and heated at 200 °C in a kugelrohr oven under a nitrogen atmosphere for 4 h. NMR analysis indicated that no change had occurred.

### 13 Attempted dehydrogenation of 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99** using selenium<sup>99</sup>

The dihydrotetrathiafulvalene **99** (0.10 g, 0.26 mmol) was mixed with selenium (0.10 g, 1.29 mmol) in a round bottomed flask and heated at 200 °C in a kugelrohr oven under a nitrogen atmosphere for 4 h. NMR analysis indicated that no change had occurred.

## C Decarboxylation Reactions of Norbornane and Norbornene-Fused Dihydrotetrathiafulvalenes

### 1 Preparation of 2,6-exo-4-(1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **117**<sup>100</sup>

The dihydrotetrathiafulvalene **99** (0.20 g, 0.52 mmol) and LiBr (0.45 g, 5.20 mmol) were heated under reflux in freshly distilled DMA (15 cm<sup>3</sup>) for 0.5 h. The reaction flask was immediately cooled in a water bath and then poured into water (30 cm<sup>3</sup>) and stirred for 10 min. A cloudy yellow solution formed immediately. The product was extracted using dichloromethane (30 cm<sup>3</sup>) which was dried and evaporated leaving a dark orange liquid. Flash column chromatography (SiO<sub>2</sub>, diethyl ether/n-hexane 70:30) gave two fractions one of which contained the product (0.24 g) which was recrystallised from chloroform and ether. The pure product **117** (0.02 g, 14%) precipitated out of the solution as yellow-orange needles, mp 134–136 °C; (Found: C, 48.8; H 4.2. C<sub>11</sub>H<sub>12</sub>S<sub>4</sub> requires C, 48.5; H 4.4%);  $\nu_{\max}/\text{cm}^{-1}$  1727, 1601, 1547, 1511, 1296, 1098, 793, 764 and 653;  $\delta_{\text{H}}$  6.23 (2 H, s, 4',5'-H), 3.85 (2 H, s, 2,6-H), 2.37 (2 H, s, 1,7-H), 1.95 (1 H, d, *J* 10, 10-H), 1.62 (2 H, d, *J* 8, 8,9-H) and 1.22 (3 H, m, 8,9,10-H);  $\delta_{\text{C}}$  120.1 (C-4, C-2'), 118.7 (C-4', C-5'), 113.4 (C-4, C-2'), 62.5 (C-2, C-6), 45.0 (C-1, C-7), 32.4 (C-10) and 27.8 (C-8, C-9); *m/z* 272 (100%), 227 (7) and 179 (7). The reaction was repeated using the same experimental procedure and the pure product **117** (0.27 g, 39%) was obtained as yellow coloured needles.

## 2 Preparation of 2,6-exo-4-(4'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **118**<sup>100</sup>

The dihydrotetrathiafulvalene **103** (0.10 g, 0.25 mmol) and LiBr were dissolved in DMA (10 cm<sup>3</sup>) and heated under reflux for 0.5 h. The flask was immediately cooled in water and the contents added to water (25 cm<sup>3</sup>) which formed a brightly coloured cloudy yellow solution. This solution was stirred for 10 minutes. The product was extracted using dichloromethane which was dried and evaporated. Kugelrohr distillation was used to remove any remaining traces of DMA giving the pure product **118** (0.07 g, 76%) as a yellow brown coloured solid, mp 130–132 °C (HRMS: found M<sup>+</sup> 348.0140. C<sub>17</sub>H<sub>16</sub>S<sub>4</sub> requires M<sup>+</sup> 348.0135);  $\nu_{\max}/\text{cm}^{-1}$  1593, 1313, 1231, 1188, 744 and 691;  $\delta_{\text{H}}$  7.39 (5 H, m, Ar-H), 6.48 (1 H, s, 5'-H), 3.89 (2 H, d, *J* 2, 2,6-H), 2.39 (2 H, br s, 1,7-H), 1.97 (1 H, d, *J* 9, 1-H *syn*), 1.62 (1 H, d, *J* 9, 10-H *anti*) and 1.24 (4 H, m, 8,9-H);  $\delta_{\text{C}}$  135.3 (Ar-C-1 or C-4'), 132.5 (Ar-C-1 or C-4'), 128.7 (Ar-C-2, Ar-C-6), 128.2 (Ar-C-4), 126.1 (Ar-C-3, Ar-C-5), 119.0 (C-4 or C-2'), 114.4 (C-4 or C-2'), 113.1 (C-5'), 62.6 and 62.5 (C-2, C-6), 44.9 (C-1, C-7), 32.4 (C-10) and 27.8 (C-8, C-9); *m/z* 348 (M<sup>+</sup>, 100%), 222 (35), 178 (21), 102 (81), 84 (23) and 49 (26).

## 3 Preparation of 2,6-exo-4-(1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **119**<sup>100</sup>

The dihydrotetrathiafulvalene **101** (0.11 g, 0.30 mmol) and LiBr (0.26 g, 3.00 mmol) were dissolved in DMA (10 cm<sup>3</sup>) and heated under reflux for 0.5 h. The flask was immediately cooled in water and the contents added to water (25 cm<sup>3</sup>) which produced a cloudy red coloured solution. This solution was stirred for 10 minutes. The product was extracted with dichloromethane which was dried and evaporated. Kugelrohr distillation was used to remove any remaining traces of DMA giving the pure product **119** (0.07 g, 79%) as a

dark brown coloured solid, mp 94–96 °C (HRMS: found  $M^+$  269.9679.  $C_{11}H_{10}S_4$  requires  $M^+$  269.9665);  $\nu_{\max}/\text{cm}^{-1}$  1319, 1282, 739 and 645;  $\delta_{\text{H}}$  6.29 (2 H, s, HC=CH), 6.20 (2 H, t,  $J$  2, HC=CH), 3.91 (2 H, d,  $J$  2, 2,6-H), 2.95 (2 H, s, 1,7-H), 1.99 and 1.65 (2 H, AB pattern,  $J$  10, 10-H *syn* and *anti*);  $\delta_{\text{C}}$  138.0 (HC=CH), 118.5 (HC=CH), 59.9 (C-2, C-6), 50.5 (C-1, C-7) and 42.5 (C-10);  $m/z$  (270  $M^+$ , 45%), 204 (100), 159 (6), 146 (17), 122 (8), 102 (23), 84 (6), 76 (10) and 66 (8).

#### 4 Preparation of 2,6-exo-4-(4'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **120**<sup>100</sup>

The dihydrotetrathiafulvalene **105** (0.10 g, 0.25 mmol) and LiBr (0.11 g, 1.24 mmol) were dissolved and heated under reflux in DMA for 0.5 h. The flask was immediately cooled in water and the contents added to water (25 cm<sup>3</sup>) producing a cloudy yellow coloured solution. This solution was stirred for 10 minutes. The product was extracted using dichloromethane which was dried and evaporated. Kugelrohr distillation was used to remove any remaining traces of DMA. The pure product (0.08 g, 98%) **120** was obtained as a dark brown solid, mp 70–71 °C (HRMS: found  $M^+$  345.9965. requires  $M^+$  345.9978);  $\nu_{\max}/\text{cm}^{-1}$  1595, 1320, 1285, 1261 and 737;  $\delta_{\text{H}}$  7.32 (5 H, m, Ar-H), 6.47 (1 H, s, 5'-H), 6.19 (2 H, t,  $J$  2, 8,9-H), 3.92 (2 H, d,  $J$  2, 2,6-H), 2.97 (2 H, m, 1,7-H), 2.00 (1 H, half AB pattern,  $J$  10, 10-H *syn*) and 1.63 (1 H, half AB pattern of t,  $J$  10, 2, 10-H *anti*);  $\delta_{\text{C}}$  138.0 (C-8, C-9), 135.2 (Ar-C-1 or C-4'), 132.44 (Ar-C-1 or C-4'), 128.7 (Ar-C-2, Ar-C-6), 128.2 (Ar-C-4), 126.0 (Ar-C-3, Ar-C-5), 119.2 (C-4 or C-2'), 116.15 (C-5'), 113.0 (C-4 or C-2'), 60.0 and 59.8 (C-2, C-6), 50.5 (C-1, C-7) and 42.5 (C-10);  $m/z$  346 ( $M^+$ , 25%), 280 (45), 270 (44), 204 (100), 146 (17), 102 (28), 86 (23) and 66 (16).

**5 Preparation of 2,6-exo-8,9-exo-4,10-bis(1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridec-4-diene **121**<sup>100</sup>**

Compound **102** (1.00 g, 1.45 mmol) was reacted with LiBr (2.59 g, 29.00 mmol) in DMA (100 cm<sup>3</sup>) and heated under reflux for 0.5 h. The solution was then cooled in a water bath and the contents added to water (100 cm<sup>3</sup>) in a conical flask and stirred for 0.5 h. The brown coloured solution was poured into a separating funnel and dichloromethane was added. A scum formed at the interface of the two layers, which was reduced by swirling the funnel. The organic layer was collected and the aqueous layer and the scum were run into a conical flask and put back into the separating funnel. Chloroform was added and the organic layer was collected. The solvent partly was evaporated off the combined organic layer, which gave a suspended solid in solution. This was filtered off giving a yellow brown coloured solid **121** (0.13 g). Investigation into the solubility of the product revealed that it was only soluble in pyridine. Vacuum sublimation was used to purify the product to give **121** (0.002 g, 0.9%) as a pale coloured solid (HRMS: found M<sup>+</sup>, 447.8694. C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>S<sub>2</sub> requires M<sup>+</sup>, 447.8705). NMR analysis using d<sub>5</sub>-pyridine indicated that the reaction had worked,  $\nu_{\max}/\text{cm}^{-1}$  1737, 1635, 1316, 1267, 1016, 798, 735 and 639;  $\delta_{\text{H}}$  6.58 (4 H, s, 4',5'-H), 3.87 (4 H, s, 2,6,8,12-H), 2.36 (2 H, s, 1,7-H) and 1.83 (2 H, s, 13-H);  $\delta_{\text{C}}$  119.9 (C-4', C-5'), 60.7 (C-2, C-6, C-8, C-12), 54.2 (C-1, C-7) and -15.9 (C-13);  $m/z$  448 (M<sup>+</sup>, 56%), 396 (9), 368 (10), 270 (51), 239 (6), 204 (100), 178 (6), 146 (25), 132 (9), 102 (28), 91 (8), 76 (14) and 57 (24).

**6 Attempted decarboxylation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **110**<sup>100</sup>**

Compound **110** (0.50 g, 1.00 mmol) and LiBr (0.56 g, 6.40 mmol) were heated under reflux in DMA (12 cm<sup>3</sup>) for 0.5 h. During this time the solution lightened in colour and

bubbles began to form. The solution was allowed to cool overnight and was then poured into a separating funnel with water (30 cm<sup>3</sup>) which gave a cloudy yellow solution. The product was extracted with dichloromethane (30 cm<sup>3</sup>), dried and evaporated to give, after kugelrohr distillation a yellow brown oil. NMR analysis indicated that partial decarboxylation had occurred. An acid base extraction was carried out using diethyl ether and 1M NaOH. The aqueous layer was acidified using concentrated hydrochloric acid and extracted with dichloromethane. Drying and evaporation followed by NMR analysis indicated the carboxylic acid had been formed. Attempted recrystallisation failed however. The experiment was not pursued any further.

#### **D Preparation of Charge Transfer Complexes**

##### **1 Formation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(ethoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane Iodine Charge Transfer Complex **122**<sup>88</sup>**

Iodine (0.55 g, 2.17 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>). A solution of the bis dihydrotetrathiafulvalene **112** (0.20 g, 0.27 mmol) dissolved in methylene chloride (5 cm<sup>3</sup>) was added dropwise and the solution was left stirring overnight. The stirring was stopped and the solution was allowed to settle. Then the solution was filtered and the solid was washed with dichloromethane to give the CTC **122** (0.58 g) as a black crystalline solid, mp 166–167 °C (Found: C, 14.5; H, 1.1; S, 10.3. C<sub>27</sub>H<sub>28</sub>S<sub>8</sub>O<sub>8</sub>I<sub>12</sub> requires C, 14.4; H, 1.3; S, 11.4%);  $\nu_{\max}/\text{cm}^{-1}$  1758 (C=O), 1205, 1097, 1022, 948 and 729;  $\delta_{\text{H}}$  4.50 (8 H, br s) and 1.35 (12 H, br s).

**2 Attempted formation of an Iodine Charge Transfer Complex with 2,6-exo-8,12-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10-oxa-3,5-dithiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane-9,11-dione **114**<sup>88</sup>**

Iodine (0.33 g, 1.30 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>). A solution of the dihydrotetrathiafulvalene **114** (0.10 g, 0.22 mmol) in dichloromethane (5 cm<sup>3</sup>) was added dropwise and the solution was left stirring overnight. The solution was filtered to give a solid that was then washed with dichloromethane giving a bright yellow powder (0.79 g), mp 272–273 °C (lit.,<sup>97</sup> 272–273 °C) (Found: C, 44.9; H, 2.7; S, 27.6. C<sub>17</sub>H<sub>14</sub>O<sub>7</sub>S<sub>4</sub> requires: C, 44.5; H, 3.1; S, 28.0%). These results showed that the starting material **114** had been recovered unchanged and the reaction had not occurred.

**3 Formation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene Iodine Charge Transfer Complex **123**<sup>88</sup>**

Iodine (0.61 g, 2.39 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>). A solution of the dihydrotetrathiafulvalene **110** (0.20 g, 0.40 mmol) in dichloromethane (5 cm<sup>3</sup>) was added dropwise to the solution which was left stirring overnight. The solution was filtered and the resulting solid was washed with dichloromethane. The CTC **123** (0.59 g) was obtained as a black crystalline solid, mp 166–167 °C (Found: C, 14.2; H, 0.7; S, 6.6. C<sub>19</sub>H<sub>18</sub>O<sub>8</sub>S<sub>4</sub>I<sub>9</sub> requires: C, 13.9; H, 1.1; S, 7.8%),  $\nu_{\max}/\text{cm}^{-1}$  1730, 1622, 1262 and 722;  $\delta_{\text{H}}$  3.83 (3 H, s) and 3.80 (3 H, s).

**4 Formation of 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane Iodine Charge Transfer Complex 124<sup>88</sup>**

Iodine (0.02 g, 0.09 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>). A solution of the bis dihydrotetrathiafulvalene **102** (0.01 g, 0.02 mmol) in dichloromethane (5 cm<sup>3</sup>) was added dropwise to the iodine solution which was left stirring overnight. The solution was filtered leaving a solid which had some unreacted iodine present. This was removed under vacuum to give the CTC **124** (0.06 g) as a black crystalline solid, mp 291–292 °C (Found: C, 9.4; H, 0.5; S 11.5. C<sub>23</sub>H<sub>20</sub>O<sub>8</sub>S<sub>8</sub>I<sub>18</sub> requires C, 9.3; H, 0.7; S, 8.7%).

**5 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(ethoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane 112**

The bis dihydrotetrathiafulvalene **112** (0.20 g, 0.27 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>) and added dropwise to a solution of bromine (0.26 g, 1.63 mmol) in dichloromethane (5 cm<sup>3</sup>). A product (0.16 g) was obtained as dark brown crystals, which subsequently decomposed (Found: C, 15.5; H, 2.6; S, 10.8. C<sub>27</sub>H<sub>28</sub>O<sub>8</sub>S<sub>8</sub>Br<sub>12</sub> requires C, 19.1; H, 1.7; S, 15.1%),  $\nu_{\max}/\text{cm}^{-1}$  1734 and 744. The product also did not dissolve well in CDCl<sub>3</sub> or in d<sub>6</sub>-DMSO for NMR analysis which would suggest that the desired reaction had not occurred.

**6 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,12-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10-oxa-3,5-dithiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane-9,11-dione 114**

The dihydrotetrathiafulvalene **114** (0.09 g, 0.19 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>). This was then added dropwise to a solution of bromine (0.21 g, 1.31 mmol) in dichloromethane (5 cm<sup>3</sup>). The solution was filtered but no product was obtained. The solvent was evaporated off and a brown oil was obtained. Proton NMR analysis indicated there was not much material present in the sample suggesting that the desired reaction had not occurred.

**7 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,9-bis(methoxycarbonyl)-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 110**

The dihydrotetrathiafulvalene **110** (0.10 g, 0.20 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>) and was added dropwise to a solution of bromine (0.19 g, 1.19 mmol) in dichloromethane. The solution was filtered but no solid was obtained. The solvent was evaporated off under reduced pressure and an orange oily substance was obtained. The oil was applied to a preparative thin layer chromatography plate (SiO<sub>2</sub>, ethyl acetate:ether 70:30) and four bands were obtained. Each band was collected separately and added to a solution of dichloromethane. The solution was filtered, then the solvent was removed and analysis was carried out using proton NMR. Only the first band was kept which consisted mostly of unreacted starting material **110**.

**8 Attempted formation of a Bromine Charge Transfer Complex with 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane 102**

The dihydrotetrathiafulvalene **102** (0.01 g, 0.02 mmol) was dissolved in dichloromethane (25 cm<sup>3</sup>) and was added dropwise to a solution of bromine (0.01 g, 0.090 mmol) in dichloromethane (25 cm<sup>3</sup>). The solution was left stirring overnight with constant stirring. The solvent and excess bromine were removed under reduced pressure and a brown gummy solid was obtained. The CHN analysis indicated that the starting product had changed, but the proton and carbon NMR analysis showed mostly decomposition products, suggesting that the desired reaction had not occurred.

**9 Attempted formation of a charge transfer complex involving TCNQ and 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane 102**

The bis dihydrotetrathiafulvalene **102** (0.20 g, 0.27 mmol) and TCNQ (0.06 g, 0.27 mmol) were dissolved in acetonitrile (15 cm<sup>3</sup>) and were left stirring overnight resulting in a solution with an orange coloured solid present. The mixture was filtered and the orange residue was washed with cold acetonitrile. Proton NMR analysis showed that the solid consisted of starting material. The solvent was removed from the filtrate leaving yellow coloured crystals behind. The IR spectrum showed the presence of cyano and carbonyl groups in the orange coloured solid. There were problems dissolving up the yellow solid (in CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>SO) for NMR analysis. It was assumed that the reaction had not occurred.

## 10 Attempted formation of a charge transfer complex with TCNQ and 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane **99**

Compound **99** (0.12 g, 0.31 mmol) and TCNQ (0.74 g, 0.35 mmol) were dissolved separately in acetonitrile (15 cm<sup>3</sup>). The TCNQ was not completely soluble in acetonitrile. The solution was left stirring for three days and a red coloured solution was obtained with some precipitate. The solution was filtered to give a solid product (a) and the solvent was removed under reduced pressure from the filtrate giving a red crystalline solid (b). The residue (a) was a yellow-brown crystalline solid. IR analysis showed that it only contained a cyano group and was probably unreacted TCNQ. NMR showed (b) to be mainly the starting material. There were problems dissolving both (a) and (b) for NMR analysis. IR analysis showed the presence of cyano and carbonyl groups. The NMR spectrum of product (b) was run using d<sub>3</sub>-acetonitrile. This showed the starting material and a tiny peak for TCNQ.<sup>101</sup> This would suggest that the desired reaction had not occurred,  $\nu_{\max}/\text{cm}^{-1}$  (a) 2223 (CN), 1670, 1539, 1354, 1126 and 862; (b) 2223 (CN) and 1723; (TCNQ) 2223, 1672, 1543, 1354, 1126 and 859.

## 11 Formation of 2,6-exo-4(1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane Iodine Charge Transfer Complex **125**

The dihydrotetrathiafulvalene **117** (0.01 g, 0.02 mmol) and iodine (0.03 g, 0.11 mmol) were dissolved separately in dichloromethane (5 cm<sup>3</sup>). The two solutions were mixed together forming a red coloured solution which contained a black solid (0.02 g). CHN analysis indicated that a CTC **125** may have been formed, (Found: C; 14.9, H, 1.15; S 14.3. C<sub>11</sub>H<sub>12</sub>S<sub>4</sub>I<sub>5</sub> requires C, 14.6; H, 1.33; S, 14.1%).

**12 Attempted preparation of a quinone charge transfer complex with 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane 102**

The dihydrotetrathiafulvalene **102** (0.10 g, 0.15 mmol) and benzoquinone (0.03 g, 0.30 mmol) were both dissolved in acetonitrile (30 cm<sup>3</sup>) forming an orange coloured solution. The solution was allowed to evaporate until precipitation began to occur. The solution was filtered giving red and black coloured platelets, mp 281–283 °C. X-ray analysis showed that they only contained the dihydrotetrathiafulvalene but this has been fortuitously obtained in two different crystalline forms. Further details are given in section D in the discussion.

**13 Attempted preparation of a quinone charge transfer complex with 2,6-exo-4-(4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane 99**

The dihydrotetrathiafulvalene **99** (0.05 g, 0.13 mmol) and benzoquinone (0.01 g, 0.13 mmol) were both dissolved in acetonitrile (10 cm<sup>3</sup>) forming an orange coloured solution which turned red. The solution was allowed to evaporate until crystals began to precipitate from solution. The solution was filtered giving red needle like platelets (0.08 g), mp 108–110 °C. NMR analysis showed that the crystals were that of the starting dihydrotetrathiafulvalene **99** but existed as dichroic crystals which had previously been unseen.

## E X-Ray Structure Determinations

### 1 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane 99

Crystal data for C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>S<sub>4</sub>,  $M = 388.52$ , red plate, crystal dimensions  $0.1 \times 0.1 \times 0.02$  mm, monoclinic, space group P2<sub>1</sub>/c,  $a = 17.490$  (10),  $b = 10.435$  (1),  $c = 9.855$  (2) Å,  $\beta = 96.32(10)^\circ$ ,  $V = 1788(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.443$  Mg m<sup>-3</sup>,  $T = 293$  K,  $R = 0.037$ ,  $R_w = 0.090$  for 1862 reflections with  $I > 2\sigma(I)$  and 209 variables. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\alpha = 0.71073$  Å). The structure was solved by direct methods and refined using full-matrix least squares methods. Atomic coordinates and bond lengths and angles are listed in the Appendix in tables 10-12 and the structure is shown in the discussion (Figure 10).

### 2 2,6-exo-4-(1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane 117

Crystal data for 117: C<sub>11</sub>H<sub>12</sub>S<sub>4</sub>,  $M = 272.45$ , yellow prism, crystal dimensions  $0.13 \times 0.1 \times 0.1$  mm, monoclinic, space group P2<sub>1</sub>/n,  $a = 6.338$  (5),  $b = 18.423$  (15),  $c = 10.315$  (8) Å,  $\beta = 90.33$  (2)°,  $V = 1205$  (17) Å<sup>3</sup>,  $D_c = 1.502$  Mg m<sup>-3</sup>,  $T = 293$  K,  $R = 0.033$ ,  $R_w = 0.066$  for 1058 reflections with  $I > 2\sigma(I)$  and 137 variables. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\alpha = 0.71073$  Å). The structure was solved by direct methods and refined using full-matrix least squares methods. Atomic coordinates and bond lengths and angles are listed in Appendix in tables 16-18 and the structure is shown in the discussion (Figure 12).

**3 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane 99** (second crystal form)

Crystal data for **99**: C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>S<sub>4</sub>, *M* = 388.52, red/yellow plate, crystal dimensions 0.19 × 0.10 × 0.03, monoclinic, space group P2(1)/n, *a* = 5.910 (8), *b* = 32.412 (4), *c* = 9.092 (12) Å, β = 104.641 (2)°, *V* = 1685(4) Å<sup>3</sup>, *D*<sub>c</sub> 1.531 Mg m<sup>-3</sup>, *R* = 0.033, *R*<sub>w</sub> = 0.080 for 2736 reflections with *I* > 2σ(*I*) and 211 variables. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (α = 0.71073 Å). The structure was solved by direct methods and refined using full-matrix least squares methods. Atomic coordinates and bond lengths and angles are listed in Appendix in tables 13-15 and the structure is shown in the discussion (Figure 18).

**4 2,6-exo-8,12-exo-4,10-bis(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5,9,11-tetrathiacyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>]tridecane 102** (second crystal form)

Crystal data for **102**: C<sub>23</sub>H<sub>20</sub>O<sub>8</sub>S<sub>8</sub>, *M* = 680.87, orange platelet, crystal dimensions 0.10 × 0.10 × 0.03, triclinic, space group P-1, *a* = 11.611 (4), *b* = 12.873 (5), *c* = 19.580 (6) Å, α = 95.74 (2), β = 106.029 (17), γ = 92.87 (2)°, *V* = 2789(16) Å<sup>3</sup>, *D*<sub>c</sub> 1.621 Mg m<sup>-3</sup>, *R* = 0.221, *R*<sub>w</sub> = 0.458 for 3758 reflections with *I* > 2σ(*I*) and 666 variables. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (α = 0.71073 Å). The structure was solved by direct methods and refined using full-matrix least squares methods. Atomic coordinates and bond lengths and angles are listed in Appendix in tables 19-21 and the structure is shown in the discussion (Figure 15).

**5 11-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10,12-dithiahexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradec-2(7),4(5)-diene-3,10-dione 91**

Crystal data for **91**: C<sub>19</sub>H<sub>14</sub>O<sub>6</sub>S<sub>4</sub>, *M* = 466.54, black block, crystal dimensions 0.13 × 0.13 × 0.01 mm, monoclinic, space group P2<sub>1</sub>/c, *a* = 9.753 (2), *b* = 17.667 (4), *c* = 11.711 (3) Å, β = 105.46 (4)°, *V* = 1945, *D<sub>c</sub>* = 1.593 Mg m<sup>-3</sup>, *T* = 293 K, *R* = 0.033, *R<sub>w</sub>* = 0.073 for 2170 reflections with *I* > 2σ(*I*) and 265 variables. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (α = 0.71073 Å). The structure was solved by direct methods and refined using full-matrix least squares methods. Atomic coordinates and bond lengths and angles are listed in Appendix in tables 22-24 and the structure is shown in the discussion (Figure 20).

**6 2-tri-*n*-butylphosphonio-2-methoxy-3,4,5-tri(methoxycarbonyl)cyclopent-2-en-1-ion-4-ide 203**

Crystal data for **203**: C<sub>25</sub>H<sub>39</sub>O<sub>8</sub>P, *M* = 486.52, yellow prism, crystal dimensions 0.19 × 0.1 × 0.1 mm, monoclinic, space group P2<sub>1</sub>/c, *a* = 8.450(10), *b* = 35.479(11), *c* = 9.174(3), β = 99.527(10)°, *V* = 2712(13) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.192 Mg m<sup>-3</sup>, *T* = 293 K, *R* = 0.060, *R<sub>w</sub>* = 0.131 for 1993 reflections with *I* > 2σ(*I*) and 317 variables. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (α = 0.71073 Å). The structure was solved by direct methods and refined using full-matrix least squares methods. Atomic coordinates and bond lengths and angles are listed in Appendix in tables 25-27 and the structure is shown in the discussion (Figure 24).

## F Construction of Norbornane-Fused Dihydrotetrathiafulvalene-Quinone Compounds

### 1 Formation of a Donor- $\sigma$ -Acceptor Compound

#### a Preparation of 2,11-endo-4,9-endo-pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]hexadeca-6,13-diene-3,10-dione **132**<sup>102</sup>

Freshly distilled cyclopentadiene was prepared by thermal cracking of dicyclopentadiene. *p*-Benzoquinone (18.43 g, 0.17 mol) was added to a solution of cyclopentadiene (22.54 g, 0.34 mol) and the mixture was stirred overnight. The solvent was partially removed under reduced pressure. The solution was then allowed to stand for 1 h by which time the product had crystallised out of solution. The product was filtered off and washed with hexane and dried overnight to give the pure product **132** (24.58 g, 71%) as colourless needles, mp 152–154 °C (lit.,<sup>102</sup> 157–158 °C);  $\delta_{\text{H}}$  6.19 (4 H, s, 6,7,13,14-H), 3.35 (4 H, s, 1,5,8,12-H), 2.88 (4 H, s, 2,4,9,11-H), 1.47 and 1.30 (4 H, AB pattern, *J* 10, 15,16-H, *syn* and *anti*);  $\delta_{\text{C}}$  212.6 (C-3, C-10), 136.3 (C-6, C-7, C-13, C-14), 53.2 (C-1, C-5, C-8, C-12), 49.5 (C-2, C-4, C-9, C-11) and 48.2 (C-15, C-16).<sup>102</sup>

#### b Preparation of 15-(4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene)-14,16-dithiahexacyclo[10.5.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]nonadec-6-ene-3,10-dione **134**

The adduct  $\text{Bu}_3\text{P} \cdot \text{CS}_2$  **92** (14.10 g, 51.00 mmol),  $\text{CS}_2$  (3.78 g, 51.00 mmol) and the quinone adduct **132** (6.00 g, 25.00 mmol) were dissolved in dichloromethane (10 cm<sup>3</sup>) and left stirring for 1 h. DMAD (8.52 g, 51.00 mmol) was added and the mixture was allowed to stir for 6 days. Flash column chromatography ( $\text{SiO}_2$ , 100% DCM) gave the impure compound. The product was recolumned ( $\text{SiO}_2$ , diethyl ether/ pet. ether 70:30) to give the pure product **134** (2.32 g, 18%) as an orange solid, mp 150–152 °C (lit.,<sup>88</sup> 136–137 °C);  $\delta_{\text{H}}$  6.34 (2 H, t, *J* 2, 6,7-H), 3.86 (2 H, s, 13,17-H), 3.83 (6 H, s, 2  $\times$  OMe), 3.41 (2 H, s), 3.12 (2

H, t,  $J$  2), 2.84 (2 H, t,  $J$  2), 2.66 (2 H, t,  $J$  2), 1.89 (1 H, d of t,  $J$  10, 2, 18-H *syn*), 1.61 (1 H, d,  $J$  10, 19-H *anti*), 1.44 (1 H, d,  $J$  10, 19-H *syn*) and 1.19 (1 H, d,  $J$  10, 18-H *anti*);  $\delta_C$  211.1 ( $2 \times C=O$ ), 160.0 ( $2 \times CO_2Me$ ), 135.4 (C-6, C-7), 131.4 (C-4', C-5'), 118.1 and 115.2 (C-15, C-2'), 57.6 (C-13, C-17), 54.2 (C-5, C-8), 53.3 ( $2 \times OMe$ ), 52.1 (C-19), 51.7 (C-1, C-12), 50.7 (C-2, C-11), 48.7 (C-4, C-9) and 31.6 (C-18).

**c Attempted retro-Diels Alder reaction of compound 134 using FVP**

Compound **134** (0.45 g, 0.84 mmol) was subjected to FVP at 500 °C. The product was washed out with dichloromethane which was then removed under reduced pressure. The product, a brown oil was applied to a preparative TLC plate. Using diethyl ether as the solvent a red and an orange band were produced. The bands were scraped off and the product extracted using dichloromethane. The solvent was removed from the filtrate, which was then subjected to NMR analysis. Fractions A and B both contained starting material plus a few other peaks.

**d Preparation of 11-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10,12-dithiatetracyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradeca-2,4,6-triene-3,6-diol **135** using a retro Diels Alder reaction<sup>103</sup>**

The product **134** (2.32 g, 4.34 mmol) was dissolved in xylene (100 cm<sup>3</sup>) and heated under reflux for 48 h. The colour of the solution had changed from orange-red to black. The solvent was removed and flash column chromatography (SiO<sub>2</sub>, 40-60° hexane/diethyl ether 40:60) was used to purify the crude product giving 4 fractions the last of which contained the pure product **135** (0.92 g, 45%) as an orange-red coloured solid, mp 186–188 °C (Found: C, 48.5; H, 3.2. C<sub>19</sub>H<sub>16</sub>O<sub>6</sub>S<sub>4</sub> requires C, 48.7; H, 3.4%);  $\nu_{max}/cm^{-1}$  1741, 1692, 1572, 1280, 1021 and 741;  $\delta_H$  6.48 (2 H, s, 4,5-H), 5.09 (2 H, br s, OH), 3.89 (2 H, s, 9,13-H), 3.84 (6 H,

s, 2 × OMe), 3.60 (2 H, d, *J* 1, 1,8-H), 2.18 and 1.89 (2 H, AB pattern, *J* 10, 14-H);  $\delta_C$  165.1(2 × CO), 160.1 (2 × CO<sub>2</sub>Me), 143.4 (C-3, C-6), 132.4 (C-4', C-5'), 131.5 (C-2, C-7), 119.7 (C-2' or C-11), 115.6 (C-4, C-5), 114.6 (C-2' or C-11), 60.9 (C-9, C-13), 53.3 (2 × OMe), 48.6 (C-1, C-8) and 42.7 (C-14).

**e Attempted oxidation of compound 135 using silver oxide**<sup>104</sup>

Compound **135** (0.28 g, 0.60 mmol) was dissolved in tetrahydrofuran (THF) giving a brown coloured solution. Silver oxide (0.56 g, 4.00 mmol) and magnesium sulfate (0.29 g, 1.32 mmol) were added to form a suspension. This mixture was stirred overnight at RT resulting in a brown coloured solution with suspended solids present. The solution was filtered using celite giving a brown coloured filtrate. The solvent was evaporated off under vacuum leaving a brown coloured oil (0.66 g). NMR and MS analysis indicated that it had a THF type structure. The singlet appearing at 6.48 ppm in the <sup>1</sup>H-NMR spectrum of the starting material was not present. The oil was applied to a preparative TLC plate and developed using THF as solvent which gave three bands. These were dissolved off the silica using a 95:5 ratio of dichloromethane:methanol with heating. NMR analysis showed only one of these bands to have some product. The spectrum was similar to that of the starting material but in addition there was a set of smaller peaks indicating the presence of butyrolactone from oxidation of the THF.

**f Attempted oxidation of compound 135 using CrO<sub>3</sub>**<sup>93</sup>

Compound **134** (0.14 g, 0.26 mmol) was dissolved in xylene and heated under reflux for 2 days. The solvent was removed leaving a dark red brown oily solid (0.22 g). Analysis of this solid indicated that the desired product **135** had been formed. The crude product was dissolved in acetic acid (10 cm<sup>3</sup>) with stirring. A solution of CrO<sub>3</sub> (2.00 g, 10.20 mmol)

dissolved in acetic acid (10 cm<sup>3</sup>) and water (2 cm<sup>3</sup>) was added dropwise to the solution, which was then allowed to stir for 48 h. The solvent was evaporated off leaving an oily black solid (4.33 g). The solid did not dissolve in CDCl<sub>3</sub> and d<sub>6</sub>-DMSO was used instead. The <sup>1</sup>H-NMR spectrum indicated that the oxidation had not occurred.

**g Attempted oxidation of compound 135 using benzoquinone<sup>45</sup>**

Compound **134** (0.16 g, 0.30 mmol) was heated in xylene under reflux for 2 days. The solvent was removed under reduced pressure and subsequent NMR analysis indicated that the desired product **135** had been formed. p-Benzoquinone (0.03 g, 0.30 mmol) was added and the solution was heated under reflux for 30 min. A TLC indicated that no reaction had occurred. The solution was heated under reflux for a further 24 hours but TLC analysis indicated that no reaction had occurred. The solvent was removed and NMR analysis showed that the starting material **135** was still present indicating that the oxidation had not occurred.

**h Preparation of 11-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-10,12-dithiatetracyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradeca-2(7),4-diene-3,6-dione **91**<sup>105</sup>**

The retro Diels-Alder product **135** (0.50 g, 1.07 mmol) and DDQ (0.24 g, 1.07 mmol) were dissolved together in toluene (100 cm<sup>3</sup>). The orange red solution was heated under reflux for 30 min by which time a dark red solution had formed with a precipitate in the bottom of the flask. The solution was filtered and the solvent was removed from the filtrate in vacuo leaving the crude product as a red-brown coloured oily solid. Flash column chromatography (SiO<sub>2</sub>, diethyl ether/hexane 70:30) gave 4 fractions one of which contained the product (0.32 g, 64%) as a dark green solid. The colour of the compound changed to dark red when dissolved in CDCl<sub>3</sub>. The product was recrystallised from ether and dichloromethane giving the pure product **91** (0.17 g, 34%) as shiny black crystals, mp 168-

170 °C (Found: C, 48.8; H, 2.7. C<sub>19</sub>H<sub>14</sub>O<sub>6</sub>S<sub>4</sub> requires C, 48.9; H, 3.0%);  $\nu_{\max}/\text{cm}^{-1}$  1737, 1651, 1576, 1259, 1090, 1031 and 723;  $\delta_{\text{H}}$  6.66 (2 H, s, HC=CH), 4.01 (2 H, d, *J* 2, 9,13-H), 3.84 (6 H, s, 2 × OMe), 3.54 (2 H, d, *J* 1, 1,8-H), 2.18 (1 H, half AB pattern of d, *J* 11, 1, 14-H) and 1.91 (1 H, half AB pattern, *J* 11, 14-H);  $\delta_{\text{C}}$  183.3 (2 × CO), 159.8 (2 × CO<sub>2</sub>Me), 151.7 (C-2, C-7), 136.1 (HC=CH), 131.3 (C-4', C-5'), 118.2 and 116.7 (C-11, C-2'), 59.3 (C-9, C-13), 53.3 (2 × OMe), 49.1 (C-1, C-8) and 42.2 (C-14); *m/z* 466 (M<sup>+</sup>, 46%), 320 (100), 275 (7), 231 (6), 181 (16), 146 (13), 131 (17), 102 (7) and 69 (40).

**i Preparation of 11-(1',3'-dithiol-2'-ylidene)-10,12-dithiahexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>9,13</sup>]tetradeca-2(7),4-diene-3,6-dione 143<sup>100</sup>**

The oxidised product **91** (0.15 g, 0.33 mmol) was dissolved with LiBr (0.14 g, 1.63 mmol) in DMA (15 cm<sup>3</sup>) and the solution was heated under reflux for 30 min. The solution was added to water (25 cm<sup>3</sup>) and allowed to stir for 10 min. The product was extracted using dichloromethane which was dried and evaporated. Kugelrohr distillation was used to remove any remaining DMA leaving the pure product **143** as a black solid (0.06 g, 55%); (HRMS: found M<sup>+</sup>, 350.9650. C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>S<sub>2</sub> requires M<sup>+</sup>, 350.9642),  $\nu_{\max}/\text{cm}^{-1}$  1603, 1543, 1278, 1154, 1019, 797 and 647;  $\delta_{\text{H}}$  6.48 (2 H, s, HC=CH), 6.26 (2 H, s, 4',5'-H), 3.98 (2 H, d, *J* 2, 9,13-H), 3.60 (2 H, t, *J* 2, 1,8-H) and 2.28 and 1.87 (2 H, AB pattern of d, *J* 10, 2, 14-H);  $\delta_{\text{C}}$  (in CDCl<sub>3</sub>) 118.6 (C-4,C-5), 115.5 (C-4', C-5'), 60.7 (C-9, C-13), 48.5 (C-1, C-8) and 42.8 (C-14),  $\delta_{\text{C}}$  (in d<sub>5</sub> pyridine) 145.4 (2 × C=O), 133.3 (C-2,C-7), 120.6 (C-2', C-11), 118.6 (C-4, C-5), 115.5 (C-4', C-5'), 115.2 (C-2', C-11), 60.7 (C-9, C-13), 48.5 (C-1, C-8) and 42.8 (C-14); *m/z* 351 (MH<sup>+</sup>, 45%), 350 (51), 265 (71), 219 (23) and 205 (100).

## 2 Attempted formation of the donor- $\sigma$ -acceptor compound using alternative routes

### a Preparation of *endo*-tricyclo[6.2.1.0<sup>2,7</sup>]undeca-4,9-diene-3,6-dione **148**<sup>106</sup>

*p*-Benzoquinone was purified by dissolving it in dichloromethane, filtering through celite and evaporating off the solvent to give shiny yellow crystals. Freshly distilled cyclopentadiene (8.30 cm<sup>3</sup>, 6.70 g, 0.10 mol) was added dropwise over 30 min to a stirred solution of *p*-benzoquinone (10.84 g, 0.10 mol) in dichloromethane (50 cm<sup>3</sup>). The solution was kept in an ice bath and was allowed to stir for 1 h. The ice bath was taken away and the solution was evaporated leaving a yellow-brown coloured liquid. Hexane was added dropwise until the solution became cloudy. The flask was cooled in ice for 10 min and then swirled, immediately producing a bright yellow coloured solid. This was washed with hexane (30 cm<sup>3</sup>) and allowed to dry in air. The product was recrystallised from methanol to give the pure product **148** (3.45 g, 20%) as yellow-brown needle shaped crystals, mp 70–71 °C (lit.,<sup>106</sup> 77–78 °C);  $\delta_{\text{H}}$  6.57 (2 H, s, HC=CH, 4,5-H), 6.07 (2H, t, *J* 2, HC=CH, 9,10-H), 3.56 (2 H, t, *J* 2, 1,8-H), 3.20 (2 H, dd, *J* 2, 1, 2,7-H), 1.55 (1 H, half AB pattern of d, *J* 9, 2, 11-H *syn*), 1.43 (1 H, half AB pattern, *J* 9, 11-H *anti*).

### b Improved preparation of *endo*-tricyclo[6.2.1.0<sup>2,7</sup>]undeca-4,9-diene-3,6-dione **148**<sup>107</sup>

Freshly distilled cyclopentadiene (8.30 cm<sup>3</sup>, 6.70 g, 0.10 mol) was added to a suspension of *p*-benzoquinone (10.84 g, 0.10 mol) in methanol at 0 °C. The ice bath was then removed and the flask was allowed to warm up to room temperature. The solution was allowed to stand for one hour but no crystals precipitated. Some of the solvent was removed and the solution was seeded which then produced crystals. The solution was filtered giving

the pure product **148** (13.53 g, 78%) as yellow-brown needles, mp 71–72 °C(lit.,<sup>107</sup> 76 °C);  $\delta_{\text{H}}$  as in **a** above.

**c Attempted formation of an unsaturated quinone adduct 150**<sup>93</sup>

Benzoquinone monocyclopentadiene adduct **148** (10.59 g, 0.06 mol) was dissolved in acetic anhydride (75 cm<sup>3</sup>) and heated under reflux at 150 °C for two hours. The brown coloured solution was allowed to cool overnight by which time crystals had come out of solution. This solution was filtered giving pale brown coloured crystals with red coloured needles present. These were washed with diethyl ether and then recrystallised from ethyl acetate. However an insoluble solid would not dissolve in ethyl acetate. The solution was filtered and the insoluble white solid was collected. No analysis could be carried out on the solid due to its insolubility in organic solvents. A second white solid precipitated out of the filtrate which was also collected. MS and NMR analysis suggested that the correct compound **149** had been formed but this was not confirmed using HRMS, mp 220 °C;  $\delta_{\text{H}}$  6.80 (2 H, d, *J* 1, HC=CH), 6.73 (2 H, d, *J* 1, HC=CH), 3.79 (4 H, s, 1,5,8,12-H), 2.33 (6 H, s, 2 × COMe) and 2.20 (4 H, s, 15,16-H), *m/z* 322 (76), 280 (34), 238 (100), 221 (19), 212 (13), 195 (17), 165 (14), 152 (7), 119 (11) and 91 (6).

The white solid was heated under reflux with KOH (2.00 g) in ethanol (15 cm<sup>3</sup>) for 20 minutes. The solution was left standing for three days but no crystals had precipitated out of solution. The solution was cooled in ice but no crystals precipitated out either. Water was added slowly until crystals appeared to precipitate out of solution. However a black gummy solid also began to precipitate out of the solution. Attempts to filter this solid off were unsuccessful and the solid clogged up the funnel. The synthesis was assumed to have been unsuccessful.

**d Preparation of 2,5-dichloro-1,4-benzoquinone 152**<sup>108</sup>

Hydrochloric gas was bubbled into concentrated hydrochloric acid (250 cm<sup>3</sup>) at 0 °C until no more was absorbed. Hydroquinone (50.00 g, 0.45 mol) was added and the suspension was stirred at 80 °C in a water bath. Potassium chlorate (37.00 g, 0.30 mol) was added very slowly and cautiously in small portions over 0.5 h. The stirrer was turned off and the mixture was left standing overnight. The resulting precipitate of dichlorohydroquinone **151** was filtered off, washed with water and sucked dry. The crude product **151** was stirred in 2 M H<sub>2</sub>SO<sub>4</sub> (500 cm<sup>3</sup>). Potassium dichromate (100.00 g, 0.34 mol) was dissolved in water (500 cm<sup>3</sup>) and added to the mixture which was then stirred continuously for 2 h. The solution was filtered giving a yellow solid with a phenolic smell, which was washed with water and then sucked dry. The solid was recrystallised from ethanol and acetone in a 3:1 ratio giving the pure product **152** (21.20 g, 27%) as shiny yellow platelets, mp 154–156 °C (lit.,<sup>108</sup> 161 °C);  $\delta_{\text{H}}$  7.13 (2 H, s, 3,6-H),  $\delta_{\text{C}}$  177.5 (C=O), 145.0 (C-2, C-5) and 133.4 (C-3, C-6).

**e Synthesis of 4-chlorotricyclo[6.2.1.0<sup>2,7</sup>]undeca-2(7),4,9-triene-3,6-dione 154**<sup>109</sup>

Freshly distilled cyclopentadiene (8.00 g, 0.12 mol) was added dropwise to a suspension of 2,5-dichlorobenzoquinone **152** (10.00 g, 56.60 mmol) in dichloromethane (80 cm<sup>3</sup>). The mixture was stirred at room temperature for 48 h giving a yellow coloured solution. The solvent was removed in vacuo leaving a brown coloured solid. This was taken up in hexane (20 cm<sup>3</sup>) and the solution was filtered leaving a clear yellow coloured solution. This solution was left standing overnight and the resulting crystals were filtered off giving the pure product 2,5-dichlorotricyclo[6.2.1.0<sup>2,7</sup>]undeca-4,9-diene-3,6-dione **153** (5.19 g, 38%) as yellow platelets, mp 96–98 °C (lit.,<sup>109</sup> 110–112 °C);  $\delta_{\text{H}}$  7.02 (1 H, d, *J* 3, 4-H), 6.21 (1 H, dd, *J* 6, 2, 10-H), 6.07 (1 H, dd, *J* 6, 3, 9-H), 3.62 (2 H, s, 1,8-H), 3.57 (2 H, d, *J* 1, 7-H) and 2.15 and 1.88 (2 H, AB pattern, *J* 9, 11-H);  $\delta_{\text{C}}$  189.7 (C-3), 188.0 (C-6), 150.1 (C-5),

138.6, 138.4 and 135.9 (C-4, C-9, C-10), 70.0 (C-2), 61.5 (C-7), 55.5 (C-1), 48.7 (C-8) and 47.0 (C-11). The product **153** (5.19 g, 21.26 mmol) was dissolved in dichloromethane (10 cm<sup>3</sup>) and subjected to flash column chromatography using alumina and dichloromethane giving the pure product **154** (4.06 g, 93%) as a yellow solid, mp 76–78 °C (lit.,<sup>88</sup> 76–78 °C);  $\delta_{\text{H}}$  6.88 (2 H, d, *J* 1, 9,10-H), 6.80 (1 H, s, 5-H), 4.16 (1 H, s, 1-H), 4.11 (1 H, s, 8-H), 2.38 and 2.32 (2 H, m, 11-H);  $\delta_{\text{C}}$  181.9 (C=O), 176.2 (C=O), 162.1 and 160.8 (C-2, C-7), 143.7 (C-4), 142.9 and 142.8 (C-9, C-10), 132.8 (C-5), 74.3 (C-11), 49.9 and 49.0 (C-1, C-8).

**f Synthesis of pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]hexadeca-2(11),4(9),6,13-tetraene-3,10-dione **144**<sup>110</sup>**

The previously made product **154** (3.00 g, 14.50 mmol) was dissolved in dichloromethane (30 cm<sup>3</sup>). Freshly distilled cyclopentadiene (1.06 g, 16.00 mmol) was added and the solution was allowed to stir over 3 days. The solvent was evaporated off and a bright yellow solid 2-chloropentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]hexadeca-4(9),6,13-triene-3,10-dione **155** (2.73 g, 10.00 mmol) was obtained. The solid was dissolved in dichloromethane and subjected to flash column chromatography using alumina and dichloromethane. This gave the pure product **144** (3.28 g) as a bright orange coloured solid, mp 172–176 °C (lit.,<sup>110</sup> 250 °C);  $\delta_{\text{H}}$  (mixture of two stereoisomers) 6.86 (4 H, t, *J* 3, 6,7,13,14-H), 6.82 (4 H, t, *J* 3, 6,7,13,14-H), 4.03 (8 H, m, 1,5,8,12-H), 2.38-2.32 (6 H, m, 15,16-H), 2.26 (2 H, d, *J* 9, 15,16-H),  $\delta_{\text{C}}$  (mixture of two stereoisomers) 180.0 (C-3, C-10), 160.0 (C-2, C-4, C-9, C-11), 142.4 and 142.3 (C-6, C-7, C-13, C-14), 73.9 and 73.8 (C-1, C-5, C-8, C-12) and 48.1 (C-15, C-16).

**g Attempted preparation of 8-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-7,9-dithiahexacyclo[13.2.1.1<sup>5,11</sup>.0<sup>2,14</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>]nonadeca-2(14),4(12),16-triene-3,13-dione 146**

Compound **144** (0.26 g, 1.11 mmol) and tri-*n*-butylphosphoniodithioformate (0.61 g, 2.22 mmol) were dissolved in dichloromethane (30 cm<sup>3</sup>). Carbon disulfide (0.17 g, 2.22 mmol) was added to the solution which was stirred for 4.5 h. DMAD (0.32 g, 2.22 mmol) was then added and the mixture was stirred overnight. The colour of the solution was still dark red. A TLC of the reaction mixture indicated that a change from the starting material had occurred. The solvent was removed under reduced pressure and a thick red oil remained. NMR analysis of the oil indicated that a byproduct **156** had been formed instead of the desired product **146**,  $\delta_{\text{H}}$  3.92 (3 H, s), 3.90 (3 H, s), 3.75 (3 H, s), 3.55 (3 H, s), 2.00-1.83 (6 H, m), 1.61-1.42 (12 H, m) and 0.90 (9 H, t);  $\delta_{\text{P}}$  50.3 (Bu<sub>3</sub>PO), 49.6 (Bu<sub>3</sub>PS), 23.1 (unknown) and 22.0 (byproduct).

**h Attempted preparation of 8-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-7,9-dithiahexacyclo[13.2.1.1<sup>5,11</sup>.0<sup>2,14</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>]nonadeca-2(14),4(12),16-triene-3,13-dione 146**

The same procedure was used as in **e** except acetonitrile was used instead of dichloromethane and DMAD was added after 24 h rather than 4.5 h. An insoluble solid precipitated from solution. The solution was filtered. The insoluble solid would not dissolve in CDCl<sub>3</sub>. The solvent was removed from the filtrate and NMR analysis of the residue indicated that the desired product may have been formed. Flash column chromatography (SiO<sub>2</sub>, diethyl ether) was used in an attempt to purify the product. However Bu<sub>3</sub>PS could not be separated from the product.

### 3 Formation of an unsaturated quinone adduct using another alternative route

#### a Preparation of tricyclo[6.2.1.0<sup>2,7</sup>]undeca-2(7),4,9-triene-3,6-dione **158**<sup>107</sup>

Compound **148** (25.00 g, 0.14 mol) was dissolved in ethyl acetate (500 cm<sup>3</sup>). Basic alumina (125.00 g) was added to the solution which was then stirred for two days with a mechanical stirrer. The alumina was filtered off and the solvent was removed under reduced pressure. Attempted crystallisation by removing the residual solvent or by adding toluene failed. It was therefore decided to proceed with the next step using the crude material. The crude brown product was dissolved with difficulty in dichloromethane (3000 cm<sup>3</sup>). Vanadium pentoxide (99.98 g, 0.55 mmol) was added to the solution and oxygen gas was bubbled through the solution for 5 days. Filtration of the solution gave an orange filtrate. This was evaporated to give a dark green coloured crude material. The crude product was purified using flash column chromatography (SiO<sub>2</sub>, hexane/diethyl ether 70:30) to give the pure product **158** (7.18 g, 29%) as a yellow orange solid, mp 62–63 °C (lit.,<sup>107</sup> 66 °C);  $\delta_{\text{H}}$  6.87 (2 H, *J* 2, HC=CH), 6.58 (2 H, s, HC=CH), 4.10 (2 H, dd, *J* 2, 1, 1,8-H), 2.33 and 2.27 (2 H, AB pattern of t, *J* 7, 2, 11-H).

#### b Preparation of pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]hexadeca-2(11),6,13-triene-3,10-dione **159**<sup>107</sup>

The compound **158** (3.50 g, 20.33 mmol) was dissolved in toluene (60 cm<sup>3</sup>) and the solution was kept at –78 °C. Freshly distilled cyclopentadiene (1.98 g, 30.00 mmol) was cooled to –78 °C and added to the solution. The stirred orange solution was transferred to an ice-water bath and allowed to warm up to room temperature. The solvent was removed leaving a yellow coloured solid which was washed with cyclohexane. NMR analysis indicated that the solid was a mixture of two isomers **159a,b**. The isomers were separated by repetitive recrystallisation in hot methanol. The endo-syn isomer **159a** (0.24 g, 5%) was

collected as yellow needles, mp 150–152 °C (lit.,<sup>107</sup> 155 °C);  $\delta_{\text{H}}$  6.78 (2 H, d,  $J$  2, 13,14-H), 5.79 (2 H, t,  $J$  2, 6,7-H), 3.97 (2 H, dd,  $J$  3, 2, 4,9-H), 3.49 (2 H, s, 1,12-H), 3.24 (2 H, d,  $J$  2, 5,8-H), 2.21 and 2.15 (2 H, AB pattern,  $J$  7, 15-H) and 1.49 and 1.41 (2 H, AB pattern,  $J$  9, 16-H).

**c Attempted preparation of pentacyclo[10.2.1.1<sup>5,8</sup>.0<sup>4,11</sup>.0<sup>4,9</sup>]hexadeca-2(11),4(9),6,13-tetraene-3,10-dione 160<sup>107</sup>**

The dione **159a** (0.10 g, 0.42 mmol) was dissolved in ethanol (15 cm<sup>3</sup>). Aqueous NaOH (2M) was added dropwise to the solution until it turned orange. This solution was allowed to stir for 5 min. Hydrochloric acid (2M) was added dropwise until the solution decolourised indicating that it had been neutralised. A saturated solution of FeCl<sub>3</sub> in ethanol (2 cm<sup>3</sup>) was added to the solution. The solution was then heated for 4 h without stirring. However no crystals precipitated from the solution. The organic product was extracted using dichloromethane which was dried and evaporated. NMR analysis of the residue indicated that the desired product may have been formed. Recrystallisation was attempted using ethanol but no crystals were obtained. The experiment was assumed to have failed.

**d Preparation tetracyclo[10.2.1.0<sup>2,11</sup>.0<sup>4,9</sup>]pentadeca-4(9),5,7,13-tetraene-3,10-dione 162**

1,4-Naphthoquinone was purified by dissolving it in dichloromethane, filtering off any insoluble material and evaporating. Cyclopentadiene (12.60 g, 0.19 mol) was added to a stirred solution of 1,4-naphthoquinone (30 g, 0.19 mol) in dichloromethane (50 cm<sup>3</sup>) in an ice bath. The ice bath was removed and the solution was left stirring for 24 h. The solvent was evaporated under reduced pressure leaving a solid. The crude product was recrystallised from hexane and ethyl acetate to give the pure product **162** (28.41 g, 67%) as pink needles, mp

110–111 °C (lit., <sup>111</sup> 108–9 °C);  $\delta_{\text{H}}$  8.01 (2 H, m, 5,8-H), 7.69 (2 H, m, 6,7-H), 5.98 (2 H, *J* 2, 14,15-H), 3.66 (2 H, m, 2,11-H), 3.46 (2 H, dd, *J* 2, 1, 1,12-H) and 1.59–1.54 (2 H, m, 15-H);  $\delta_{\text{C}}$  198.1 (C=O), 136.1 (C-4, C-9), 135.9 and 134.4 (C-5, C-6, C-7, C-8), 127.2 (C-13, C-14), 49.9 (C-1, C-2, C-11, C-12) and 49.6 (C-15).

**e Attempted preparation of 15-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-14,16-dithiapentacyclo[10.5.1.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]octadeca-4(9),5,7-triene-3,10-dione 163**

The dione **162** (2.00 g, 8.93 mmol) was dissolved in dichloromethane (40 cm<sup>3</sup>). Bu<sub>3</sub>PCS<sub>2</sub> (2.49 g, 8.93 mmol) and CS<sub>2</sub> (0.68 g, 8.93 mmol) were added to the solution which was allowed to stir overnight. DMAD (1.27 g, 8.93 mmol) was added to the solution which was then allowed to stir for 12 days. Flash column chromatography (SiO<sub>2</sub>, dichloromethane /hexane 50:50) of the crude product gave five fractions which consisted mostly of Bu<sub>3</sub>PO and of the starting material **162**.

**f Attempted preparation of 15-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-14,16-dithiapentacyclo[10.5.1.0<sup>2,11</sup>.0<sup>4,9</sup>.0<sup>13,17</sup>]octadeca-4(9),5,7-triene-3,10-dione 163**

The dione **162** (2.00 g, 8.93 mmol) was added to Bu<sub>3</sub>CS<sub>2</sub> (2.49 g, 8.93 mmol) in acetonitrile (60 cm<sup>3</sup>). CS<sub>2</sub> (0.68 g, 8.93 mmol) was added to the solution which was then allowed to stir overnight. DMAD (1.27 g, 8.93 mmol) was added to the solution which was stirred 24 hours. The crude product was purified using flash column chromatography (SiO<sub>2</sub>, hexane/dichloromethane 30:70, gradient elution dichloromethane /methanol 90:10) which gave 5 fractions the last of which appeared to contain the compound of interest. Kugelrohr distillation was used in an attempt to remove the Bu<sub>3</sub>PO but was unsuccessful. Further analysis on the unknown compound could not be carried out.

## **G Convenient two-step conversion of aldehydes into 2-arylmethylene-1,3-dithioles**

### **1 Synthesis of 1,3-dithiolanes via a Wittig reaction**

#### **a Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-phenylmethylene-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **173****<sup>92</sup>

The adduct **109** (2.30 g, 11.10 mmol) was added to a solution of tri-*n*-butylphosphoniodithioformate **92** (3.08 g, 11.10 mmol) in dichloromethane (30 cm<sup>3</sup>). Benzaldehyde (1.17 g, 11.10 mmol) was added after 30 min forming a red coloured solution and the solution was allowed to stir overnight. The solvent was evaporated off under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, dichloromethane 100%) was used to purify the crude product giving 2 fractions. The second one proved to be the pure product **173** (2.27 g, 55%) as a yellow coloured oil from which pale yellow platelets later formed, mp 78–80 °C (HRMS: Found  $M+H^+$ , 375.0724. C<sub>19</sub>H<sub>19</sub>O<sub>4</sub>S<sub>2</sub> requires  $M+H^+$ , 375.0725);  $\nu_{\max}/\text{cm}^{-1}$  1707, 1628, 1585, 1155, 1094, 1013, 970, 919, 748 and 690 ;  $\delta_{\text{H}}$  7.34 (5 H, s, Ar-H), 6.60 (1 H, s, =CH), 4.29 (1 H, d,  $J$  1, 2 or 6-H), 4.02 (1 H, d,  $J$  1, 2 or 6-H), 3.79 (3 H, s, OMe), 3.78 (3 H, s, OMe), 3.29 (2 H, m 1,7-H), 2.12 (1 H, half AB pattern of t,  $J$  10, 1, 10-H) and 1.81 (1 H, half AB pattern of t,  $J$  10, 2, 10-H);  $\delta_{\text{C}}$  164.1 and 164.0 (2  $\times$  C=O), 144.8 and 144.2 (C-8, C-9), 140.0 and 136.8 (Ar-C1', C-4), 128.2 (Ar-C-2, Ar-C-6), 127.7 (Ar-C-3, Ar-C-5), 126.3 (Ar-C-4), 117.4 (=CH), 60.1 and 54.2 (C-2, C-6), 53.9 and 53.8 (C-1, C-7), 52.2 and 52.1 (2  $\times$  OMe) and 41.4 (C-10);  $m/z$  375 ( $[M+H]^+$ , 100%), 317 (12), 301 (29), 287 (33), 235 (92), 219 (44), 192 (6) and 183 (15).

**b Preparation of 2,6-exo-(8,9-bis(methoxycarbonyl)-4-(3'-formylphenylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 175**

The substituted norbornadiene **109** (1.49 g, 7.20 mmol) was added to Bu<sub>3</sub>P·CS<sub>2</sub> **92** (2.00 g, 7.20 mmol) in dichloromethane (15 cm<sup>3</sup>). The solution was allowed to stir for a short time and isophthalaldehyde (0.96 g, 7.20 mmol) was then added and the solution was allowed to stir for 2 days. The solvent was removed under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, ethyl-acetate/hexane, 45:55) gave the product and some starting material in one fraction. The starting material **109** was removed using kugelrohr distillation giving the pure product **175** (1.64 g, 57%) as an oily brown solid (HRMS: Found M<sup>+</sup>, 402.0592. C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>S<sub>2</sub> requires M<sup>+</sup>, 402.0596);  $\nu_{\max}/\text{cm}^{-1}$  1712, 1625, 1566, 1150, 1093, 971 and 732;  $\delta_{\text{H}}$  10.02 (1 H, s, CHO), 7.89 (1 H, s, 2'-H), 7.70 (1 H, d, *J* 8, 4' or 6'-H), 7.59 (1 H, d, *J* 8, 4' or 6'-H), 7.50 (1 H, t, *J* 8, 5'-H), 6.60 (1 H, s, =CH), 4.31 (1 H, d, *J* 2, 2 or 6-H), 4.04 (1 H, d, *J* 2, 2 or 6-H), 3.81 (3 H, s, OMe), 3.80 (3 H, s, OMe), 3.38 (2 H, s, 1,7-H) and 2.17 and 1.90 (2 H, AB pattern of t, *J* 10, 1, 10-H);  $\delta_{\text{C}}$  192.2 (Ar-CO), 164.1 and 164.0 (2 × CO), 144.8 and 144.1 (C-8, C-9), 142.6, 137.8 and 136.4 (C-4, Ar-C-1, Ar-C-3), 133.4, 129.0, 128.6 and 127.2 (Ar-C-2, Ar-C-4, Ar-C-5, Ar-C-6), 115.4 (=CH), 60.4 and 54.5 (C-2, C-6), 53.9 and 53.8 (C-1, C-7), 52.3 (2 × OMe) and 41.4 (C-10), *m/z* 402 (M<sup>+</sup>, 13%), 234 (7), 220 (100), 178 (9), 151 (6), 122 (19) and 69 (13).

**c Preparation of 2,6-exo-(8,9-bis(methoxycarbonyl)-4-(4'-formylphenylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 174**

To a stirred solution of Bu<sub>3</sub>PCS<sub>2</sub> **92** (2.00 g, 7.20 mmol) in dichloromethane the carboxylated adduct **109** (1.49 g, 7.20 mmol) was added. This solution was allowed to stir for a short time and terephthalaldehyde (0.96 g, 7.20 mmol) was then added and the solution was

stirred for 2 days. The solvent was removed under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane 30:70) gave the product in two fractions, B (0.22 g) and C (1.88 g). B was slightly impure and kugelrohr distillation was used to remove the impurities. The two fractions were combined to give the pure product **174** (1.17 g, 41%) as yellow coloured oil from which crystals later formed mp 78–80 °C (Found: C, 59.3; H 4.8. C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>S<sub>2</sub> requires C, 59.7; H 4.5%) (HRMS: found M<sup>+</sup>, 402.0592. C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>S<sub>2</sub> requires M<sup>+</sup>, 402.0596);  $\nu_{\max}/\text{cm}^{-1}$  1717, 1549, 1161, 1093, 850 and 787;  $\delta_{\text{H}}$  9.95 (1 H, s, CHO), 7.84 (2 H, d, *J* 8, Ar-H), 7.48 (2 H, d, *J* 8, Ar-H), 6.57 (1 H, s, =CH), 4.37 (1 H, d, *J* 2, 2 or 6-H), 4.08 (1 H, d, *J* 2, 2 or 6-H), 3.813 (3 H, s, OMe), 3.808 (3 H, s, OMe), 3.36 (2 H, t, *J* 2, 1,7-H) and 2.13 and 1.91 (2 H, AB pattern of t, *J* 10, 2, 10-H);  $\delta_{\text{C}}$  191.3 (CHO), 164.0 and 163.9 (2 × CO), 145.3, 144.6, 143.9 and 142.7 (Ar-C-4', C-8, C-9, C-4), 133.5 (Ar-C-1'), 129.8 and 127.8 (Ar-C-2', C-6', C-3', C-5'), 115.3 (=CH), 60.7 and 54.5 (C-2, C-6), 53.8 and 53.7 (C-1, C-7), 52.2 (2 × OMe) and 41.4 (C-10); *m/z* 402 (M<sup>+</sup>, 15%), 234 (10), 220 (100), 178 (15), 122 (32) and 69 (18).

**d Preparation of 1',4'-phenylenebis(4-methylenyl-8,9-bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene) 176<sup>112</sup>**

The substituted norbornadiene **109** (1.50 g, 7.20 mmol) and Bu<sub>3</sub>PCS<sub>2</sub> **92** (2.00 g, 7.20 mmol) were dissolved in dichloromethane forming a red coloured solution which was allowed to stir for 30 minutes. Terephthalaldehyde (0.48 g, 3.60 mmol) was added to the solution, which was allowed to stir for 3 days. NMR analysis indicated that only the mono product had been formed. 2.5 molar equivalents of the 2 starting materials were added to the solution which was allowed to stir for a further 4 days and then evaporated. Flash column chromatography (SiO<sub>2</sub>, dichloromethane) gave the impure product. The impure product was rechromatographed (SiO<sub>2</sub>, hexane-diethyl ether, 1:1) giving 3 fractions one of which

contained the pure product **176** (0.20, 8%) as an oily brown solid,  $\delta_{\text{H}}$  7.31 (4 H, s, Ar-H), 6.53 (2 H, s, =CH), 4.29 (2 H, d,  $J$  2, 2 or 6-H), 4.00 (2 H, d,  $J$  2, 2 or 6-H), 3.800 (6 H, s, 2  $\times$  OMe), 3.795 (6 H, s, 2  $\times$  OMe), 3.32 (4 H,  $J$  2, 1,7-H), 2.12 (2 H, half AB pattern of d,  $J$  11, 2, 10-H) and 1.84 (2 H, half AB pattern of t,  $J$  11, 2, 10-H).

**e Preparation of 1',3'-phenylenebis(4-methylenyl-8,9-bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene) 177<sup>112</sup>**

The substituted norbornadiene **109** (1.50 g, 7.20 mmol) and  $\text{Bu}_3\text{P}\cdot\text{CS}_2$  **92** (2.00 g, 7.20 mmol) were dissolved in dichloromethane (15  $\text{cm}^3$ ) forming a red coloured solution which was allowed to stir for 30 minutes. Isophthalaldehyde (0.48 g, 3.60 mmol) was added to the solution, which was stirred for a further three days. NMR analysis indicated that only the mono product had been formed. 2.5 molar equivalents of each starting material were added to the solution and the solution was allowed to stir for a further 3 days and then evaporated. NMR analysis of the crude material indicated that the desired product had been formed. Flash column chromatography ( $\text{SiO}_2$ , dichloromethane 100%) gave the impure product. The impure product was rechromatographed ( $\text{SiO}_2$ , hexane/diethyl ether 40:60) and gave 3 fractions one of which contained the product **177** (0.07 g, 3%) as an oily brown solid,  $\delta_{\text{H}}$  7.32 (2 H, m, Ar-H), 7.20 (2 H, m, Ar-H), 6.56 (2 H, s, =CH), 4.30 (2 H, d,  $J$  2, 2 or 6-H), 4.01 (2 H, d,  $J$  2, 2 or 6-H), 3.803 (6 H, s, 2  $\times$  OMe), 3.795 (6 H, s, 2  $\times$  OMe), 3.33 (4 H, d,  $J$  1, 1,7-H), 2.13 (2 H, m, 10-H) and 1.85 (2 H, dm,  $J$  10, 10-H).

**f Preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(1'-butylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 178**

The adduct  $\text{Bu}_3\text{P}\cdot\text{CS}_2$  **92** (1.00 g, 3.60 mmol) and the substituted norbornadiene **109** (0.75 g, 3.60 mmol) were dissolved separately in dichloromethane (50  $\text{cm}^3$ ) and stirred

together in a round-bottomed flask for 20 minutes. Butyraldehyde (0.26 g, 3.60 mmol) was added and the red coloured solution was stirred for 4 days. The solvent was removed under reduced pressure and the crude product was purified using flash column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane 40:60) which gave 2 fractions one of which contained the pure product **178** (0.71 g, 58%) as a light brown coloured oil (HRMS: found M<sup>+</sup>, 340.0800. C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub> requires M<sup>+</sup>, 340.0803);  $\nu_{\max}/\text{cm}^{-1}$  1717, 1627, 1155, 1094, 923 and 786;  $\delta_{\text{H}}$  5.50 (1 H, t, *J* 7, =CH), 4.08 (1 H, d, *J* 2, 2 or 6-H), 3.98 (1 H, d, *J* 2, 2 or 6-H), 3.791 (3 H, s, OMe), 3.788 (3 H, s, OMe), 3.29 (1 H, d, *J* 2, 1 or 7-H), 3.27 (1 H, d, *J* 2, 1 or 7-H), 2.10 (3 H, m, 10,1'-H), 1.85 (1 H, half AB pattern of t, *J* 10, 2, 10-H), 1.42 (2 H, m, 2'-H) and 0.92 (3 H, t, *J* 7, 3'-H);  $\delta_{\text{C}}$  163.9 and 163.8 (2 × CO), 144.6 and 144.2 (C-8, C-9), 137.0 (C-4), 119.0 (=CH), 57.3 and 55.7 (C-2, C-6), 53.8 and 53.7 (C-1, C-7), 51.8 (2 × OMe), 41.2 (C-10), 34.5 (C-1'), 22.1 (C-2') and 13.3 (C-3'); *m/z* 340 (M<sup>+</sup>, 19%), 285 (6), 182 (17), 158 (100), 151 (21) and 129 (97).

**g Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(2'-thienylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 179**

The substituted norbornadiene **109** (1.00 g, 4.81 mmol) and Bu<sub>3</sub>PCS<sub>2</sub> **92** (1.34 g, 4.81 mmol) were dissolved separately in dichloromethane (15 cm<sup>3</sup>) and then added together forming a red coloured solution. This solution was allowed to stir for 1 h. Thiophene-2-carboxaldehyde (0.54 g, 4.81 mmol) was added to the solution, which was allowed to stir for a further 5 days. The reaction was monitored using TLC. Evaporation followed by flash column chromatography (SiO<sub>2</sub>, hexane/diethyl ether 70:30) gave 4 fractions one of which contained the pure product **179** (0.32 g, 18%) as a dark green oily solid (HRMS: found M<sup>+</sup>, 380.0224. C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S<sub>3</sub> requires M<sup>+</sup>, 380.0211);  $\nu_{\max}/\text{cm}^{-1}$  1724, 1626, 1572, 1262, 1154,

1093, 1019, 971, 733 and 699;  $\delta_{\text{H}}$  7.25 (1 H, dd,  $J$  5, 1, 3'-H), 7.01 (1 H, dd,  $J$  5, 4, 4'-H), 6.96 (1 H, dd,  $J$  4, 1, 5'-H), 6.72 (1 H, s, =CH), 4.31 (1 H, d,  $J$  2, 2 or 6-H), 4.06 (1 H, d,  $J$  2, 2 or 6-H), 3.80 (6 H, s, 2  $\times$  OMe), 3.36 (2 H, d,  $J$  2, 1,7-H) and 2.15 and 1.88 (2 H, AB pattern of t,  $J$  10, 2, 10-H);  $\delta_{\text{C}}$  163.8 and 163.7 (2  $\times$  CO), 144.6 and 144.0 (C-8, C-9), 140.6 and 137.8 (C-2', C-4), 126.8 (C-3'), 125.2 (C-4'), 124.4 (C-5'), 110.7 (=CH), 60.2 and 55.3 (C-2, C-6), 53.8 and 53.6 (C-1, C-7), 52.0 (2  $\times$  OMe) and 41.3 (C-10);  $m/z$  380 ( $M^+$ , 11%), 198 (41), 151 (12), 104 (100), 84 (22) and 59 (6).

#### **h Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(3'-thienylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 180**

The substituted adduct **109** (1.00g, 4.81 mmol) and  $\text{Bu}_3\text{PCS}_2$  **92** (1.34 g, 4.81 mmol) were dissolved separately in dichloromethane (15  $\text{cm}^3$ ) and then added together forming a red coloured solution which was allowed to stir for 1 h. Thiophene-3-carboxaldehyde (0.54 g, 4.81 mmol) was added to the solution, which was allowed to stir for 5 days. The reaction was monitored using TLC. Evaporation followed by flash column chromatography ( $\text{SiO}_2$ , hexane/diethyl ether 70:30) of the crude product gave 5 fractions one of which contained the pure product **180** (0.26 g, 14%) as a yellow oily solid (HRMS: found  $M^+$ , 380.0200.  $\text{C}_{17}\text{H}_{16}\text{O}_4\text{S}_3$  requires  $M^+$ , 380.0211);  $\nu_{\text{max}}/\text{cm}^{-1}$  1728, 1629, 1261, 1155, 1093, 911 and 736;  $\delta_{\text{H}}$  7.26 (1 H, dd,  $J$  5, 3, 4'-H), 7.22 (1 H, dd,  $J$  3, 1, 2'-H), 7.12 (1 H, dd,  $J$  5, 1, 5'-H), 6.55 (1 H, s, =CH), 4.27 (1 H, d,  $J$  2, 2 or 6-H), 4.02 (1 H, d,  $J$  2, 2 or 6-H), 3.79 (6 H, s, 2  $\times$  OMe), 3.32 (2 H, d,  $J$  1, 1,7-H), 2.14 (1 H, half AB pattern of t,  $J$  10, 1, 10-H) and 1.85 (1 H, half AB pattern of t,  $J$  10, 2, 10-H);  $\delta_{\text{C}}$  164.13 and 164.08 (2  $\times$  CO), 144.8 and 144.2 (C-8, C-9), 138.7 and 138.2 (C-4, C-3'), 127.7 (C-4'), 125.1 (C-2'), 121.6 (C-5'), 111.9 (=CH), 59.8

and 54.9 (C-2, C-6), 54.0 and 53.9 (C-1, C-7), 52.2 (2 × OMe) and 41.5 (C-10);  $m/z$  380 ( $M^+$ , 22%), 198 (100), 151 (9), 121 (8), 104 (18) and 59 (7).

**i Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(4'-pyridylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 181**

The substituted norbornadiene **109** (1.00 g, 4.81 mmol) and  $Bu_3PCS_2$  **92** (1.34 g, 4.81 mmol) were dissolved separately in dichloromethane (11 cm<sup>3</sup>) and then added together forming a red coloured solution. After 20 minutes pyridine-4-carboxyaldehyde (0.52 g, 4.81 mmol) was added to the solution which was allowed to stir for a further 5 days. The progress of the reaction was monitored using TLC. Evaporation followed by flash column chromatography (SiO<sub>2</sub>, hexane-diethyl ether, 1:1) of the crude product gave 5 fractions one of which contained the pure product **181** (0.26 g, 14%) as a yellow-brown oily solid (HRMS: found  $M^+$ , 375.0595. C<sub>18</sub>H<sub>17</sub>NO<sub>4</sub>S<sub>2</sub> requires  $M^+$ , 375.0599);  $\nu_{max}/cm^{-1}$  1731, 1629, 1594, 1570, 1262, 1155, 1093 and 733;  $\delta_H$  8.52 (2 H, d,  $J$  6, 2', 6'-H), 7.20 (2 H, d,  $J$  6, 3', 5'-H), 6.41 (1 H, s, =CH), 4.38 (1 H, d,  $J$  2, 2 or 6-H), 4.07 (1 H, d,  $J$  2, 2 or 6-H), 3.81 (6 H, s, 2 × OMe), 3.36 (2 H, d,  $J$  2, 1,7-H), 2.12 (1 H, half AB pattern of t,  $J$  10, 1, 10-H) and 1.92 (1 H, half AB pattern of t,  $J$  10, 2, 10-H);  $\delta_C$  164.1 and 164.0 (2 × CO), 149.7 (C-2', C-6'), 147.3 and 144.7 (C-4, C-4'), 144.0 and 143.7 (C-8, C-9), 121.7 (C-3', C-5'), 113.6 (=CH), 60.9 and 54.6 (C-2, C-6), 54.8 and 53.8 (C-1, C-7), 52.4 (2 × OMe) and 41.5 (C-10);  $m/z$  375 ( $M^+$ , 11%) and 193 (100).

**j Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(1'-naphthylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 182**

The substituted norbornadiene **109** (1.00 g, 4.81 mmol) and Bu<sub>3</sub>PCS<sub>2</sub> **92** (1.34 g, 4.81 mmol) were dissolved separately in dichloromethane (11 cm<sup>3</sup>) and formed a red coloured solution upon mixing. After 20 min 1-naphthaldehyde (0.75 g, 4.81 mmol) was added to the solution which was left stirring for a further 5 days and was monitored by TLC. Evaporation followed by flash column chromatography (SiO<sub>2</sub>, hexane/diethyl ether 1:1) gave 5 fractions of which the fourth one contained the impure product. This was then washed with diethyl ether to give the pure product **182** (0.30 g, 15%) as a pale yellow brown solid, mp 94–96 °C (HRMS: found M<sup>+</sup>, 424.0810. C<sub>23</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub> requires M<sup>+</sup>, 424.0803);  $\nu_{\max}/\text{cm}^{-1}$  1725, 1625, 1256, 1153, 1091 and 780;  $\delta_{\text{H}}$  8.05 (1 H, m, Ar-H), 7.81 (2 H, m, Ar-H), 7.49 (4 H, m, Ar-H), 7.17 (1 H, s, =CH), 4.19 (1 H, d, *J* 2, 2 or 6-H), 4.07 (1 H, d, *J* 2, 2 or 6-H), 3.81 (3 H, s, OMe), 3.77 (3 H, s, OMe), 3.38 (1 H, d, *J* 2, 1 or 7-H), 3.23 (1 H, d, *J* 2, 1 or 7-H), 2.16 (1 H, half AB pattern, *J* 10, 10-H) and 1.83 (1 H, half AB pattern of t, *J* 10, 2, 10-H);  $\delta_{\text{C}}$  164.23 and 164.16 (2 × CO), 144.8 and 144.5 (C-8, C-9), 142.3 (C-4), 134.5, 133.4 and 131.1 (C-1', C-4a', C-8a'), 128.5, 127.9, 127.6, 126.2, 126.0, 125.9, 125.2 and 124.0 (C-2', C-3', C-4', C-5', C-6', C-7', C-8'), 115.1 (=CH), 59.9 and 54.0 (C-2, C-6), 55.0 (C-1, C-7), 52.3 and 52.2 (2 × OMe) and 41.5 (C-10); *m/z* 424 (M<sup>+</sup>, 15%), 242 (60), 182 (19), 151 (22), 104 (100) and 59 (24).

**k Preparation of 2,6-*exo*-8,9-bis(methoxycarbonyl)-4-(2'-furylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 183**

The substituted norbornadiene **109** (2.00 g, 9.62 mmol) and Bu<sub>3</sub>PCS<sub>2</sub> **92** (2.68 g, 9.62 mmol) were dissolved separately in dichloromethane (15 cm<sup>3</sup>) and then mixed together

forming a red coloured solution. 2-Furaldehyde (0.92 g, 9.62 mmol) was added to the solution after 1 h and the reaction was then heated under reflux for 7 days. Evaporation followed by flash column chromatography (SiO<sub>2</sub>, hexane/diethyl ether, 80:20) gave 4 fractions one of which contained the pure product **183** (0.69 g, 20%) as a yellow oil (HRMS: found M<sup>+</sup>, 364.0432. C<sub>17</sub>H<sub>16</sub>O<sub>5</sub>S<sub>2</sub> requires M<sup>+</sup>, 364.0439);  $\nu_{\max}/\text{cm}^{-1}$  1718, 1625, 1261, 1154, 1093, 1019, 970, 925 and 733;  $\delta_{\text{H}}$  7.36 (1 H, dd, *J* 2, 0.5, 5'-H), 6.40 (1 H, dd, *J* 4, 2, 3'-H), 6.39 (1 H, d, *J* 0.5, =CH), 6.27 (1 H, d of t, *J* 4, 0.5, 4'-H), 4.26 (1 H, d, *J* 2, 2 or 6-H), 4.07 (1 H, d, *J* 2, 2 or 6-H), 3.79 (6 H, s, 2 × OMe), 3.34 (1 H, d, *J* 2, 1 or 7-H) and 3.32 (1 H, d, *J* 2, 1 or 7-H), 2.14 (1 H, half AB pattern of t, *J* 10, 1, 10-H) and 1.87 (1 H, half AB pattern of t, *J* 10, 2, 10-H);  $\delta_{\text{C}}$  164.1 and 164.0 (2 × C=O), 152.0 (C-2'), 144.6 and 144.2 (C-8, C-9), 141.0 (C-5'), 138.4 (C-4), 111.5 (C-3), 107.4 (=CH), 105.5 (C-4'), 59.8 and 55.6 (C-2, C-6), 53.9 and 53.8 (C-1, C-7), 52.2 and 52.1 (2 × OMe) and 41.4 (C-10); *m/z* 364 (M<sup>+</sup>, 28), 205 (7), 182 (100), 151 (18), 128 (11), 104 (72), 95 (6), 84 (10), 59 (9) and 49 (11).

#### **1 Preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(3'-furylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **184****

The substituted norbornadiene **109** (2.00 g, 9.62 mmol) and Bu<sub>3</sub>PCS<sub>2</sub> **92** (2.68 g, 9.62 mmol) were dissolved separately in dichloromethane (15 cm<sup>3</sup>). The two solutions were mixed together forming a red coloured solution. After 1 h 3-furaldehyde (0.92 g, 9.62 mmol) was added to the solution which was then heated under reflux for 7 days. Evaporation followed by flash column chromatography (SiO<sub>2</sub>, hexane-diethyl ether, 70:30) gave 6 fractions. There were 2 fractions containing the product (0.22 g, 6% estimated from <sup>1</sup>H NMR spectrum), one in an impure form and the second in a pure form both of which consisted of oils; (HRMS: found M<sup>+</sup>, 364.0434. C<sub>17</sub>H<sub>16</sub>O<sub>5</sub>S<sub>2</sub> requires M<sup>+</sup>, 364.0439);  $\nu_{\max}/\text{cm}^{-1}$  1731,

1624, 1271, 1153, 1020, 971, 910 and 735;  $\delta_{\text{H}}$  7.50 (1 H, apparent quintet,  $J$  2, 1, 1, 2'-H), 7.38 (1 H, t of d,  $J$  2, 0.5, 5'-H), 6.54 (1 H, apparent quintet,  $J$  2, 1, 1, 4'-H), 6.30 (1 H, s, =CH), 4.26 (1 H, d,  $J$  2, 2 or 6-H), 4.03 (1 H, d,  $J$  2, 2 or 6-H), 3.80 (6 H, s, 2  $\times$  OMe), 3.34 (1 H, d,  $J$  2, 1 or 7-H) and 3.32 (1 H, d,  $J$  2, 1 or 7-H), 2.14 (1 H, half AB pattern of d,  $J$  10, 1, 10-H) and 1.87 (1 H, half AB pattern of d,  $J$  10, 2, 10-H);  $\delta_{\text{C}}$  165.0 and 163.9 (2  $\times$  C=O), 144.6 and 144.0 (C-8, C-9), 142.5 and 140.0 (C-2', C-5'), 138.0 (C-4), 122.8 (C-3'), 109.7 (C-4'), 107.5 (=CH), 59.9 and 55.6 (C-2, C-6), 54.1 and 54.0 (C-1, C-7), 52.3 (2  $\times$  OMe) and 41.6 (C-10);  $m/z$  364 ( $\text{M}^+$ , 15%), 287 (7), 234 (18), 208 (17), 182 (77), 151 (35), 122 (56), 105 (100), 77 (28) and 59 (35).

**m Preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(3'-methyl-2'-thienylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 185**

The substituted norbornadiene **109** (2.00 g, 9.61 mmol) and  $\text{Bu}_3\text{PCS}_2$  **92** (2.68 g, 9.61 mmol) were dissolved together in dichloromethane (15  $\text{cm}^3$ ) forming a red coloured solution. This solution was allowed to stir for 1 h. 3-Methylthiophene-2-carboxaldehyde (1.21 g, 9.61 mmol) was added to the solution which was then heated under reflux for 6 days. Evaporation followed by flash column chromatography ( $\text{SiO}_2$ , hexane/diethyl ether 80:20) of the crude product gave 6 fractions the last of which contained the product and a side product (1.20 g). A preparative TLC plate was used in an attempt to separate the two products, both oils, which were identified as the pure product **A (185)** and a side product **B**, (**A**)  $\delta_{\text{H}}$  7.19 (1 H, d,  $J$  5, 5'-H), 6.81 (1 H, d,  $J$  5, 4'-H), 6.70 (1 H, s, =CH), 4.30 (1 H, d,  $J$  2, 2 or 6-H), 4.05 (1 H, d,  $J$  2, 2 or 6-H), 3.80 (3 H, s, Me), 3.37 (1 H, d,  $J$  2, 1 or 7-H) and 3.35 (1 H, d,  $J$  2, 1 or 7-H) and 2.16 and 1.86 (2 H, AB pattern of t,  $J$  10, 2, 10-H),  $\delta_{\text{C}}$  164.2 and 164.1 (2  $\times$  C=O), 144.4 (C-8, C-9), 140.5 (C-3'), 136.9 (C-4 or C-2'), 134.1 (C-4 or C-2'), 129.8 (C-5'), 123.6

(C-4'), 110.2 (=CH), 60.4 (C-2, C-6), 55.6 (C-1, C-7), 52.3 (CO<sub>2</sub>Me), 41.6 (C-10) and 14.2 (CH<sub>3</sub>).

(B)  $\delta_{\text{H}}$  4.16 and 4.09 (2 H, AB pattern,  $J$  11, 4-H), 4.02 (2 H, d,  $J$  2, 2,6-H), 3.80 (6 H, s, OMe), 3.28 (2 H, t,  $J$  2, 1,7-H) and 2.11 and 1.88 (2 H, AB pattern of t,  $J$  10, 2, 10-H);  $\delta_{\text{C}}$  164.4 (C=O), 59.9 (C-2, C-6), 52.9 (C-1, C-7), 52.2 (OMe) and 42.9 (C-10).

## **n Attempted preparation of 2,6-exo-8,9-bis(methoxycarbonyl)-4-(1'-methyl-2'-pyrrylmethylene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 186**

The substituted norbornadiene **109** (1.00 g, 4.81 mmol) and Bu<sub>3</sub>PCS<sub>2</sub> **92** (1.34 g, 4.81 mmol) were dissolved separately in dichloromethane (15 cm<sup>3</sup>) and were then mixed together forming a red coloured solution. This solution was allowed to stir for 1 h and 1-methylpyrrole-2-carboxaldehyde (0.52 g, 4.81 mmol) was added. The solution was allowed to stir for a further 18 days and the reaction was monitored by TLC. Evaporation and NMR analysis of the crude material showed that it only contained starting materials.

## **2 Synthesis of 2-substituted-1,3-dithioles via Flash Vacuum Pyrolysis of Wittig Products**

### **a Preparation of 2-benzylidene-1,3-dithiole 171**

The Wittig product **173** (0.23 g, 0.62 mmol) was subjected to FVP at 600 °C. A dark red coloured product (0.21 g) was produced in the cold trap. The crude product was purified by flash column chromatography (SiO<sub>2</sub>, distilled hexane/ether, 80:20) which gave four products. The first fraction contained the pure product **171** (0.02 g, 17%) as yellow needles, mp 78–80 °C (HRMS: Found  $M+H^+$ , 193.0150, C<sub>10</sub>H<sub>8</sub>S<sub>2</sub> requires  $M+H^+$  193.0146);  $\delta_{\text{H}}$  7.35 (2 H, t,  $J$  7, Ar-H), 7.25 (2 H, d,  $J$  7, Ar-H), 7.14 (1 H, t,  $J$  7, Ar-H), 6.55 (1 H, br s, =C-H), 6.34 (1 H, half AB pattern of d,  $J$  7, 1, H-C=C-H) and 6.28 (1 H, half AB pattern of d,  $J$  7, 2,

$H-C=C-H$ );  $\delta_C$  136.7 (Ar-C-1), 136.3 (C-2), 128.4 (Ar-C-2, Ar-C-6), 126.4 (Ar-C-3, Ar-C-5), 125.4 (Ar C-4), 117.34 and 117.28 (C-4, C-5) and 112.8 (C=CH);  $m/z$  193 ( $M+H^+$ , 100), 123 (9), 105 (6) and 57 (10).

**b Preparation of 2-(4'-formylbenzylidene)-1,3-dithiole 187**

The Wittig product **174** (0.11 g, 0.27 mmol) was subjected to FVP at 600 °C. A red coloured product collected in the cold trap. Part of the product was insoluble in  $CDCl_3$ . NMR analysis of the crude product indicated that the intended reaction had occurred. The solvent was removed in vacuo and the crude product was purified by flash column chromatography ( $SiO_2$ , distilled hexane/ethyl acetate, 80:20) giving the pure product **187** (0.01 g, 19%) as yellow needles, mp 117–119 °C (HRMS: Found  $M+H^+$ , 221.0086.  $C_{11}H_8OS_2$  requires  $M+H^+$  221.0095);  $\nu_{max}/cm^{-1}$  1678, 1597, 1546, 1518, 1166, 790 and 658;  $\delta_H$  9.94 (1 H, s, CHO), 7.87 and 7.36 (4 H, AB pattern,  $J$  9, Ar-H), 6.64 (1 H, t,  $J$  1, C=CH), 6.47 (1 H, half AB pattern of d,  $J$  7, 1, HC=CH) and 6.41 (1 H, half AB pattern of d,  $J$  7, 2, HC=CH);  $\delta_C$  191.3 (CHO), 142.5 (C-4'), 132.7 (C-2), 130.2 (Ar-C-2, Ar-C-6 or Ar-C-3, Ar-C-5), 129.2 (C-1'), 126.4 (Ar-C-2, Ar-C-6 or Ar-C-3, Ar-C-5), 118.2 and 118.0 (C-4, C-5) and 111.2 (C=CH);  $m/z$  221 ( $M+H^+$ , 100%) and 57 (20).

**c Attempted preparation of 1',4'-phenylenebis(2-methylenyl-1,3-dithiole) 189**

The Wittig product **176** (0.10 g, 0.15 mmol) was subjected to FVP at 600 °C. A red-brown coloured product collected in the cold trap. NMR analysis of the crude material indicated that the reaction might have occurred. Preparative TLC ( $SiO_2$ , dichloromethane-hexane, 90:10) of the crude material gave 4 fractions none of which contained the desired product.

**d Attempted preparation of 1',3'-phenylenebis(2-methylenyl-1,3-dithiole) 190**

The Wittig product **177** (0.06, 0.09 mmol) was subjected to FVP at 600 °C. A red-brown coloured product formed in the cold trap. NMR analysis of the crude product indicated that the desired product had not been formed.

**e Attempted preparation of 2-butyridene-1,3-dithiole 191**

The Wittig product **178** (0.20 g, 0.59 mmol) was subjected to FVP at 600 °C. A red coloured product was produced in the cold trap. NMR analysis showed the product to be made up mainly of the substituted cyclopentadiene. The black oil remaining in the FVP tube was insoluble in CDCl<sub>3</sub>. It was therefore assumed that the desired reaction had not occurred.

**f Preparation of 2-(2'-thienylmethylene)-1,3-dithiole 192**

The Wittig product **179** (0.23 g, 0.61 mmol) was subject to FVP at 600 °C. A red coloured product collected in the cold trap. Flash column chromatography (SiO<sub>2</sub>, hexane/diethyl ether 80:20) gave 2 fractions the first of which contained the pure product **189** (0.02 g, 17%) as an oily red solid (HRMS: Found  $M^+$ , 197.9631. C<sub>8</sub>H<sub>6</sub>S<sub>3</sub> requires  $M^+$  197.9632);  $\delta_H$  7.22 (1 H, dd,  $J$  5, 1, 3'-H), 7.04 (1 H, dd,  $J$  5, 4, 4'-H), 6.89 (1 H, dd,  $J$  4, 1, 5'-H), 6.78 (1 H, s, =CH) and 6.30 (2 H, s, HC=CH);  $\delta_C$  134.9 (C-2'), 132.4 (C-2), 127.3 (C-3'), 123.03 (C-4'), 123.00 (C-5') 117.94 and 117.91 (C-4, C-5) and 106.4 (=CH);  $m/z$  198 ( $M^+$ , 100%), 153 (16), 140 (20), 122 (11), 96 (20), 84 (17), 55 (13) and 45 (11).

**g Preparation of 2-(3'-thienylmethylene)-1,3-dithiole 193**

The Wittig product **180** (0.24 g, 0.63 mmol) was subjected to FVP at 600 °C. A red coloured product collected in the cold trap. Flash column chromatography (SiO<sub>2</sub>, hexane-

diethyl ether, 80:20) of the crude product gave two fractions the first of which contained the pure product **193** (0.03 g, 24%) as red-brown platelets, mp 74–76 °C (HRMS: Found  $M+H^+$ , 198.9706.  $C_8H_6S_3$  requires  $M+H^+$  198.9710);  $\nu_{\max}/\text{cm}^{-1}$  1645, 1548, 1291, 1065, 1026, 920, 741, 698 and 651;  $\delta_H$  7.29 (1 H, dd,  $J$  5, 3, 4'-H), 7.09 (1 H, dd,  $J$  3, 1, 2'-H), 7.06 (1 H, dd,  $J$  5, 1, 5'-H), 6.61 (1 H, dd,  $J$  2, 1, =CH), 6.33 (1 H, half AB pattern of d,  $J$  7, 1, 4,5-H) and 6.28 (1 H, half AB pattern of d,  $J$  7, 2, 4,5-H);  $\delta_C$  138.3 (C-3'), 135.5 (C-2), 127.4 (C-4'), 125.0 (C-2'), 119.0 (C-5'), 117.7 and 117.2 (C-4, C-5) and 107.5 (=CH);  $m/z$  199 ( $M+H^+$ , 100).

#### **h Preparation of 2-(4'-pyridylmethylene)-1,3-dithiole 194**

The Wittig product **181** (0.23 g, 0.60 mmol) was subjected to FVP at 600 °C. A red coloured product was collected in the cold trap. Flash column chromatography ( $\text{SiO}_2$ , hexane-diethyl ether, 90:10) of the crude material gave 2 fractions the second of which contained the pure product **194** (0.002 g, 2%) as an oily solid,  $\delta_H$  8.53 (1 H, dd,  $J$  5, 2, 2',6'-H), 7.14 (1 H, dd,  $J$  5, 2, 3',5'-H), 6.52 (1 H, dd,  $J$  2, 1, =CH), 6.49 (1 H, half AB pattern of d,  $J$  7, 1, HC=CH) and 6.46 (1 H, half AB pattern of d,  $J$  7, 2, HC=CH);

#### **i Preparation of 2-(1'-naphthylmethylene)-1,3-dithiole 195**

The Wittig product **182** (0.20 g, 0.46 mmol) was subjected to FVP at 600 °C. A red coloured product formed in the cold trap. Flash column chromatography ( $\text{SiO}_2$ , hexane/diethyl ether 80:20) gave 2 fractions the first of which contained the pure product **195** (0.06 g, 52 %) as a red coloured solid, mp 59–61 °C, (HRMS: Found  $M^+$ , 242.0216.  $C_{14}H_{10}S_2$  requires  $M^+$  242.0224);  $\nu_{\max}/\text{cm}^{-1}$  1550, 1250, 1090, 800, 771, 727, 645 and 600;  $\delta_H$  8.03-7.44 (7 H, m, Ar-H), 7.11 (1 H, s, =CH), 6.30 (1 H, half AB pattern,  $J$  7, 4 or 5-H)

and 6.16 (1 H, half AB pattern of d,  $J$  7, 2, 4 or 5-H);  $\delta_C$  139.1, 134.4, 133.7, 130.6 (C-2, C-1', C-4a', C-8a'), 128.5, 126.8, 125.9, 125.4, 123.8, 123.3 (Ar-C-2' to Ar-C-8'), 117.3 and 116.9 (C-4, C-5) and 109.9 (=CH);  $m/z$  242 ( $M^+$ , 100), 209 (17), 184 (8), 171 (8), 165 (14), 152 (35), 139 (13), 121 (9), 86 (35) and 84 (38).

#### **j Preparation of 2-(2'-furylmethylene)-1,3-dithiole 196**

The Wittig product **183** (0.40 g, 1.11 mmol) was subjected to FVP at 600 °C. A brightly red coloured product had collected in the trap. NMR analysis indicated that the reaction had worked. Flash column chromatography (SiO<sub>2</sub>, hexane/diethyl ether 80:20) of the crude product gave 2 fractions, one of which contained the impure product **196** (0.04 g);  $\delta_H$  7.38 (1 H, dd,  $J$  2, 1, 5'-H), 6.45 (1 H, s, =CH), 6.43 (1 H, dd,  $J$  3, 2, 3'-H), 6.31 (2 H, d,  $J$  2, HC=CH) and 6.12 (1 H, dt,  $J$  3, 1, 4'-H);  $\delta_C$  152.3 (C-2'), 140.5 (C-5'), 135.1 (C-2), 118.4 and 118.3 (C-4, C-5), 111.6 (C-3'), 105.3 (=CH) and 101.5 (C-4').

The second contained an unknown product (0.03 g),  $\delta_C$  159.0, 136.7, 131.4, 122.4 and 121.8, 117.5, 108.9, 100.4 and 53.0

#### **k Preparation of 2-(3'-furylmethylene)-1,3-dithiole 197**

The Wittig product **184** (0.53 g, 1.46 mmol) was subjected to FVP at 600 °C. A red coloured product collected in the cold trap. Flash column chromatography (SiO<sub>2</sub>, hexane/diethyl ether 90:10) gave 3 fractions the first of which contained the impure product **197** (0.18 g) as an oily solid,  $\delta_H$  7.47 (1 H, dd,  $J$  2, 1, 2' or 5'-H), 7.39 (1 H, t,  $J$  2, 2' or 5'-H), 6.45 (1 H, dd,  $J$  2, 1, =CH), 6.29 (2 H, s, HC=CH) and 6.05 (1 H, s, 3'-H);  $\delta_C$  142.7 (C-2' or C-5'), 138.8 (C-2' or C-5'), 117.9 and 117.5 (C-4, C-5), 109.6 (=CH) and 103.2 (C-4'), C-3' and C-2 not apparent.

## **l      Attempted preparation of 2-(3'-methyl(-2'-thienylmethylene)-1,3-dithiole 198**

The Wittig product **185** (0.41 g, 1.05 mmol) was subjected to FVP at 600 °C. A red coloured product was collected in the cold trap. Flash column chromatography (SiO<sub>2</sub>, hexane-diethyl ether, 90:10) gave two fractions, the second of which contained the desired product **198** in an impure form. A preparative TLC plate (SiO<sub>2</sub>, hexane-diethyl ether, 90:10) was used in an attempt to purify the product. Two fractions were obtained. The NMR spectra indicated that the product had been formed but were not clear enough to distinguish the correct peaks for the compound.

## **m      Attempted decarboxylation of 173**

The Wittig product **173** (0.50 g, 1.34 mmol) and LiBr 1.16 g, 13.4 mmol) were heated under reflux together in DMA (30 cm<sup>3</sup>) for 30 minutes. The flask was immediately cooled in water and the contents added to water (10 cm<sup>3</sup>). This solution was allowed to stir for 10 minutes. The product was extracted with dichloromethane giving a brown coloured liquid. The solvent was removed and a brown oily liquid remained which solidified overnight. The pale brown coloured solid (0.93 g) was only slightly soluble in CDCl<sub>3</sub> and the <sup>1</sup>H NMR spectrum was obtained using d<sub>6</sub>-DMSO. This showed tiny amounts of starting material present. It was assumed that the reaction had failed.

## **H      Reaction of Bu<sub>3</sub>P with DMAD and various heterocumulenes.**

### **1      Preparation of diphenylcarbodiimide<sup>113</sup>**

Triphenylphosphine (31.40 g, 0.12 mol), *N,N'*-diphenylurea (21.20 g, 0.10 mol), triethylamine (10.10 g, 0.10 mol) and carbon tetrachloride (15.4 g, 0.10 mol) were heated in dichloromethane (50 cm<sup>3</sup>) at 40 °C for 1 h with stirring. The solids dissolved giving a clear yellow brown solution. The solution was left stirring for 1.5 h by which time most of the

Et<sub>3</sub>N<sup>+</sup>H Cl<sup>-</sup> had crystallised out of the solution. The solvent was evaporated off. Pet. ether (4 × 20 cm<sup>3</sup>) was added to the solid and heated and the mixture was stirred vigorously. The mixture was filtered and the filtrate evaporated leaving the crude product (15.41 g). Kugelrohr distillation of this gave the pure product (11.29 g, 59%) as a yellow liquid, δ<sub>H</sub> 7.16 (10 H, m, Ar-H); δ<sub>C</sub> 138.3 (Ar-C-1), 135.0 (C=N), 129.3 (Ar-C-2, Ar-C-6), 125.4 (Ar-C-4) and 124.0 (Ar-C-3, Ar-C-5).

## 2 Reaction of Bu<sub>3</sub>P and DMAD with phenyl isocyanate

Tri-*n*-butylphosphine (2.02 g, 10.00 mmol) was dissolved in dichloromethane (10 cm<sup>3</sup>) and DMAD (1.42 g, 10.00 mmol) was added. The solution began to react vigorously and more dichloromethane (10 cm<sup>3</sup>) was added. After 10 min phenyl isocyanate (0.60 g, 5.00 mmol) was added and the solution was stirred overnight. The solvent was removed under reduced pressure and the crude product was purified using flash column chromatography (SiO<sub>2</sub>, diethyl ether/ethyl acetate, 90:10, gradient elution to ethyl acetate-methanol 90:10). Five fractions were obtained one of which contained the product of interest (0.59 g) as dark brown crystals. These were recrystallised from diethyl ether giving the pure product **203** 5-tri-*n*-butylphosphonio-5-methoxy-2,3,4-tri(methoxycarbonyl)cyclopent-2-en-1-on-4-ide (0.24 g, 3 %) as dark yellow prisms, mp 138–140 °C (Found: C, 59.6; H, 8.2. C<sub>25</sub>H<sub>39</sub>O<sub>8</sub>P requires C, 59.2; H, 8.1%); ν<sub>max</sub>/cm<sup>-1</sup> 1737, 1664, 1519, 1238, 1103, 1026, 914 and 731; δ<sub>H</sub> 3.94 (3 H, s, CO<sub>2</sub>Me), 3.74 (3 H, s, CO<sub>2</sub>Me), 3.68 (3 H, s, CO<sub>2</sub>Me), 3.23 (3 H, s, OMe), 2.21 (6 H, m, Bu), 1.50 (12 H, m, Bu) and 0.96 (9 H, t, *J* 7, Bu); δ<sub>C</sub> 188.5 (d, *J* 3, C-1), 167.5 (3-CO), 165.1 (d, *J* 10, 4-CO), 163.5 and 162.1 (each d, *J* 1, 2-CO and C-3), 101.1 (C-2), 93.5 (d, *J* 2, C-4), 85.4 (d, *J* 64, C-5), 53.6 (d, *J* 13, 5-OMe), 52.1 (OMe), 50.8 (OMe), 50.6

(OMe), 24.14 (d, *J* 5, C-2'), 24.05 (d, *J* 15, C-3'), 16.5 (d, *J* 43, C-1') and 13.2 (d, *J* 1, C-4');  $\delta_p$  36.9; *m/z* 487 (M+H<sup>+</sup>, 5%), 285 (84), 253 (53), 219 (13) and 203 (100).

### 3 Reaction of Bu<sub>3</sub>P and DMAD with phenyl isothiocyanate

DMAD (2.84 g, 20.00 mmol) was added dropwise to tri-*n*-butylphosphine (2.02 g, 10.00 mmol) in dichloromethane (50 cm<sup>3</sup>) at 0 °C. The solution turned dark red and was allowed to stir for 1 h. Phenyl isothiocyanate (1.35 g, 10.00 mmol) was added and the solution was allowed to stir for 4 days and monitored by TLC. After the solvent was removed the crude product was purified by flash column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane, 1:1) which gave 6 fractions and using 100% ethyl acetate gave 2 more fractions one of which contained the product of interest (0.68 g). The crude product was recrystallised from diethyl ether giving the pure product **203** (0.39 g, 4.0 %) as yellow green prisms, mp 143–144 °C (Found: C, 59.4; H, 8.4. C<sub>25</sub>H<sub>39</sub>O<sub>8</sub>P requires C, 59.2; H, 8.1%); spectroscopic data as in 2.

### 4 Reaction of Bu<sub>3</sub>P and DMAD with dicyclohexylcarbodiimide

DMAD (2.84 g, 20.00 mmol) and tri-*n*-butylphosphine (2.02 g, 10.00 mmol) were reacted together in dichloromethane (50 cm<sup>3</sup>) at 0 °C. A dark red coloured solution was formed which was stirred for 1 h. Diphenylcarbodiimide (1.94 g, 10.00 mmol) was added and the mixture was stirred for 4 days. The solvent was removed and flash column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane 60:40, gradient elution to ethyl acetate) gave 6 fractions the first one contained diphenylcarbodiimide (1.90 g) and the last fraction contained the product of interest (1.23 g). The product was recrystallised from diethyl ether giving the pure product **203** (0.34 g, 4%) as yellow-brown prisms; mp 143–144 °C (Found: C, 59.4; H, 8.5 C<sub>25</sub>H<sub>39</sub>O<sub>8</sub>P requires C, 59.2, H, 8.1%); spectroscopic data as in 2.

## 5 Reaction of Bu<sub>3</sub>P and DMAD alone

DMAD (2.84 g, 20.00 mmol) was dissolved in dichloromethane (50 cm<sup>3</sup>) and tri-*n*-butylphosphine (2.02 g, 10.00 mmol) was added dropwise to the solution. The solution turned to a red colour and was allowed to stir for 2 days. The solvent was removed and the residue purified using flash column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane 1:1). The % yield of the product **203** (0.42 g, 4%) in the crude mixture was estimated using <sup>1</sup>H-NMR with nitromethane acting as an internal standard.

## 6 Reaction of Ph<sub>3</sub>P and DMAD alone<sup>114</sup>

Triphenylphosphine (2.00 g, 7.60 mmol) was added dropwise to DMAD (2.12 g, 14.90 mmol) in diethyl ether (30 cm<sup>3</sup>). A thick yellow-brown mixture formed which was heated under reflux for 1 h. This mixture was filtered and the solid washed with diethyl ether leaving a yellow-brown powder (3.50 g, mp 185–200 °C). This was purified using column chromatography (100% ethyl acetate) giving two products, the major product **210** (38%);  $\delta_{\text{P}}$  49.5 and the minor product **209** 2-methoxy-2,3,4-tri(methoxycarbonyl)-5-triphenylphosphoranylidene-cyclopent-3-en-1-one (13%) as yellow prisms, mp 224–226 °C (lit.,<sup>114</sup> 222–224 °C);  $\delta_{\text{H}}$  7.70–7.45 (15 H, m), 3.78 (3 H, s), 3.67 (3 H, s), 3.42 (3 H, s) and 3.10 (3 H, s, 2-OMe);  $\delta_{\text{C}}$  194.9 (d, *J* 8, CO), 168.0, 166.1 and 162.2 (3 × CO<sub>2</sub>Me), 160.0 (d, *J* 14, C-4), 134.0 (d, *J* 10, Ph C-2), 133.2 (Ph C-4), 128.9 (d, *J* 13, Ph C-5), 121.9 (d, *J* 93, Ph C-1), 107.4 (d, *J* 10, C-3), 87.0 (d, *J* 13, C-2), 70.6 (d, *J* 119, P=C), 52.3 (2 × OMe), 51.7 (OMe) and 51.0 (OMe);  $\delta_{\text{P}}$  11.7.

## **I Ring Opening Metathesis Polymerisation of Norbornene-Fused Dihydrotetrathiafulvalenes.**

### **1 Polymerisation of norbornene using “first generation” catalyst **217****<sup>115,116</sup>

Norbornene (0.02 g, 0.24 mmol) was dissolved in dichloromethane (10 cm<sup>3</sup>). Ru(Cl)<sub>2</sub>(=CHPh)(PPh<sub>3</sub>)<sub>2</sub> (0.01 g, 0.12 μmol) was dissolved in dichloromethane (10 cm<sup>3</sup>) and added to the solution under nitrogen. The solution was allowed to stir overnight and was then exposed to air. Ethyl vinyl ether (5 mg) and 2,6-di-*t*-butyl-4-methylphenol (5 mg) were added to terminate the reaction. The solution was filtered through a short column of silica and the solvent was removed under reduced pressure leaving a clear rubbery polymer, δ<sub>H</sub> 5.34 (2 H, s), 5.20 (2 H, s), 2.80 (2 H, br s), 2.43 (2 H, br s), 1.85-1.77 (6 H, br m), 1.35 (4 H, m) and 1.04 (2 H, m). This was compared with a previously published <sup>1</sup>H NMR spectrum and was shown to be in good agreement.<sup>115</sup>

### **2 Polymerisation of norbornene using “second generation” catalyst**<sup>115,116</sup>

Norbornene (0.02 g, 0.24 mmol) was dissolved in dichloromethane (10 cm<sup>3</sup>). The “second generation” Grubbs catalyst **216b** (0.01 g, 0.12 μmol) was dissolved in dichloromethane (10 cm<sup>3</sup>) and added to the solution under nitrogen. The colour of the solution turned red. The solution was allowed to stir overnight and was then exposed to air. Ethyl vinyl ether (5 mg) and 2,6-di-*t*-butyl-4-methylphenol (5mg) were added with dichloromethane to stop the reaction proceeding any further. The solution was filtered through a short column of silica and the solvent was removed under reduced pressure leaving a colourless rubbery polymer, δ<sub>H</sub> 5.34 (2 H, s), 5.20 (2 H, s), 2.80 (2 H, br s), 2.43 (2 H, br s), 1.85-1.77 (6 H, br m), 1.35 (4 H, m) and 1.04 (2 H, m). This was compared with a previously published <sup>1</sup>H NMR spectrum and was shown to be in excellent agreement.<sup>115</sup>

### 3 Polymerisation of 2,6-*exo*-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **106**

The dihydrotetrathiafulvalene **106** (0.10 g, 0.24 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>) under nitrogen. The “second generation” Grubbs catalyst **216b** (0.01 g, 11.9 μmol) was dissolved in dichloromethane (5 cm<sup>3</sup>) and added to the solution under nitrogen. The solution was allowed to stir for 3 h. Then 2,6-di-*t*-butyl-4-methylphenol (5 mg) and ethyl vinyl ether (5 mg) were added to terminate the polymerisation. The solution was filtered using a short silica gel column and the solvent was removed under reduced pressure. There was still some 2,6-di-*t*-butyl-4-methylphenol present in the product according to the <sup>1</sup>H NMR spectrum. An attempt was made to remove this using chloroform and dichloromethane but this proved unsuccessful.

### 4 Polymerisation of 2,6-*exo*-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **106**

The dihydrotetrathiafulvalene **106** (0.10 g, 0.24 mmol) was dissolved in dichloromethane (5 cm<sup>3</sup>) under nitrogen. The “second generation” Grubbs catalyst **216b** (0.04 g, 47.73 μmol) was dissolved in dichloromethane (5 cm<sup>3</sup>) and added to the solution. The solution was allowed to stir for 3 h. Then 2,6-di-*t*-butyl-4-methylphenol (5 mg) and ethyl vinyl ether (5 mg) were added. The solution was filtered using a short silica column and the solvent was removed under reduced pressure. NMR analysis indicated that the polymerisation had occurred but the product could not be analysed any further due to its insolubility.

## 5 Copolymerisation of 2,6-*exo*-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **106** with norbornene

The dihydrotetrathiafulvalene **106** (0.04 g, 0.09 mmol) and norbornene (0.04 g, 0.45 mmol) were dissolved in dichloromethane (5 cm<sup>3</sup>) under nitrogen. The “second generation” Grubbs catalyst **216b** (0.004 g, 4.48 μmol) was dissolved in dichloromethane (5 cm<sup>3</sup>) and added to the solution. This solution was allowed to stir for 3 h and then 2,6-di-*t*-butyl-4-methylphenol (5 mg) and ethyl vinyl ether (5 mg) were added. The solution was filtered using a short silica column and the solvent was removed under reduced pressure leaving the product (0.06 g) as a sticky orange coloured solid **218**. NMR analysis indicated that the polymerisation had occurred.

## 6 Copolymerisation of 2,6-*exo*-4-(4'-ethoxycarbonyl-5'-phenyl-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene **106** with norbornene

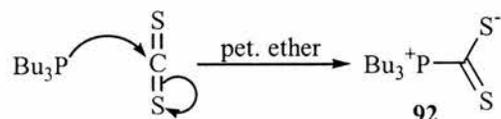
The dihydrotetrathiafulvalene **106** (0.05 g, 0.12 mmol) and norbornene (0.06 g, 0.60 mmol) were dissolved in dichloromethane (5 cm<sup>3</sup>) under nitrogen. The “second generation” Grubbs catalyst **216b** (0.005 g, 5.97 μmol) was dissolved in dichloromethane and then added to the solution which was allowed to stir for 3 h. The solution was then filtered through a short silica column into methanol with stirring. The solvent was removed leaving an orange coloured solid **218**;  $\nu_{\max}/\text{cm}^{-1}$  1727, 1700, 1287, 1254, 1198, 969 and 737;  $\delta_{\text{H}}$  7.38 (s), 5.34 (s), 4.09 (br m), 2.80 (br s), 2.44 (br s), 1.80 (br m), 1.34 (br s) and 1.10–1.00 (br m);  $\delta_{\text{C}}$  159.5 (C=O), 134.0 and 133.8 (C=C), 133.0 and 132.9 (C=C), 131.7 (Ar-C-1), 129.5 (Ar-C-4), 128.9 (Ar-C-2, Ar-C-6), 128.1 (Ar-C-3, Ar-C-5), 61.5 (CO<sub>2</sub>Et), 44.4, 44.3, 42.1, 38.6, 38.4, 33.1, 32.9, 32.3, 32.2 and 13.9 (CO<sub>2</sub>Et).

## **DISCUSSION**

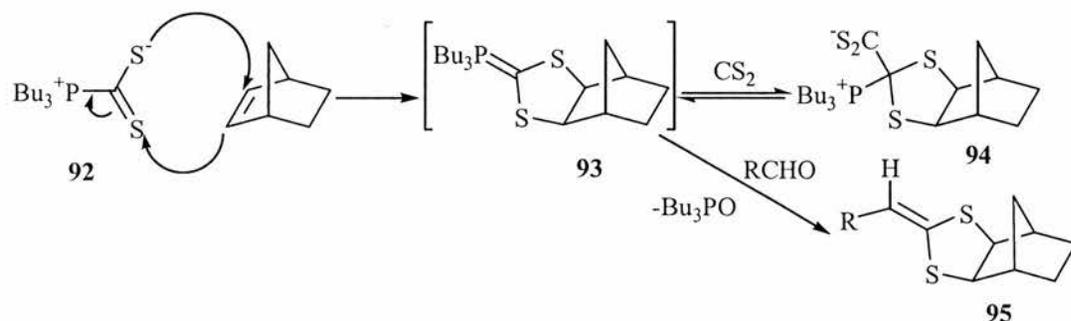
## A Norbornane and norbornene-fused dihydrotetrathiafulvalenes

### 1 Synthesis

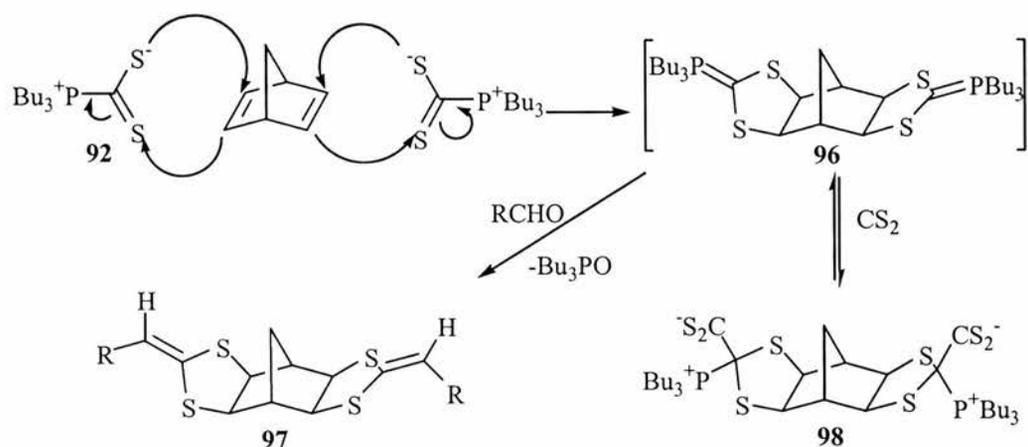
The first requirement was to prepare supplies of the various dihydroTTF derivatives using methods previously developed in this laboratory.<sup>97,98</sup> Carbon disulfide and tri-n-butylphosphine reacted together in pet. ether to give the red coloured adduct **92**.<sup>90</sup>



The adduct **92** was then used subsequently in the reactions with norbornene and norbornadiene to give the norbornene and norbornadiene adducts **94** and **98** respectively.<sup>92</sup>

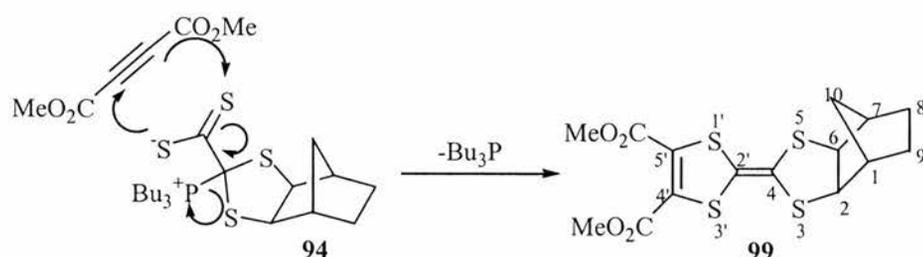


When  $\text{Bu}_3\text{P}/\text{CS}_2$  adduct **92** is reacted with norbornene a cycloaddition reaction occurs between the highly strained double bond of norbornene and the  $\text{CS}_2$  of **92**. This produces an intermediate **93** which has never been isolated but can be trapped using a Wittig reaction to give **95**. In the absence of an aldehyde, the intermediate **93** reacts with a further molecule of  $\text{CS}_2$  and the adduct **94** is formed which is isolated as a pink solid.



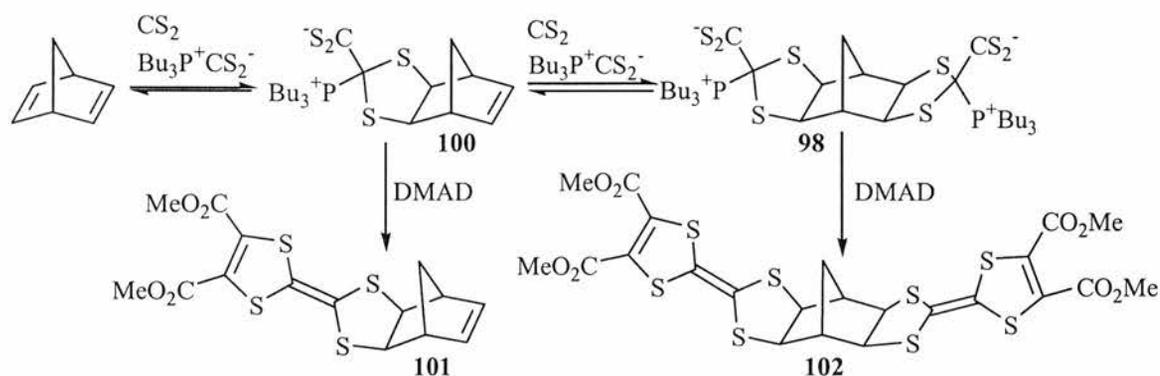
The reaction between the adduct **92** and norbornadiene occurs in the same manner giving an intermediate **96** which again was not isolated but could be trapped using a Wittig reaction to give **97**. In the absence of an aldehyde a pink coloured bis adduct **98** was obtained whose elemental composition was verified using elemental analysis. The bis adduct **98** is totally insoluble in common organic solvents.

DMAD, an acetylenic dipolarophile, was added to the solution containing **94** which changed colour from orange to red over three days.<sup>97</sup> A cycloaddition reaction is believed to occur between the adduct **94** and DMAD resulting in the formation of the dihydrotetrathiafulvalene **99** in low yield (30%) with the loss of tri-*n*-butylphosphine. The proton NMR spectrum showed only one set of signals indicating that either the exo or endo product had been formed. The *J* coupling for H<sub>2,6</sub> was small suggesting that the product existed in the exo form. The product was recrystallised from hexane and was obtained as red platelets which were subsequently used for X-ray analysis. This confirmed that the product existed in the exo form as discussed in Section D of the discussion.

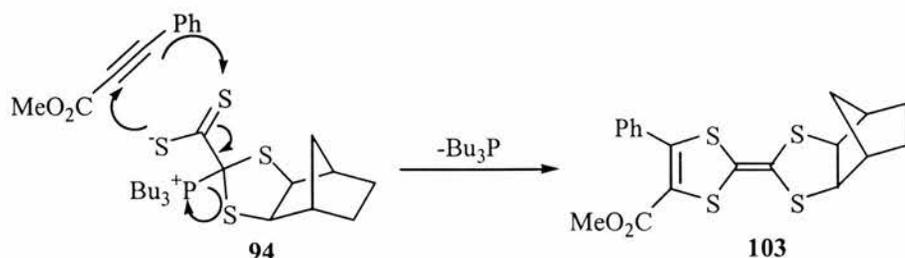


To illustrate the systematic nomenclature and numbering system used for these compounds **99** is named 2,6-exo-4-(4',5'-bis(methoxycarbonyl)-1',3'-dithiol-2'-ylidene)-3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decane and numbered as shown in the previous diagram.

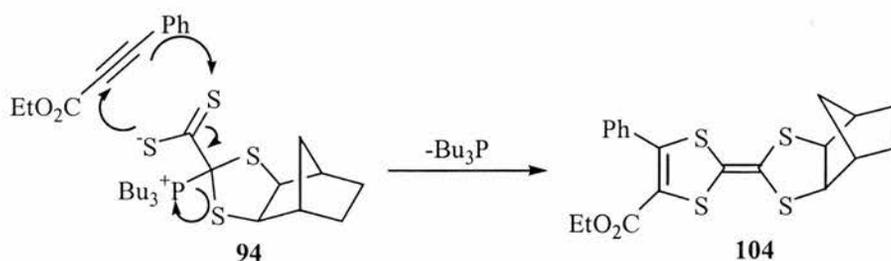
The norbornadiene adduct **98** formed a pink coloured suspension in dichloromethane. DMAD was added to the suspension changing the colour from pink to orange and after another portion of DMAD was added to a dark red colour.<sup>98</sup> The crude product was purified chromatographically producing two products of interest **101** and **102**. The first was the mono dihydrotetrathiafulvalene which was isolated as the minor product **101** (3%) and the bis dihydrotetrathiafulvalene which was isolated as the major product **102** (13%). This would therefore suggest that the adduct **98** must exist in equilibrium with a mono adduct **100**. This mono adduct has never been isolated or even trapped using a Wittig reaction with an aldehyde.



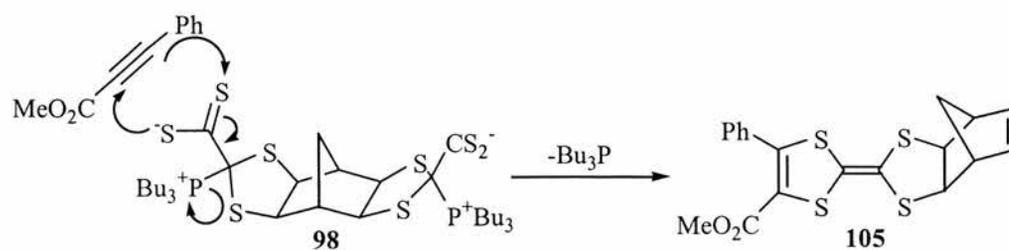
Methyl phenylpropiolate is a less highly activated dipolarophile because it only has one electron withdrawing ester group present.<sup>97</sup> This acetylenic ester was reacted with the norbornene adduct **94** to give the dihydrotetrathiafulvalene **103** in good yield (30%). The chemical shifts for the C-2 and C-6 positions in the  $^{13}\text{C}$ -NMR are different indicating that **103** is unsymmetrical. However this does not occur for C-1 and C-7 or C-8 and C-9.



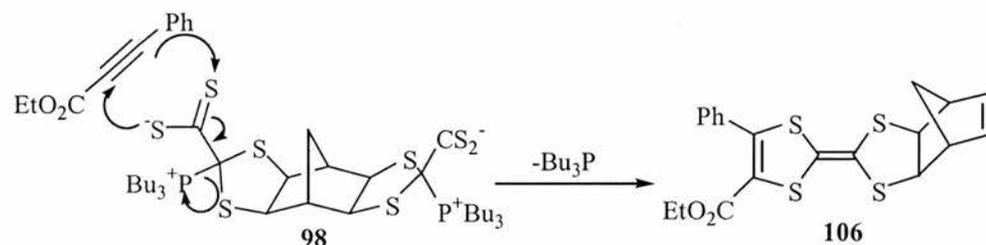
The norbornene adduct **94** was then reacted with ethyl phenylpropiolate to see if this reaction could be repeated using a different type of ester on the dipolarophile. This was the first time this reaction was carried out and gave the pure product **104** in low yield (6%). This was confirmed using spectroscopic data and elemental analysis. Two chemical shifts are obtained for both the C-2 and C-6 and for C-1 and C-7 positions in the  $^{13}\text{C}$ -NMR spectrum. This shows that the ethyl ester on the dipolarophile affects the molecule more compared with having a methyl ester on the dipolarophile.



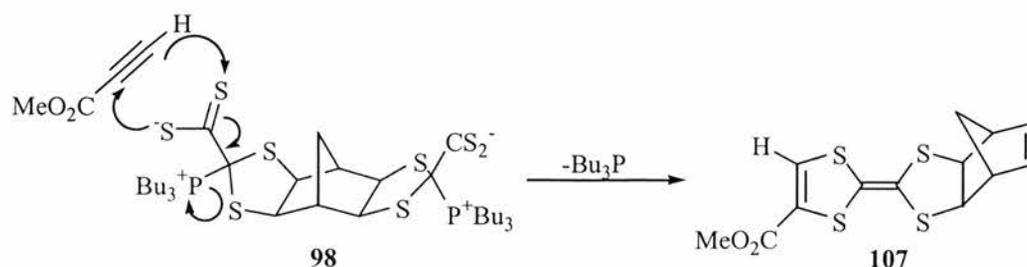
The norbornadiene adduct **98** was then reacted with methyl phenylpropiolate and in agreement with previous work, only the mono norbornene-fused dihydropentalene **105** was obtained in low yield (13%).<sup>98</sup> In the  $^{13}\text{C}$ -NMR spectrum there are two signals for the C-2 and C-6 positions and for the C-1 and C-7 positions. This is different to **103** indicating that the molecule **105** is more unsymmetrical.



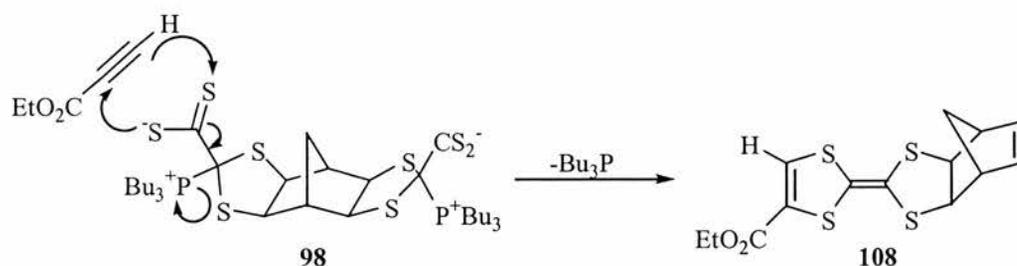
Ethyl phenylpropiolate was then reacted with the norbornadiene adduct **98** to see if the same result would be obtained using a different dipolarophile. The product **106** was obtained in low yield (4%) and its structure was proved using elemental analysis and spectroscopic data. This was the first time compound **106** had ever been synthesised. Both the C-2 and C-6 and the C-1 and C-7 positions each have two chemical shifts as expected which also was obtained for the saturated dihydrotetrathiafulvalene analogue **104**.



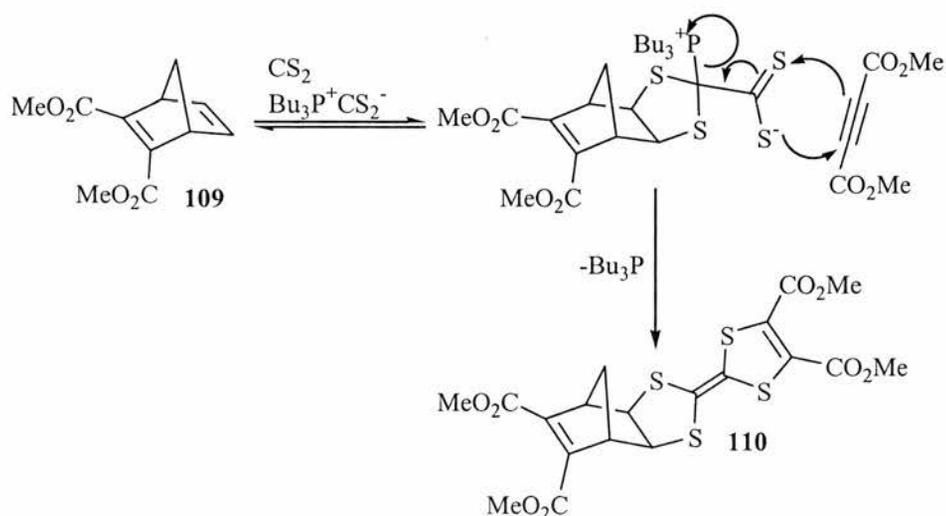
Methyl propiolate was reacted with the norbornadiene adduct **98** in dichloromethane.<sup>98</sup> As before only the mono dihydrotetrathiafulvalene **107** was obtained in low yield (3%). The <sup>13</sup>C-NMR shows two chemical shifts for the C-2 and C-6 positions indicating that the molecule **107** is unsymmetrical because of the unsymmetrical dipolarophile used.



The norbornadiene adduct **98** was then reacted with ethyl propiolate.<sup>98</sup> Only the mono dihydrotetrathiafulvalene was formed in low yield (13%).



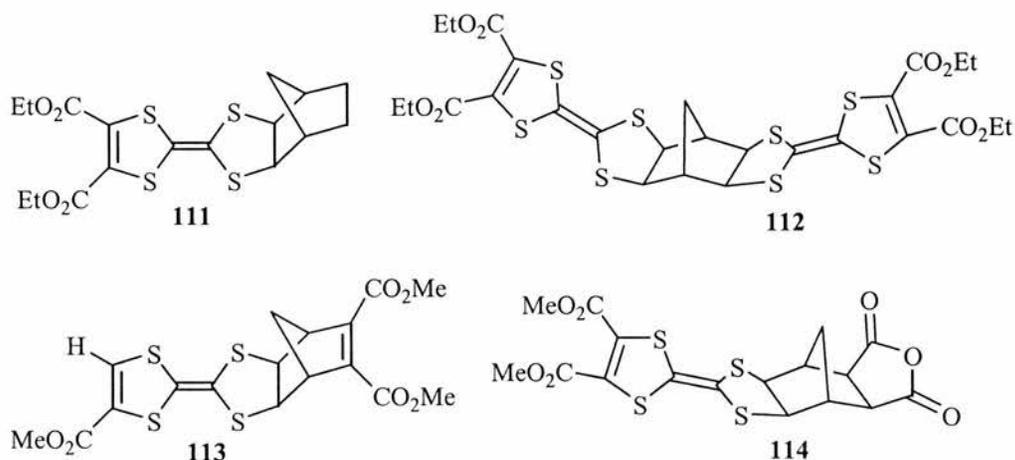
The modified norbornadiene **109**, the Diels Alder adduct of cyclopentadiene and DMAD, was reacted with the adduct **92** and carbon disulfide to form an intermediate which was then reacted with DMAD to give the dihydrotetrathiafulvalene **110** in low yield (23%).<sup>98</sup>



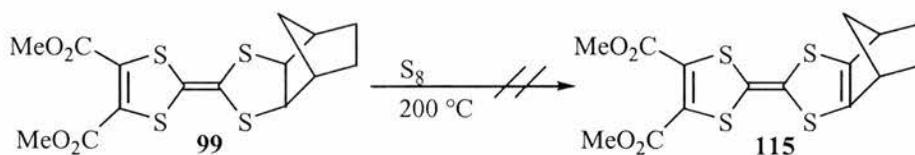
Only the mono dihydrotetrathiafulvalenes are formed when less highly activated dipolarophiles are used even though there exists an equilibrium between the mono adduct **100** and the bis adduct **98**. This may be due to solubility because the mono dihydrotetrathiafulvalene is formed faster and precipitates from the solution first. Therefore

all of the starting acetylenic ester is used up before the bis dihydrotetrathiafulvalene could be formed.

For the cyclic voltammetry studies a further four compounds **111-114** were available from previous work in the laboratory.

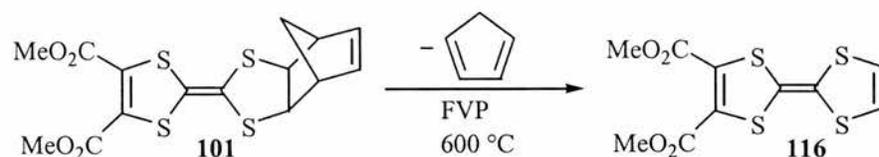


An attempt was made to dehydrogenate the dihydrotetrathiafulvalene **99** by heating with elemental sulfur or selenium in a closed atmosphere for 4 h.<sup>99</sup> It was hoped that this would give the norbornane fused tetrathiafulvalene **115** which would have lower oxidation potentials than dihydrotetrathiafulvalenes. Unfortunately the starting dihydrotetrathiafulvalene **99** remained unchanged.



Using these methods the dihydrotetrathiafulvalenes shown were readily prepared. Although the route is relatively low yielding it is convenient requiring only column chromatography for purification. This route allows access to mono and bis norbornane-fused

dihydrotetrathiafulvalenes. As previously discovered in this laboratory,<sup>98</sup> compounds such as **101** readily undergo retro Diels Alder reaction upon FVP providing a direct although low yielding route to disubstituted TTFs such as **116**.



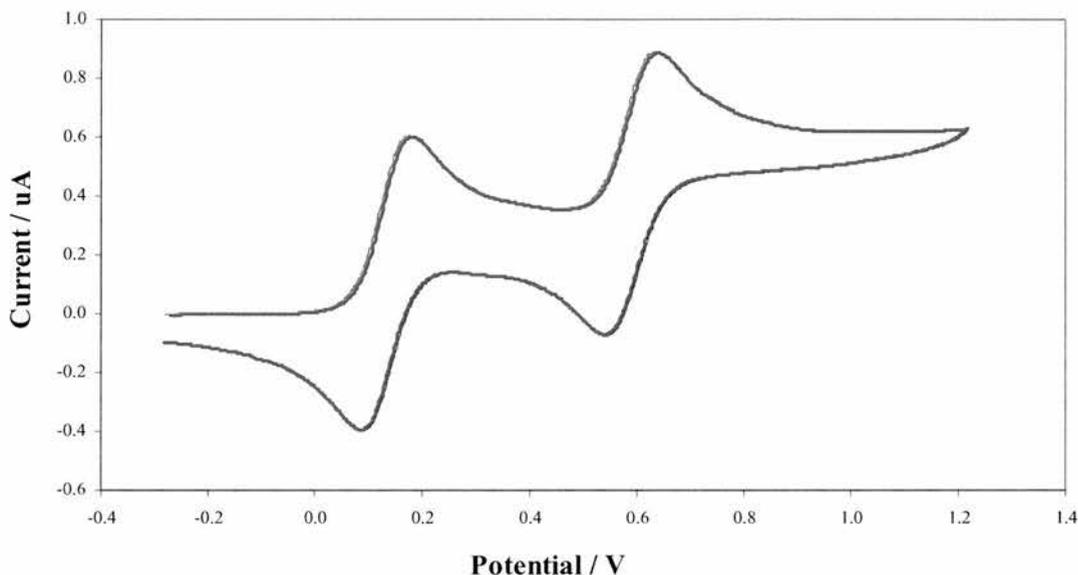
## 2 Measurement of the oxidation potentials

The oxidation potentials were measured using cyclic voltammetry (CV).<sup>117</sup> This is a simple and direct method for following the transfer of electrons during the course of a redox reaction on a voltammogram. The potential of a small, stationary working electrode is changed linearly with time starting from a potential where no electrode reaction occurs and moving to potentials where reduction or oxidation of the dihydrotetrathiafulvalene occurs. The auxiliary or counter electrode is used to maintain the correct current by conducting electricity from the signal source to the solution.

A typical cyclic voltammogram Figure 7, shows two 1 electron processes occurring. At  $I = 0$  and  $V = 0$  on the diagram, the dihydrotetrathiafulvalene is present in the solution in the neutral form. As the current is increased oxidation begins to occur at the anode and the dihydroTTF is oxidised to the cationic state as indicated by the first peak. As the current is increased further the dihydroTTF is oxidised to the dicationic state which is indicated by the second peak.

The direction of the current is reversed and the compound is reduced back to the cationic state and then to the neutral form of the dihydrotetrathiafulvalene. The first redox

potential is a measure of the ability of the donor to donate an electron ( $D^0 \rightarrow D^+$ ).  $\Delta E$  is the difference between  $E^1$  and  $E^2$  and is related with the reaction ( $D^+ \rightarrow D^{2+}$ ).

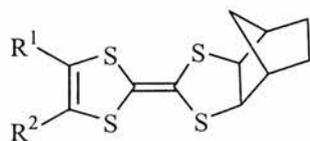


**Figure 7** CV of the dihydrotetrathiafulvalene **118**

The oxidation potential of a compound is a measure of its electron donating ability. The lower the oxidation potential the easier it is for a donor to donate an electron. The  $\Delta E$  value shows the difference between the cationic and dicationic states. The greater the  $\Delta E$  value the more difficult it is to reach the dicationic state.

In the area of cyclic voltammetry there has been some confusion over the reference used for reporting oxidation potentials. In older work these were often reported relative to the standard calomel electrode (SCE) as zero. Later many groups changed to the use of  $\text{Ag}/\text{Ag}^+$  as the reference point and most recently the favoured reference point is ferrocene/ferrocinium ( $\text{Fc}/\text{Fc}^+$ ). All CV data in this thesis are reported relative to  $\text{Fc}/\text{Fc}^+$  as zero and the voltammograms were calibrated by running with an internal ferrocene present. For comparison with literature data, values with the different reference points may be converted using  $E_{\text{Fc}/\text{Fc}^+} = E_{\text{SCE}} - 0.4 \text{ V}$ .

The results for norbornane-fused dihydrotetrathiafulvalenes are summarised in Table 1. From these it can be seen that it is harder to generate the dicationic state in **111** compared to **99** even though they are quite similar compounds. Replacing the ester group by a phenyl group lowers the oxidation potentials as shown for **103** and **104**. This is because an ester group is a good electron withdrawing group and increases the oxidation potential. However the  $\Delta E$  value still remains similar. Changing the ester group from CO<sub>2</sub>Me to CO<sub>2</sub>Et in this case does not have any significant effect on the oxidation potentials.

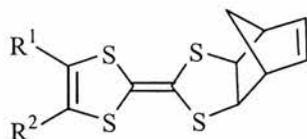


**Table 1** Oxidation potentials of norbornane-fused dihydroTTFs (V)

Compound	R <sup>1</sup>	R <sup>2</sup>	E <sup>1</sup>	E <sup>2</sup>	$\Delta E$
<b>99</b>	CO <sub>2</sub> Me	CO <sub>2</sub> Me	0.37	0.78	0.41
<b>111</b>	CO <sub>2</sub> Et	CO <sub>2</sub> Et	0.39	0.93	0.54
<b>103</b>	Ph	CO <sub>2</sub> Me	0.23	0.66	0.43
<b>104</b>	Ph	CO <sub>2</sub> Et	0.23	0.67	0.44

The oxidation potentials of norbornane-fused dihydrotetrathiafulvalenes were compared with those of norbornene-fused dihydrotetrathiafulvalenes, Table 2, to determine if the presence of a double bond in the norbornane unit of the molecule had any effect on the oxidation potentials. Comparing the data for **99** and **101**, **103** and **105** and **104** and **106**, shows there are no significant differences between E<sup>1</sup>, E<sup>2</sup> or  $\Delta E$ . Replacing one of the ester

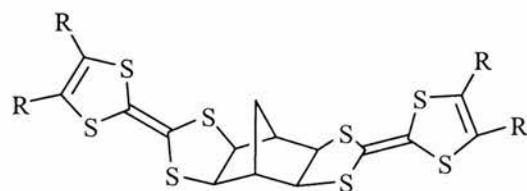
groups with a phenyl group lowers the oxidation potentials of the compound but does not change the  $\Delta E$  value. Having a hydrogen atom instead of a phenyl group also has no significant effect on the oxidation potentials of the donor as seen by comparing the values for **101** with **107** and **108**.



**Table 2** Oxidation potentials of norbornene-fused dihydrotetrathiafulvalenes (V)

Compound	R <sup>1</sup>	R <sup>2</sup>	E <sup>1</sup>	E <sup>2</sup>	$\Delta E$
<b>101</b>	CO <sub>2</sub> Me	CO <sub>2</sub> Me	0.34	0.72	0.38
<b>105</b>	Ph	CO <sub>2</sub> Me	0.25	0.69	0.44
<b>106</b>	Ph	CO <sub>2</sub> Et	0.23	0.66	0.43
<b>107</b>	H	CO <sub>2</sub> Me	0.32	0.78	0.46
<b>108</b>	H	CO <sub>2</sub> Et	0.34	0.78	0.43

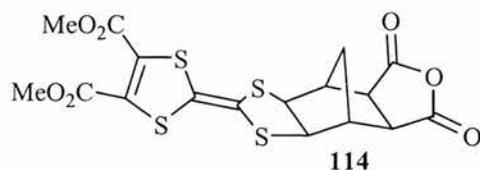
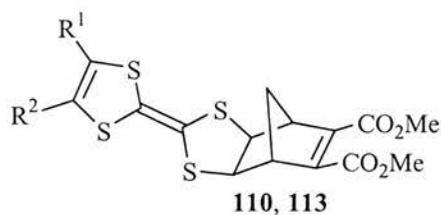
The bis norbornane-fused dihydrotetrathiafulvalenes **102** and **112** have the capacity to donate four electrons. The cyclic voltammetry measurements only show three oxidation potentials. The second oxidation potential occurred as a shoulder on the first oxidation potential peak. The close similarity of E<sup>1</sup> and E<sup>2</sup> suggests that the two separate sides of the molecule do not communicate strongly. However the fact that E<sup>1</sup>  $\neq$  E<sup>2</sup> shows that they do communicate to a small extent. The third oxidation potential occurred on the second peak and was broad and partially irreversible. Ester groups are known to reduce irreversibly and these groups may be interfering with the accurate measurement of the oxidation potentials.



**Table 3** Oxidation potentials of bis dihydrotetrathiafulvalenes (V)

Compound	R	E <sup>1</sup>	E <sup>2</sup>	E <sup>3</sup>	ΔE
<b>102</b>	CO <sub>2</sub> Me	0.40	0.42	0.81	0.42, 0.39
<b>112</b>	CO <sub>2</sub> Et	0.38	0.44	0.85	0.47, 0.41

The effect of having remote electron withdrawing groups present was now investigated by looking at compounds **110**, **113** and **114**. The presence of ester groups on the norbornene portion of the molecule exerts an electron withdrawing effect through the molecule which is shown through an increase in the oxidation potentials of **110** and **114**. The ΔE values are still quite similar to those of **101**. Substituting one of the ester groups with a hydrogen in **113** reduces the oxidation potentials but does not alter the ΔE value. The acid anhydride group exerts an electron withdrawing effect through the norbornane group which is indicated by an increase in the oxidation potentials in the donor portion of **114**.



**Table 4** Oxidation potentials of modified dihydrotetrathiafulvalenes

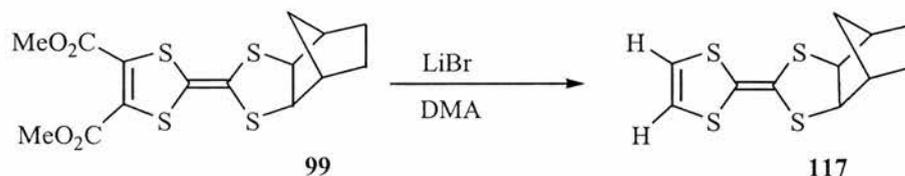
Compound	R <sup>1</sup>	R <sup>2</sup>	E <sup>1</sup>	E <sup>2</sup>	ΔE
<b>110</b>	CO <sub>2</sub> Me	CO <sub>2</sub> Me	0.48	0.90	0.42
<b>113</b>	CO <sub>2</sub> Me	H	0.40	0.81	0.41
<b>114</b>			0.48	0.90	0.41

In summary the presence of ester groups on the donor portion of the molecules seems to have an adverse effect on the oxidation potentials of the dihydrotetrathiafulvalene donors: **110**, **113** and **114**. Replacing the ester groups with other groups such as phenyl has lowered the oxidation potentials. Accordingly by removing the ester groups the oxidation potentials should be lowered significantly. The presence of electron withdrawing groups on the norbornane portion of the molecule also has an adverse effect on the oxidation potentials of the dihydrotetrathiafulvalene donors. With this in mind removal of the ester groups was now investigated.

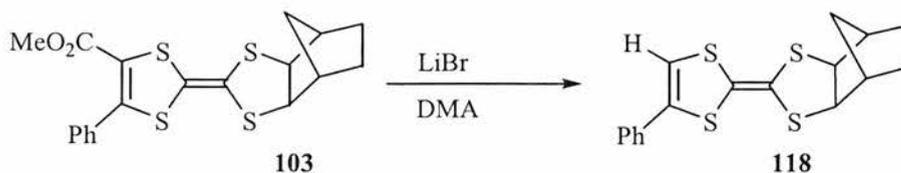
## B Decarboxylation of the norbornane and norbornene-fused dihydrotetrathiafulvalenes.

According to a literature procedure the ester groups could be removed through a decarboxylation reaction involving lithium bromide in DMA.<sup>100</sup> This allowed the preparation of a range of completely new dihydrotetrathiafulvalenes which were fully characterised.

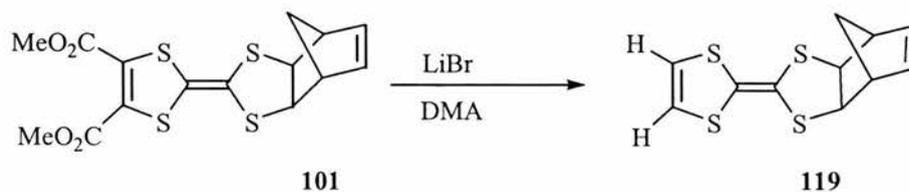
This reaction was used to remove the ester groups from compound **99** to give the decarboxylated product **117** in low yield (39%). The crystals obtained were of very high quality and were subsequently used in X-ray analysis.



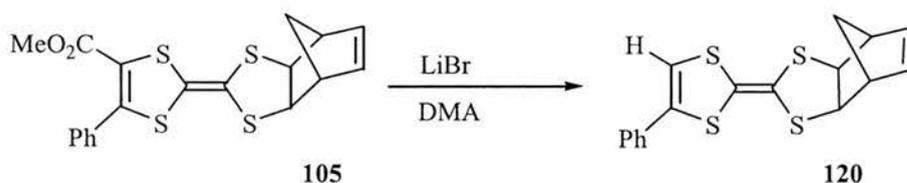
This reaction was then used to remove the ester group from **103** to give **118** in good yield (76%). Some traces of the solvent remained after rotary evaporation and Kugelrohr distillation was used to remove these.



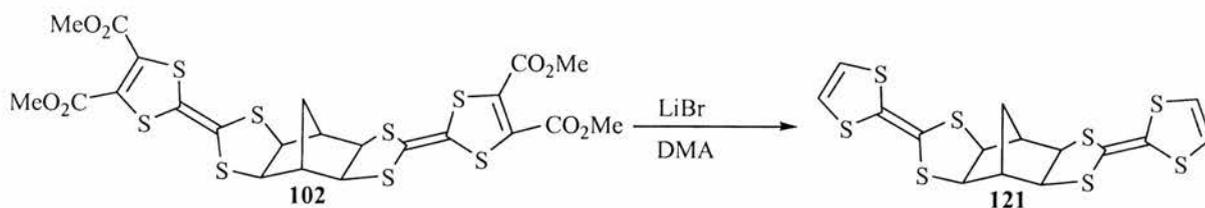
Compound **101** was also decarboxylated to give the dihydrotetrathiafulvalene **119** in good yield (79%). Comparing the <sup>13</sup>C NMR spectra for **117** and **119** the C-2 and C-6 positions are equivalent indicating that both compounds are symmetrical as would be expected.



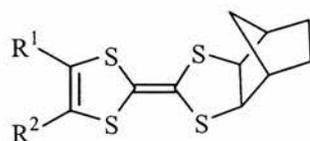
The dihydrotetrathiafulvalene **120** was obtained from the decarboxylation of **105** in excellent yield (98%). The C-2 and C-6 positions have two different chemical shifts as shown in the  $^{13}\text{C}$  NMR spectra for **118** and **120**. This would be expected because both molecules are unsymmetrical.



The decarboxylation was also carried out for the bis dihydrotetrathiafulvalene **102**. The reaction was successful, but the decarboxylated product **121** was highly insoluble in any common solvents and was only slightly soluble in pyridine. Therefore it was not possible to determine its cyclic voltammetry properties. This reaction illustrates the role that ester groups play in the solubility of large molecules such as the bis dihydrotetrathiafulvalenes.

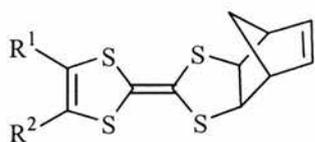


The oxidation potentials of these compounds were now determined and the results are shown in Tables 5 and 6.



**Table 5** Oxidation potentials of norbornane-fused dihydrotetrathiafulvalenes (V)

Compound	R <sup>1</sup>	R <sup>2</sup>	E <sup>1</sup>	E <sup>2</sup>	ΔE
<b>117</b>	H	H	0.08	0.55	0.47
<b>118</b>	H	Ph	0.15	0.60	0.45

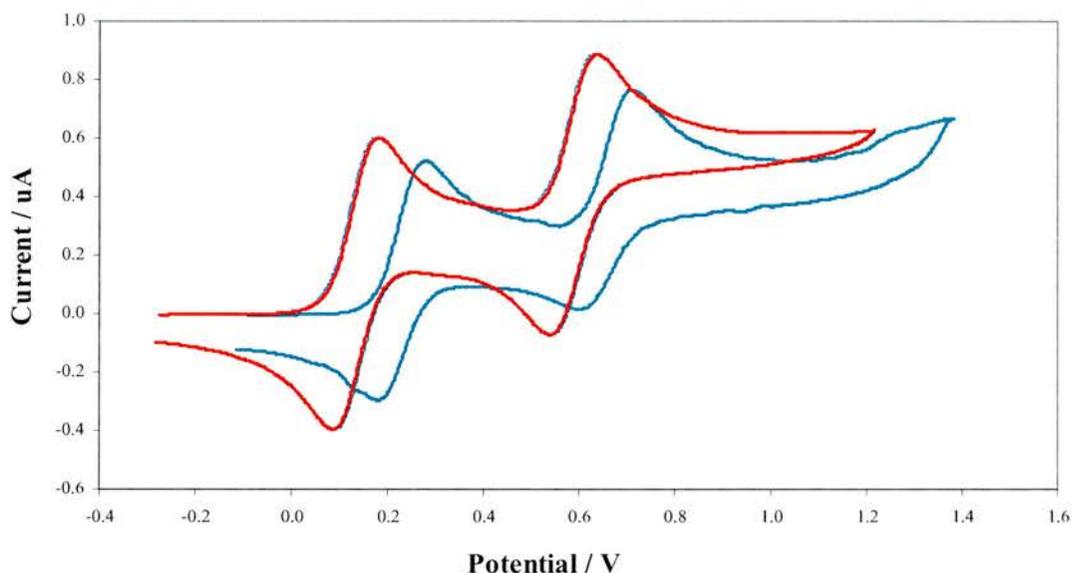


**Table 6** Oxidation potentials for norbornene-fused dihydrotetrathiafulvalenes (V)

Compound	R <sup>1</sup>	R <sup>2</sup>	E <sup>1</sup>	E <sup>2</sup>	ΔE
<b>119</b>	H	H	0.07	0.55	0.48
<b>120</b>	H	Ph	0.13	0.59	0.46

As found before for compounds **101**, **105**, **106**, **107** and **108**, the presence of a double bond on the norbornene portion of the molecule has no adverse effect on the oxidation potentials of the donors **119** and **120**. The E<sup>1</sup>, E<sup>2</sup> and ΔE values are similar to those of the fully saturated dihydrotetrathiafulvalene donors **117** and **118**.

Removing the ester groups has reduced the oxidation potentials of the dihydrotetrathiafulvalenes significantly. This is illustrated by comparing the cyclic voltammetry data for **103** (blue) and **118** (red) in Figure 8.

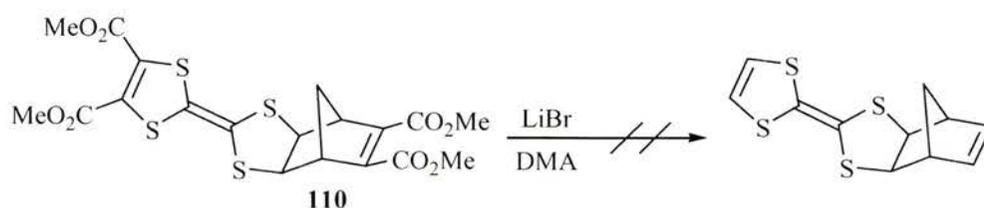


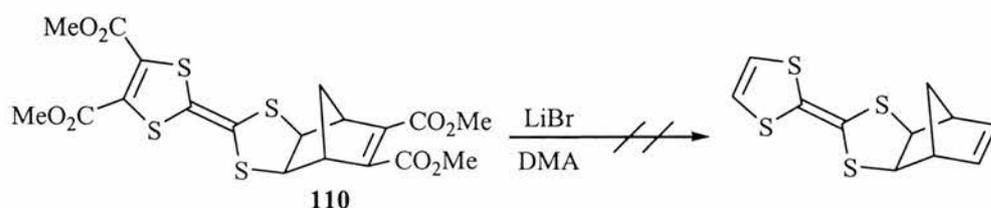
**Figure 8** Effect of decarboxylation of the Oxidation Potentials of Dihydrotetrathiafulvalene Donors

The separation between  $E^1$  and  $E^2$  is still similar though which means that both the first and second oxidation processes are equally affected. The presence of a phenyl group also increases the oxidation potential slightly.

In conclusion removing the ester groups has made a significant enhancement to the donor ability of the norbornane fused dihydrotetrathiafulvalene donors.

This reaction was also attempted on the dihydrotetrathiafulvalene **110** as shown below. Unfortunately the reaction did not work which may indicate that this reaction is only suitable for removing ester groups from the 1,3-dithiole portion of the molecule.





The cyclic voltammetry values obtained for the dihydrotetrathiafulvalenes were compared with some well known donors in Table 7. Some of the conditions used to measure the oxidation potentials are slightly different and may alter the E values slightly so an exact comparison cannot be made.

Tetrathiafulvalene (TTF) itself has excellent oxidation potentials. Comparing TTF with compounds such as **101**, **117** and **119** show that it is a better electron donor. Its oxidation potentials are even lower than those of the decarboxylated products and the  $\Delta E$  value is smaller. The second oxidation potential of the dihydrotetrathiafulvalenes is also higher which is probably due to having a  $\sigma$  bond as opposed to a  $\pi$  bond which means the ring only has 4  $\pi$  electrons as opposed to six which would allow it to achieve aromaticity and therefore planarity more easily.

Synthesising molecules such as tetraselenafulvalene (TSF) and tetratelerafulvalene (TTeF) were undertaken because they would have increased dimensionality. This was believed to reduce on site Coulombic repulsion in the dicationic state which is indicated by a smaller  $\Delta E$  value, but was accompanied by an increase in the  $E^1$  value.<sup>10</sup> BEDT-TTF has similar oxidation potentials to TTF and also has increased dimensionality.

Yamada and co-workers have shown that it is not necessary to have fully unsaturated TTF donors in order to form charge transfer complexes for potential organic superconductors.<sup>16,18</sup> Therefore these norbornane fused dihydrotetrathiafulvalenes should not be dismissed as possible potential donors for charge transfer complexes. Comparing the values of **117** and **119** with those of DODHT shows that the oxidation potentials are lower

and the  $\Delta E$  value is only slightly higher indicating that these molecules are good electron donors.

**Table 7** Comparison of the oxidation potentials (V) of dihydroTTFs and other TTF donors

Donor	$E^1$	$E^2$	$\Delta E$	Conditions
<b>99</b>	0.37	0.78	0.41	refer to experimental for <b>99-120</b>
<b>111</b>	0.39	0.93	0.54	
<b>103</b>	0.23	0.66	0.43	
<b>104</b>	0.23	0.67	0.44	
<b>101</b>	0.34	0.72	0.38	
<b>105</b>	0.25	0.69	0.44	
<b>106</b>	0.23	0.66	0.43	
<b>107</b>	0.32	0.78	0.46	
<b>108</b>	0.34	0.78	0.43	
<b>102</b>	0.40	0.42	0.81	0.42, 0.39
<b>112</b>	0.38	0.44	0.85	0.47, 0.41
<b>110</b>	0.48	0.90	0.42	
<b>113</b>	0.40	0.81	0.41	
<b>114</b>	0.48	0.90	0.41	
<b>117</b>	0.08	0.55	0.47	
<b>118</b>	0.15	0.60	0.45	
<b>119</b>	0.07	0.55	0.48	
<b>120</b>	0.13	0.59	0.46	
TTF <sup>118,119</sup>	0.08	0.30	0.22	0.1 M Et <sub>4</sub> NClO <sub>4</sub> in MeCN
TSF <sup>120</sup>	0.08	0.36	0.28	0.1 M Bu <sub>4</sub> NPF <sub>6</sub> in MeCN
TTeF <sup>118,119</sup>	0.19	0.44	0.25	0.2 M Bu <sub>4</sub> NBF <sub>4</sub> in MeCN
BEDT-TTF <sup>118,119</sup>	0.09	0.34	0.25	0.1 M Et <sub>4</sub> NClO <sub>4</sub> in MeCN
DODHT <sup>18</sup>	0.24	0.68	0.44	In PhCN/CS <sub>2</sub>
BDA-TTP <sup>16</sup>	0.32	0.50	0.18	0.1 M n-Bu <sub>4</sub> ClO <sub>4</sub> in PhCN/CS <sub>2</sub> , Pt electrode

NOTE: all values are given relative to Fc/Fc<sup>+</sup>

## C Formation of Charge transfer complexes

The cyclic voltammetry studies in Section A and B have allowed the oxidation potentials of the various dihydroTTF donors to be determined for the first time. Comparison of these values with the electron affinities of common electron acceptors (oxidising agents) allows a planned approach to the formation of charge-transfer (donor-acceptor) complexes.

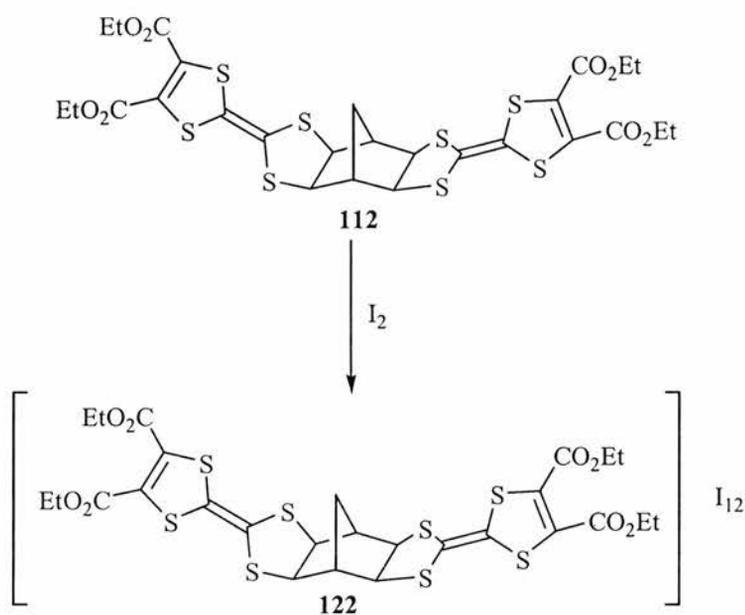
**Table 8** Electron affinities of common acceptors (V)

Acceptor	Electron affinity
Br <sub>2</sub>	1.07
I <sub>2</sub>	0.54
Benzoquinone	0.70
DDQ	1.00

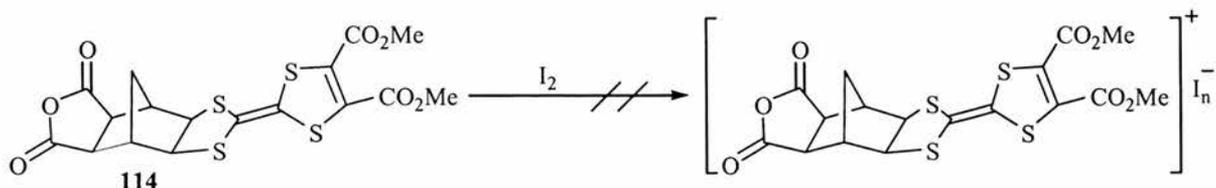
Since the dihydroTTFs have first oxidation potentials in the range 0.23-0.47 V they can potentially form CTCs with any of the donors in Table 8. The simplest approach to the formation of CTCs relies on the fact that these are often less soluble than the individual components and so simply mixing solutions of the donor and acceptor leads to precipitation of the CTC.

The dihydrotetrathiafulvalene **112** was dissolved in dichloromethane forming a solution which was mixed with a solution of iodine in dichloromethane. A black solid precipitated from the solution and was filtered off and washed leaving a black crystalline solid. Elemental analysis showed the solid had a molecular formula equivalent to that of **112** + I<sub>12</sub>. The <sup>1</sup>H NMR spectrum had certain peaks missing which could be due to paramagnetic effects, due to the presence of unpaired electrons in the dihydrotetrathiafulvalene thus

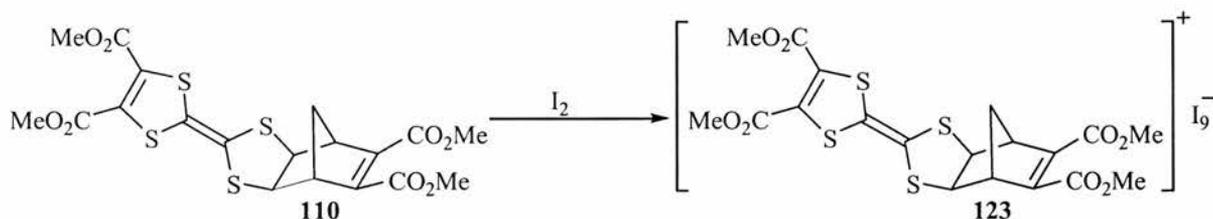
indicating that electrons were donated to the acceptor. On the basis of this evidence, the structure of the black solid is believed to be that of the charge transfer complex **122**. The structure could only be confirmed by an X-ray diffraction study. It has been reported previously in the literature that  $I_{12}$  systems have two negative charges.<sup>121</sup> This would suggest that two electrons have been donated from the dihydrotetrathiafulvalene donor. If the acceptor is  $I_{12}^{2-}$  then the acceptor could occur as two antiparallel pentaiodides which are linked by an iodine molecule to form a twisted sawhorse geometry or as an  $I_4^{2-}$  unit interacting with two iodine molecules at each end forming a twisted H geometry.<sup>122</sup>



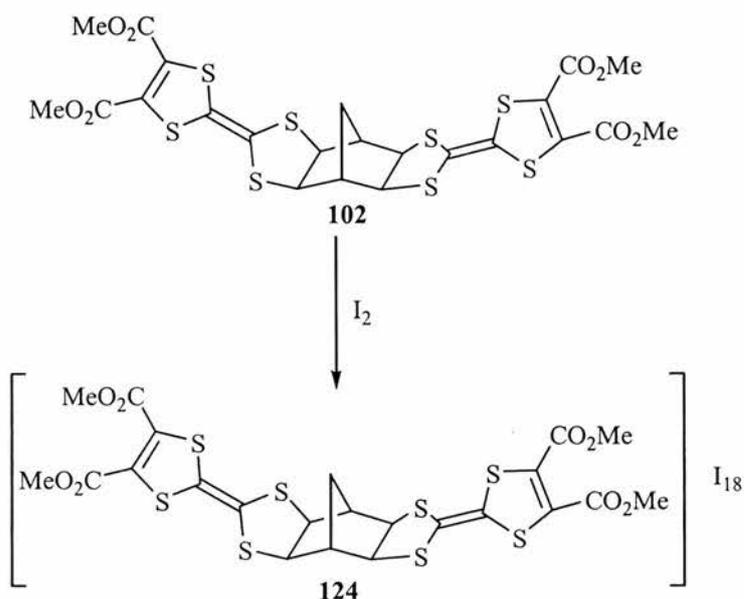
The dihydrotetrathiafulvalene **114** was dissolved in dichloromethane and mixed with a solution of iodine in dichloromethane. The solution was left stirring overnight, then filtered and the solid washed with dichloromethane. The melting point of the product was the same as the starting material. CHN analysis indicated that the product had the same molecular formula as the starting material and a CTC had not been formed.



A solution of iodine in dichloromethane and a solution of the dihydrotetrathiafulvalene **110** were mixed together. A black solid precipitated from the solution and was filtered off and washed leaving a black crystalline solid **123**. The  $^1\text{H}$  NMR spectrum showed that some peaks from the starting material were missing suggesting that a CTC had been formed. Elemental analysis showed that the molecular formula contained  $\text{I}_9$ . The structure of the iodine acceptor in **123** could be a V-shaped pentaiodide molecule coordinated to two iodine molecules,<sup>123</sup> or a nonaiodide of  $[(\text{I}_3^-)_3\text{I}_2]$  composition<sup>124</sup> or a pyramidal  $\text{I}_7^-$  linked by an iodine molecule<sup>125</sup> as previously reported in the literature.

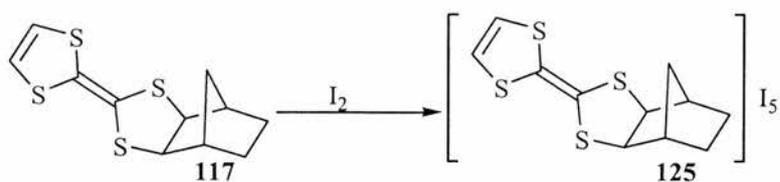


The same type of experimental procedure was used when iodine and the dihydrotetrathiafulvalene **102** reacted together. After filtration and washing the black crystalline solid **124** was analysed using elemental analysis. This showed that the black solid had  $\text{I}_{18}$  present. The CTC **124** could have the  $\text{I}_{18}^{2-}$  network formed from the interaction of three  $\text{I}_2$  molecules, a V-shaped pentaiodide anion and a pyramidal  $\text{I}_7^-$  anion as has been previously published in the literature.<sup>126</sup>

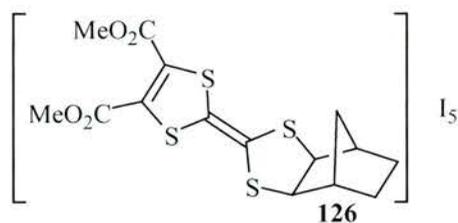


Attempts to form complexes from these donors using bromine, benzoquinone, DDQ and TCNQ were unsuccessful and the starting materials were recovered unchanged. However in the course of the repeated crystallisations involved, a new second crystalline form was discovered for both **99** and **102**. These are presented and discussed in detail in Section D of the Discussion.

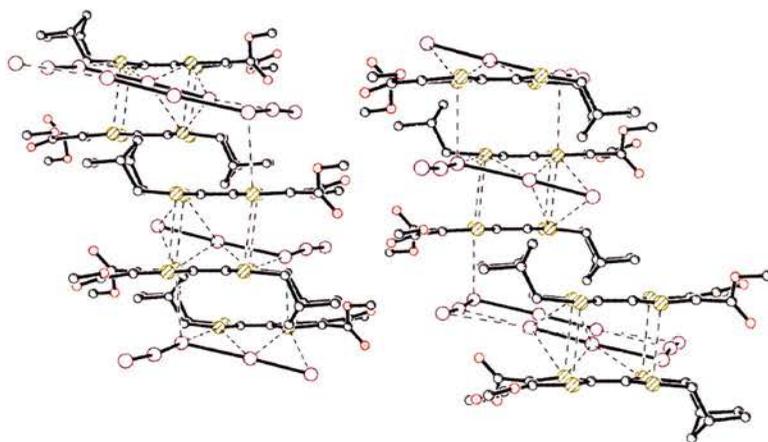
The decarboxylated dihydrotetrathiafulvalene **117** was dissolved in dichloromethane and added to a solution of iodine in dichloromethane which produced a black solid. This was filtered off and washed with dichloromethane giving a black solid. Elemental analysis indicated that the solid contained  $I_5$ .



An X-ray structure of a CTC complex **126** comprising the dihydrotetrathiafulvalene **99** and iodine was obtained by a previous worker as shown in Figure 9.<sup>88</sup>



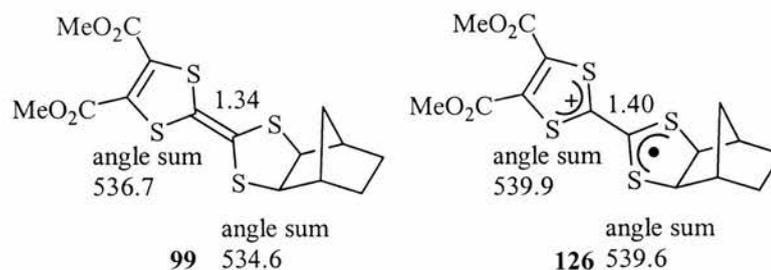
The elemental analysis showed the presence of a pentaiodide anion. From the X-ray data this was shown to occur in a V-shape. This has previously been reported in the literature.<sup>127</sup> If an X-ray structure could be obtained of **125** then it would be possible to see if the iodide acceptor also existed in the V-shaped form. Unfortunately crystals of suitable quality for X-ray diffraction were not obtained for any of the CTCs formed in this work but further attempts could be made to obtain X-ray structures of CTCs of **122-124** to examine if there are any trends for the amount of iodine being present for each CTC.



**Figure 9** X-Ray of the Iodine CT Complex **126**

The X-ray structure of **126** determined previously was compared with an X-ray structure of the norbornane-fused dihydrotetrathiafulvalene **99** obtained in the course of the present work to examine how complexation affected the donor molecule. The length of the double bond between the two rings had increased suggesting a radical cation has been

formed. The carbon-sulfur bonds attached to the central double bond have shortened by 0.04 Å. The sums of the angles for the dithiole and dithiolane rings are both essentially 540°. This indicates that both rings are planar making it easier for the electrons to delocalise over the molecule.



In the starting donor **99** the 1,3-dithiolane ring attached to the norbornane section of the molecule has 5 $\pi$  electrons and is less planar than the peripheral ring. This peripheral ring has 7 $\pi$  electrons and is almost planar (537°). When the charge transfer complex is formed a number of changes occur within the donor. The 1,3-dithiole ring donates 1 $\pi$  electron and the ring becomes planar. Charge is now delocalised over the ring. The length of the double bond between the two rings has become 0.06 Å longer suggesting the formation of a radical cation species. The 1,3-dithiolane ring also becomes planar to allow the charge to be distributed over the two rings.

In the TTF molecule both of the rings have 7  $\pi$  electrons. If each of the rings loses one electron each therefore both will have become aromatic, according to Hückel's Rule, and this will be accompanied by a change from a bent conformation to a planar conformation. These conformational changes are due to TTF being oxidised from a neutral state to a cation state and then to a dication state as shown in Table 8. The second oxidation potential for the dihydrotetrathiafulvalene donor is higher because the ring only contains 5 $\pi$  electrons. It is harder to oxidise a donor so that the second ring only contains 4 $\pi$  electrons. This is shown by

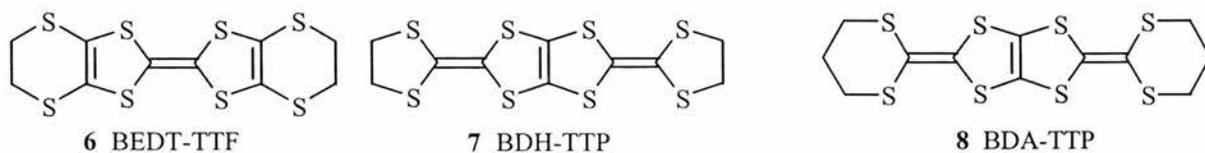
the lower second oxidation potential for TTF which is due to the ring losing 1 $\pi$  electron to get 6 $\pi$  electrons which fulfil Hückel's Rule for aromaticity.

**Table 9** Oxidation potentials (V) of **99** and TTF

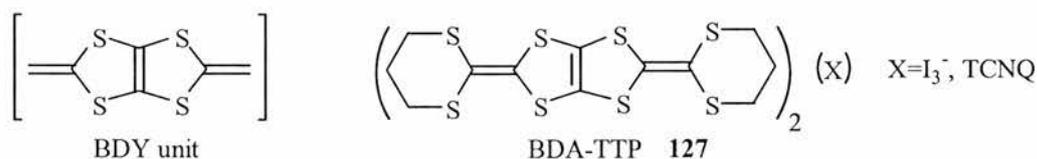
Compound	E <sup>1</sup>	E <sup>2</sup>	$\Delta E$
<b>99</b>	0.37	0.78	0.41
TTF <sup>118,119</sup>	0.08	0.30	0.22

As described in more detail in section D, the dihydrotetrathiafulvalene **99** and its decarboxylated derivative **117** both have a packing arrangement, the  $\kappa$ -phase which also occurs in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>.<sup>128</sup> The BEDT-TTF donor **6** has formed many CTCs and some of these have shown superconducting properties.<sup>7,8</sup>

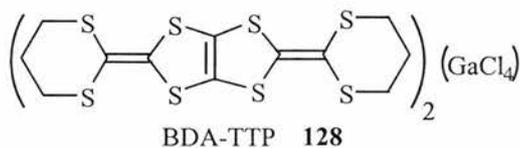
The attempts to form CTCs here by simple precipitation have generally given disappointing results. However the recent work of Yamada shows that further work in this direction is worthwhile since CTCs of this type may have useful electrical properties including superconductivity. Yamada and co-workers found that many BDH-TTP salts were stable down to low temperatures. BDH-TTP **7** is a structural isomer of BEDT-TTF **6** and is not a TTF containing donor. There was no superconductivity observed in BDH-TTP salts whereas there was for BEDT-TTF salts. This was believed to be due the fact that BDH-TTP **7** was planar and composed of rigid five membered rings while those of BEDT-TTF **6** had more flexible six-membered rings which allowed the molecule to adopt a number of different conformations.



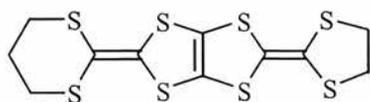
BDA-TTP **8** was synthesised because it still contained the BDY (bis-fused 1,3-dithiol-2-ylidene) unit and was believed to be more flexible thus offering a better chance of obtaining an organic superconductor.<sup>16</sup> A number of charge transfer complexes **127** were prepared using the current controlled electrocrystallisation method.<sup>129</sup> Charge transfer complexes using **8** as the donor and acceptors such as iodine or TCNQ were also prepared but did not show any superconducting properties. Superconductivity at ambient pressure was observed in complexes **127** with  $X = \text{AsF}_6^-$  and  $\text{PF}_6^-$ .



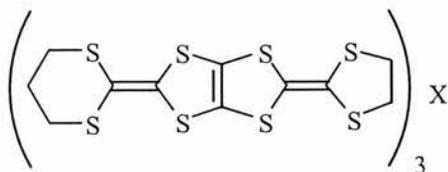
More recently the charge transfer complex  $(\text{BDA-TTP})_2(\text{GaCl}_4)$  **128** was prepared where superconductivity under applied pressure was also observed.<sup>130</sup>



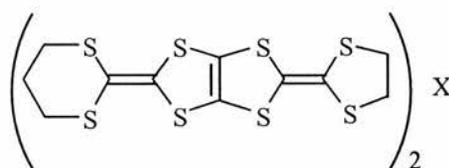
Both BEDT-TTF **6** and BDA-TTP **8** are symmetrical donors. An unsymmetrical donor, BHDA-TTP **9** was synthesised in an effort to extend the superconductivity observed in previously prepared charge transfer complexes **127** and **128**. A number of different complexes **129** and **130** were prepared.



BHDA-TTP **9**



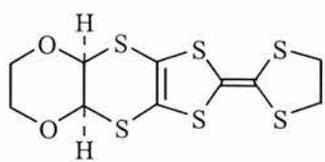
BHDA-TTP **129**  
X = TCNQ, I<sub>3</sub><sup>-</sup>



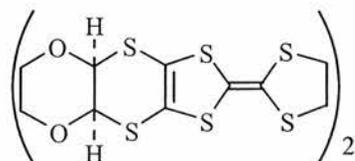
BHDA-TTP **130**  
X = PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>

However the CTCs **130** exhibited metal-insulator transitions instead of superconducting transitions at room temperature.<sup>17</sup>

The BDY unit has a similar  $\pi$ -electron system as tetrachalcogenafulvalene (TCF) derivatives. DODHT **10** was synthesised in an attempt to ascertain whether or not it is possible to produce superconductors from donors with a less extended  $\pi$ -system than TCF derivatives. This donor, containing only a 1,3-dithiol-2-ylidene unit as a  $\pi$ -system, was used to make charge transfer complexes with various counterions. Two of these CTCs **131** were shown to act as organic superconductors under induced pressure.<sup>18</sup>



DODHT **10**



**131**

(X) X = AsF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>

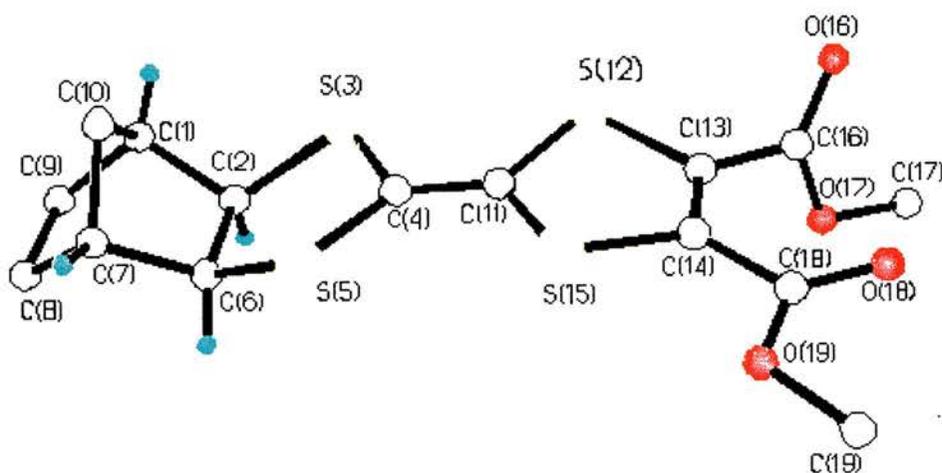
Comparing the formation of CTCs from Yamada and from the norbornane fused dihydrotetrathiafulvalenes leads to some important conclusions:

1. Halide and TCNQ complexes have not been shown to produce superconductors for partially unsaturated donors.
2. Electrocrystallisation should be considered as a viable alternative to the chemical oxidation method of preparing charge transfer complexes.
3. Preparing CTCs using counter ions such as  $\text{PF}_6^-$  and  $\text{AsF}_6^-$  should be carried out as Yamada has shown that they can produce organic superconductors under the right conditions.
4. Further work on obtaining good quality crystals of the iodine CTCs should be carried out to see if there is any link between the type of dihydrotetrathiafulvalene and the number of iodine atoms present in the CTC.

## D X-Ray structures of the dihydrotetrathiafulvalenes

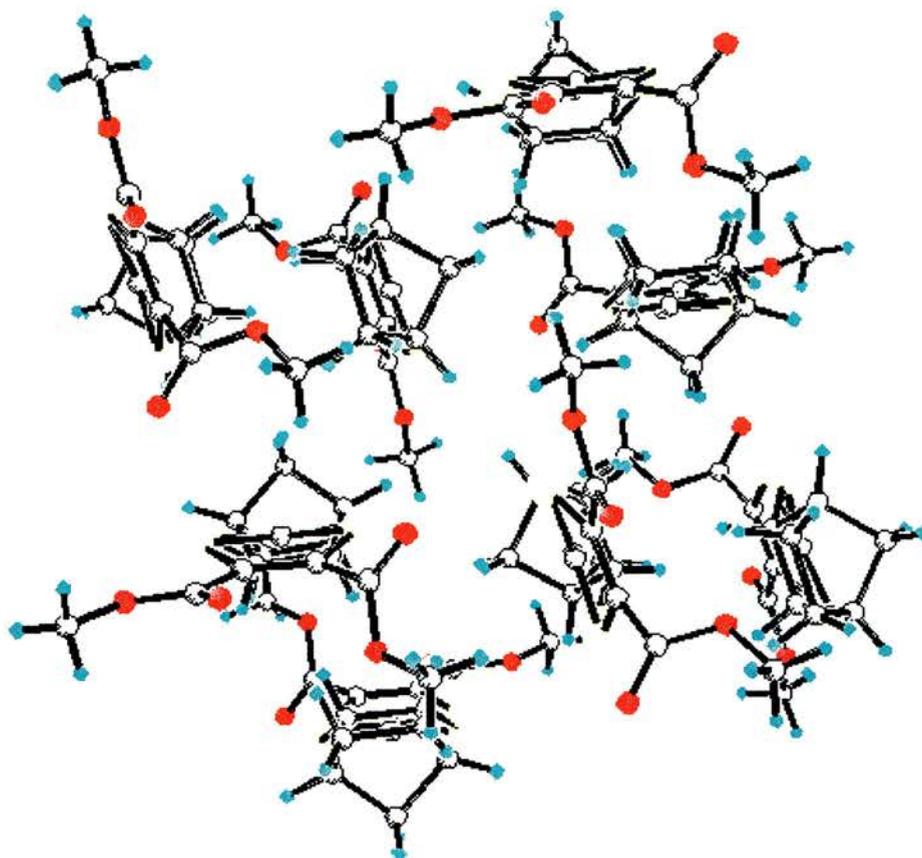
Crystals of excellent quality were obtained for two of the norbornane-fused dihydrotetrathiafulvalenes **99** and **117** and were used to obtain X-ray structures. The X-ray structures confirmed the exo-configuration of the dihydrotetrathiafulvalenes. The degree of planarity of both of the 1,3-dithiole rings could also be measured.

In the dihydrotetrathiafulvalene **99**, Figure 10 the angle sums of the dithiolane and dithiole rings are  $535^\circ$  and  $537^\circ$  respectively. The proximity of these values to the ideal  $540^\circ$  indicates that they are almost planar.



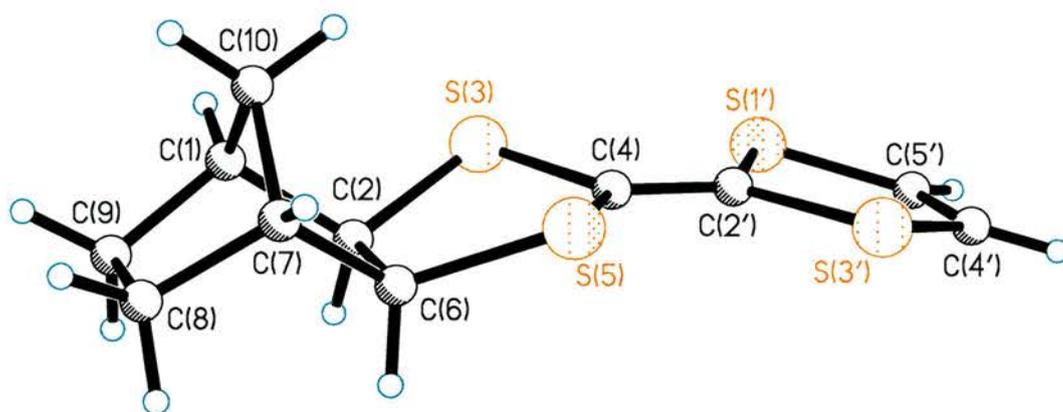
**Figure 10:** X-ray structure of the dihydrotetrathiafulvalene **99** showing the crystallographic numbering scheme. Selected bond lengths and angles; C(4)–C(11) 1.334(4), C(4)–S(3) 1.751(3), C(4)–S(5) 1.738(3), C(11)–S(15) 1.760(3), C(11)–S(12) 1.760(3) Å; S(3)–C(4)–S(5) 115.19(16), C(4)–S(5)–C(6) 97.38(13), S(5)–C(6)–C(2) 111.96(19), C(6)–C(2)–S(3) 112.62(18), C(2)–S(3)–C(4) 97.10(12), C(11)–S(15)–C(14) 93.61(15), S(15)–C(14)–C(13) 117.1(3), C(14)–C(13)–S(12) 117.9(3), C(13)–S(12)–C(11) 93.88(16), S(12)–C(11)–S(15) 114.16(17)°.

An unusual packing arrangement was also found, Figure 11, consisting of interacting orthogonal dimers. In this phase there are no stacks. This has previously been observed for  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>.<sup>128</sup>



**Figure 11:** X-ray structure of the dihydrotetrathiafulvalene **99** showing the packing arrangement of the molecules in space.

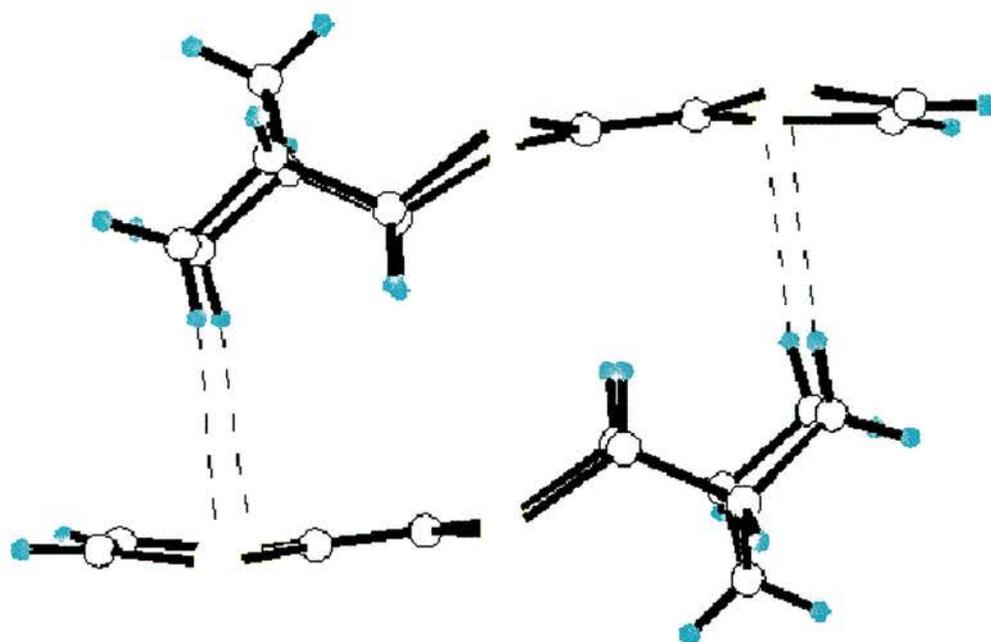
An X-ray structure was also obtained for crystals of the decarboxylated dihydrotetrathiafulvalene **117**, Figure 12. The angle sums for the 1,3-dithiolane and 1,3-dithiole rings had changed to 531° and 539° respectively. This indicated that one ring had become less planar and the other more planar.



**Figure 12:** X-ray structure of the dihydrotetrathiafulvalene **117** showing crystallographic numbering scheme. Selected bond lengths and angles; C(4)-C(2') 1.341(4), S(3)-C(4) 1.751(3), S(5)-C(4) 1.749(3), C(2')-S(1') 1.765(3), C(2')-S(3') 1.758(3) Å; C(2)-S(3)-C(4) 96.54(15), S(3)-C(4)-S(5) 113.53(19), C(4)-S(5)-C(6) 96.38 (15), S(5)-C(6)-C(2) 112.5(2), C(6)-C(2)-S(3) 111.8(2), C(5')-S(1')-C(2') 94.42(17), S(1')-C(2')-S(3') 113.69(19), C(2')-S(3')-C(4') 94.46(17), S(3')-C(4')-C(5') 118.4(3), C(4')-C(5')-S(1') 117.9°.

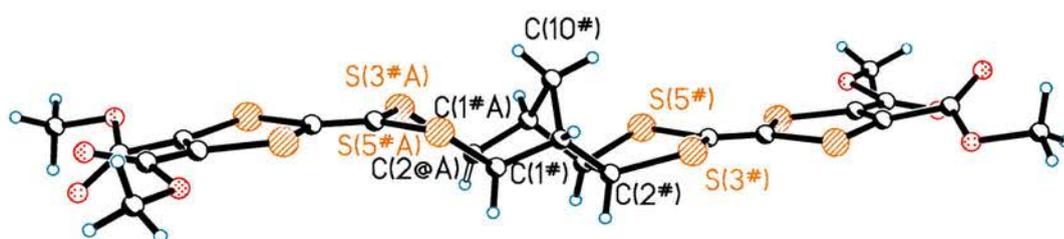
The same type of packing arrangement consisting of orthogonal dimers was again found in the decarboxylated product **117**. There were also apparent interactions between the sulfur atoms and the CH bonds within the orthogonal dimers as shown in Figure 13. This type of CH-S hydrogen bonding is very unusual and the existence of a genuine interaction as opposed to simple close contact is debatable.

The degree of planarity for the 1,3 dithiole and dithiolane rings is of some significance in the dihydrotetrathiafulvalenes. It is a useful indicator for the formation of charge transfer complexes. A good organic conductor is planar. In the case of tetrathiafulvalene both rings have 7  $\pi$  electrons and need to lose one electron each in order to attain aromaticity and hence planarity. This can be used as an indication to confirm that electron transfer has occurred and that a charge transfer complex has been formed.



**Figure 13:** Apparent CH-S interactions between the dihydrotetrathiafulvalenes

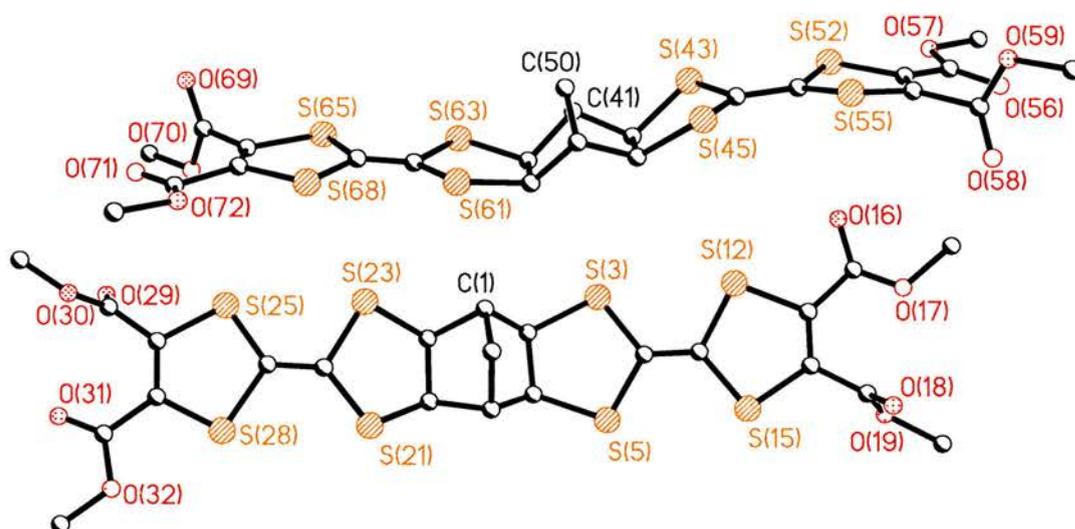
An X-ray structure has previously been obtained of the dihydrotetrathiafulvalene **102** as shown in Figure 14.<sup>97</sup>



**Figure 14** X-ray structure of the dihydrotetrathiafulvalene **102** showing crystallographic numbering scheme. Selected bond lengths and angles; S(3)-C(4) 1.788(7), C(4)-S(5) 1.731(7), C(4)-C(11) 1.314(9), C(11)-S(12) 1.753(7), C(11)-S(15) 1.769(7) Å; C(2)-S(3)-C(4) 97.8(5), S(3)-C(4)-S(5) 113.6(4), C(4)-S(5)-C(6) 100.3(5), S(5)-C(6)-C(2) 113.5(8), C(6)-C(2)-S(3) 114.4(9), C(11)-S(12)-C(13) 95.2(3), S(12)-C(13)-C(14) 118.1(5), C(13)-C(14)-S(15) 117.2(5), C(14)-S(15)-C(11) 95.5(3), S(15)-C(11)-S(12) 113.8(12)°.

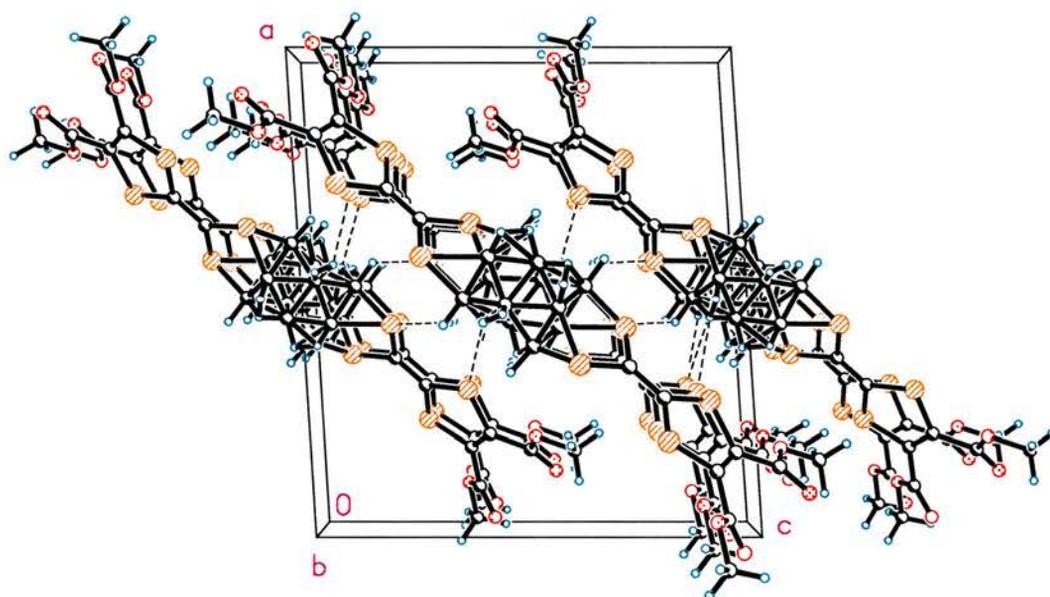
The sum of the angles for both the 1,3-dithiolane ring and the 1,3-dithiole ring are both  $539.6^\circ$ , indicating that both rings are almost planar.

An attempt was made to form a CTC between the bis dihydrotetrathiafulvalene **102** and benzoquinone by dissolving both of them in acetonitrile. The solution was allowed to evaporate until red and black crystals began to precipitate from solution. X-ray structures were obtained for both crystals showing that a CTC had not formed and the bis dihydrotetrathiafulvalene had itself crystallised. The X-ray structure of the black crystals was similar to the previously published X-ray structure of **102** as shown in Figure 14.<sup>97</sup> The X-ray structure of the red crystals is shown in Figure 15.



**Figure 15** X-ray structure of the dihydrotetrathiafulvalene **102** (new form) showing crystallographic numbering scheme. Selected bond lengths and angles; S(3)-C(4) 1.773(19), C(4)-S(5) 1.791(17), C(4)-C(11) 1.27(3), C(11)-S(12) 1.84(2), C(11)-S(15) 1.75(3) Å; C(2)-S(3)-C(4) 101.7(10), S(3)-C(4)-S(5) 113.4(11), C(4)-S(5)-C(6) 98.2(6), S(5)-C(6)-C(2) 116.4(15), C(6)-C(2)-S(3) 109.0(17), C(11)-S(12)-C(13) 94.5(11), S(12)-C(13)-C(14) 114.5(17), C(13)-C(14)-S(15) 122.4(16), C(14)-S(15)-C(11) 94.3(9), S(15)-C(11)-S(12) 113.8(12)°.

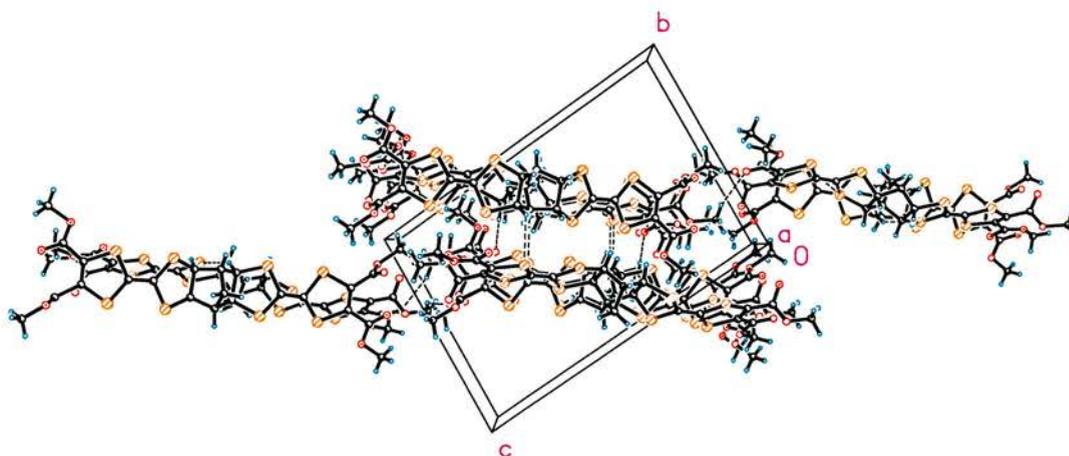
The sum of the angles for the 1,3-dithiolane ring has decreased to  $538.7^\circ$  indicating that this ring has become slightly less planar. The sum of the angles for the 1,3-dithiole ring remained unchanged. The bond lengths have changed. The central double bond C(4)-C(11) has become shorter. This has been accompanied by an increase in three of the carbon-sulfur bonds, C(4)-S(5), C(11)-S(12) and C(11)-S(15).



**Figure 16** Diagram of the packing arrangement in the previously published structure of bis dihydrotetrathiafulvalene **102**<sup>97</sup>

Figure 16 shows how the bis dihydrotetrathiafulvalenes pack together in regular stacks. Referring to the Figure 5 in Section C of the Introduction this type of packing arrangement could be assigned to type IV. The molecules pack directly on top of each other forming stacks which are arranged diagonally away from each other.

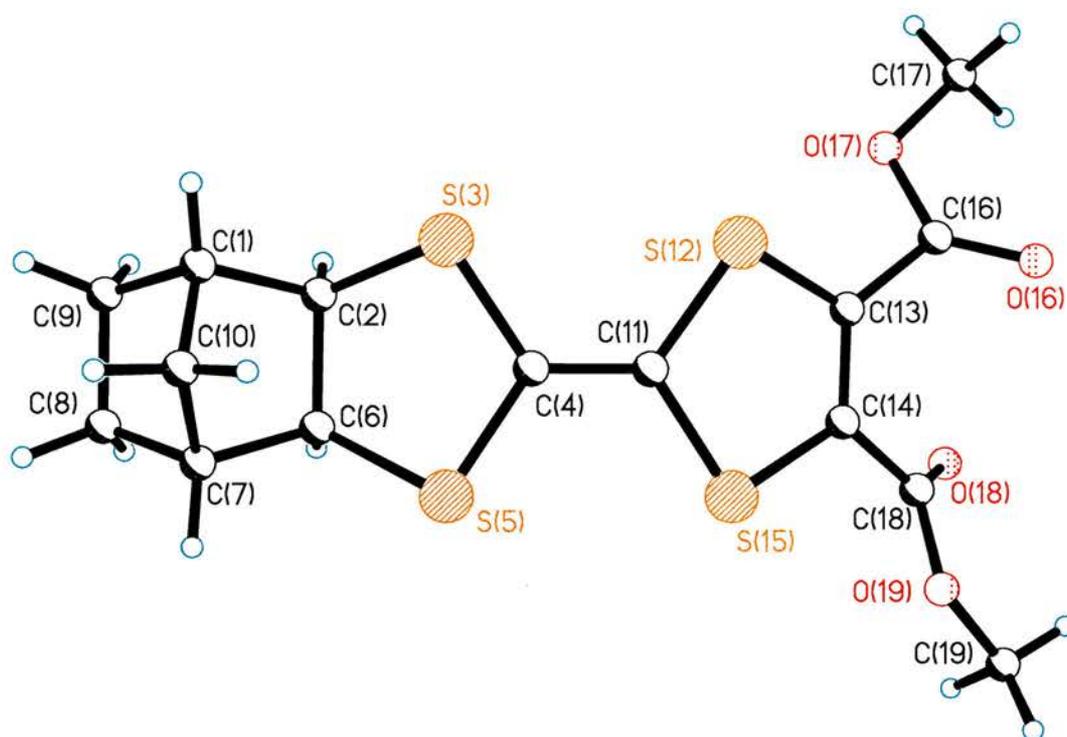
An unusual type of packing arrangement was observed in the X-ray structure of the red crystals of **102** as shown in Figure 17. Comparing this with Figure 5 in Section C of the Introduction could lead to the packing arrangement being assigned as type II. The molecules of **102** pack on top of each other in a less ordered fashion but the stacks still occur in the same diagonal pattern.



**Figure 17** Diagram showing the unusual packing arrangement of the red crystals of the bis dihydrotetrathiafulvalene **102**

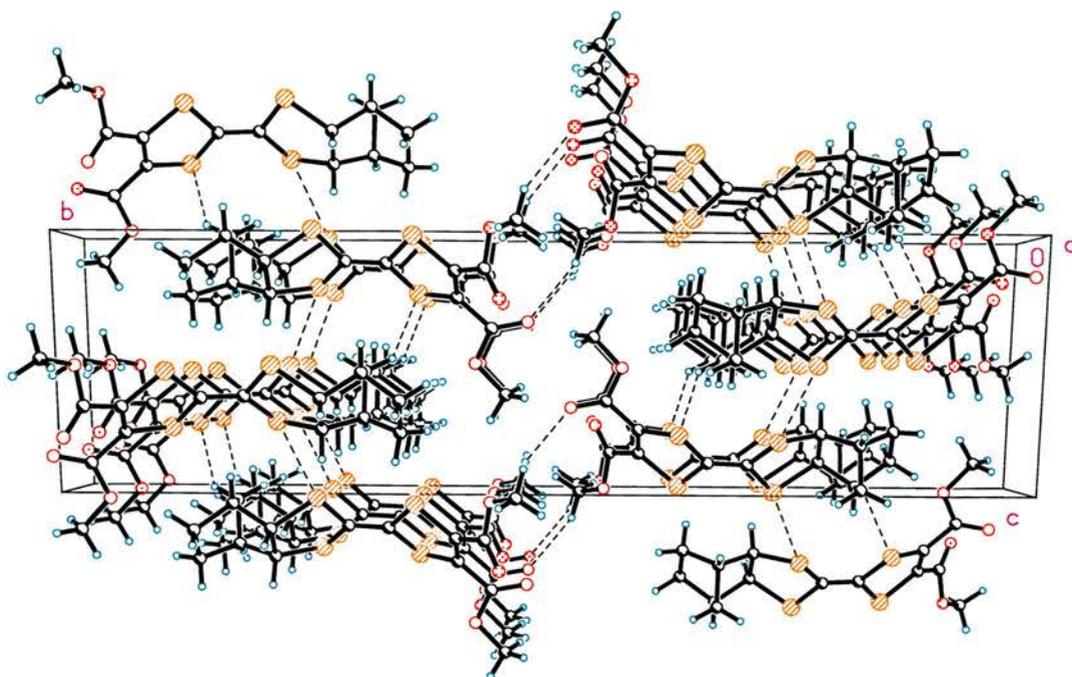
Benzoquinone and the dihydrotetrathiafulvalene **99** were dissolved in acetonitrile in an attempt to form a benzoquinone CTC. Red needle shaped crystals were obtained. An X-ray structure of the crystals, as shown in Figure 18 indicated that they were those of the dihydrotetrathiafulvalene **99** but in a different crystalline form to that previously obtained.

As compared to the structure of the conventional form shown in Figure 10, the central double bond C(4)-C(11) has increased in length by 0.01 Å. The carbon-sulfur bonds have decreased slightly in length by 0.002 Å. The sum of the angles for the 1,3-dithiolane ring and the 1,3-dithiole ring have changed significantly from 535° and 537° in Figure 10 to 530° and 534° in Figure 15. This indicates that both rings have become less planar.



**Figure 18** X-ray structure of the dihydrotetrathiafulvalene **99** (new form) showing crystallographic numbering scheme. Selected bond lengths and angles; S(3)-C(4) 1.750(18), C(4)-S(5) 1.747(18), C(4)-C(11) 1.343(11), C(11)-S(12) 1.762(18), C(11)-S(15) 1.758(18) Å; C(2)-S(3)-C(4) 95.55(9), S(3)-C(4)-S(5) 114.06(10), C(4)-S(5)-C(6) 96.13(9), S(5)-C(6)-C(2) 112.06(13), C(6)-C(2)-S(3) 111.57(12), C(11)-S(12)-C(13) 93.19(9), S(12)-C(13)-C(14) 116.63(14), C(13)-C(14)-S(15) 117.35(14), C(14)-S(15)-C(11) 93.16(8), S(15)-C(11)-S(12) 113.27(10)°.

There was an unusual packing pattern in the new crystalline form of **99** as shown in Figure 19 which had previously been referred to a type II packing arrangement as illustrated in Figure 5 in Section C of the Introduction. The molecules of **99** pack directly on top of each other and form stacks that occur diagonally to each other. The packing arrangement previously observed for **99** was a type V packing arrangement. This type of packing arrangement was also observed in the decarboxylated dihydrotetrathiafulvalene **117**.



**Figure 19** Diagram showing the packing arrangement for the new crystalline form of dihydrotetrathiafulvalene **99**

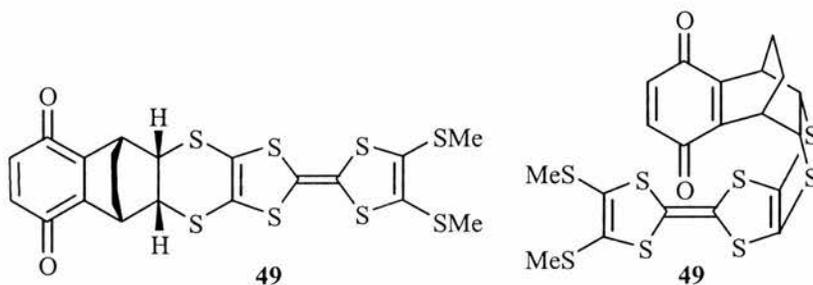
The crystals of this new form of **99** were also observed to be dichroic. This rare phenomenon means that when they were observed in transmitted light at a certain angle some appeared red and some yellow. By varying the angle of observation the red crystals changed to yellow and the yellow ones to red. This phenomenon was rather difficult to capture photographically but the existence of two different colours of crystals is obvious in the photographs on the following page which show compound **99** in both (top) transmitted and (bottom) reflected light.



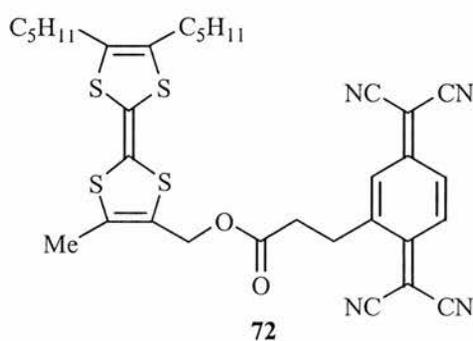
## E Donor- $\sigma$ -acceptor compound

### 1 Formation of a Donor- $\sigma$ -acceptor compound

As described in section B of the Introduction, components in which a  $\pi$ -donor is separated from a  $\pi$ -acceptor by a  $\sigma$ -bonded framework have been of interest ever since the pioneering paper of Aviram and Ratner in 1974.<sup>34</sup> Several previous attempts, such as that of Becker and co-workers, have been frustrated by having too flexible a  $\sigma$ -bonded portion which allows intramolecular interaction of the donor and acceptor as shown in **49**.<sup>45</sup>

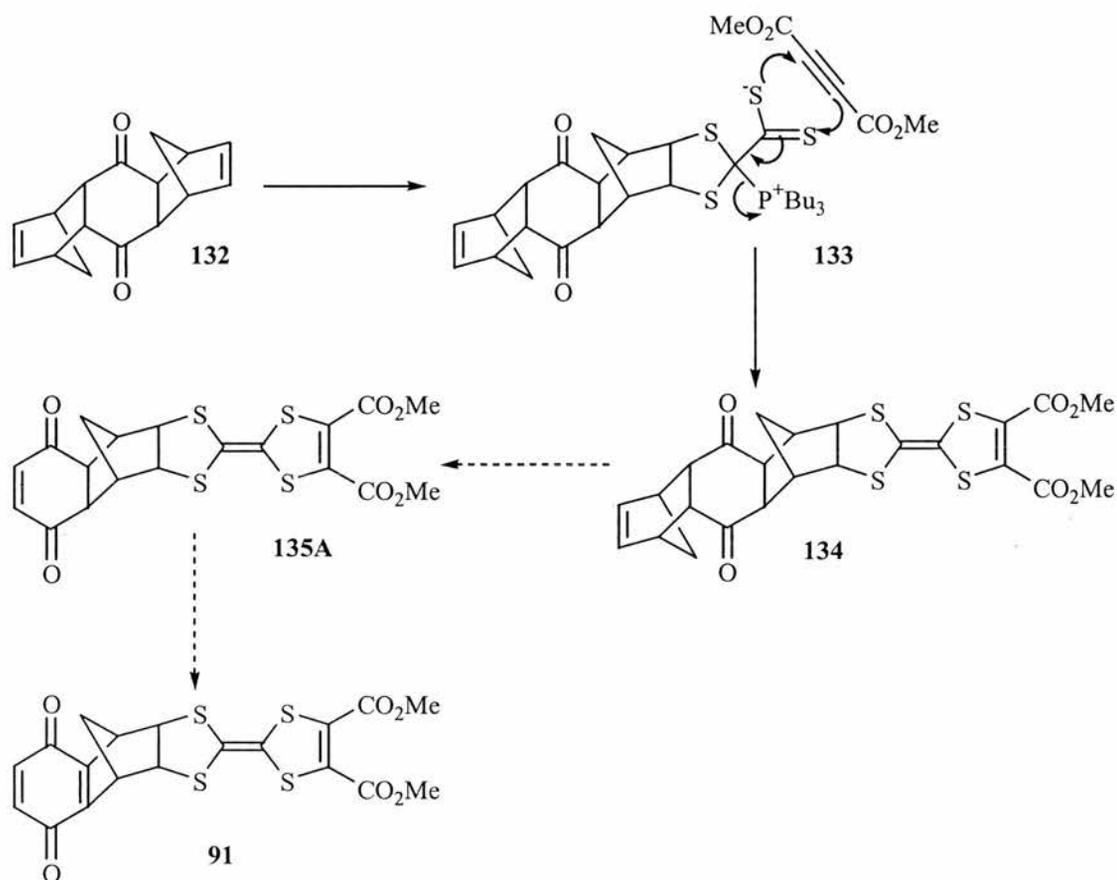


In the late stages of preparation of this Thesis, a highly significant paper appeared by Bryce and co-workers,<sup>61</sup> describing the synthesis and properties of the donor-acceptor compound **72** shown below.

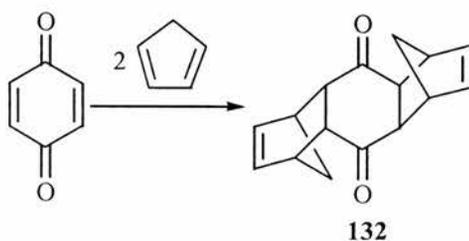


This showed two oxidation and two reduction processes using cyclic voltammetry with values of -0.77, -0.26, -0.09 and 0.37 V. The separation of the middle two of these at only 0.17 V was said to be the lowest ever recorded for an organic compound. This also led to two

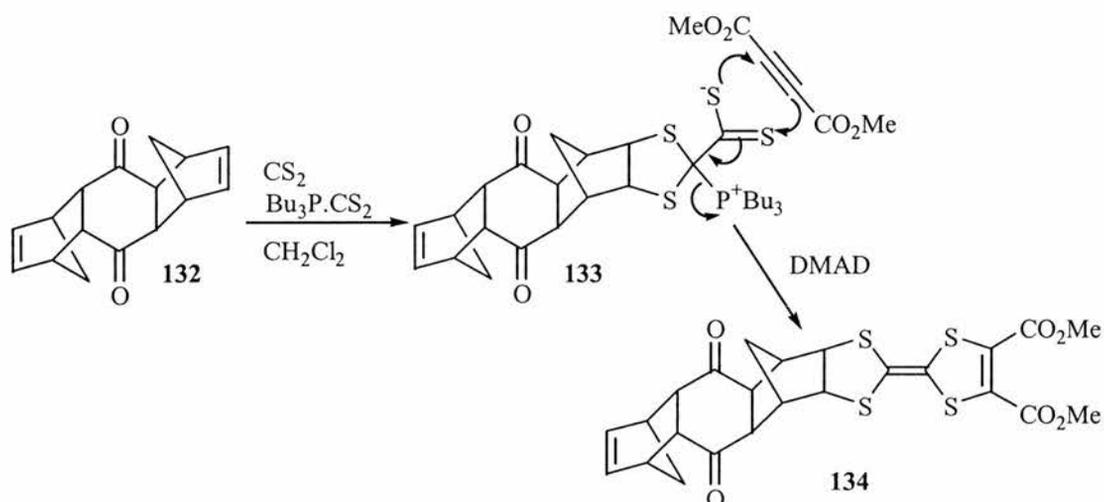
ESR signals being observed due to thermal population of the radical anion-radical cation state at room temperature. Our objective here was to prepare a donor- $\sigma$ -acceptor compound with a norbornene spacer which would act as an effective  $\sigma$ -bonded spacer group but also be sufficiently rigid to stop such intramolecular interactions. The synthetic plan for the target **91** is shown below.



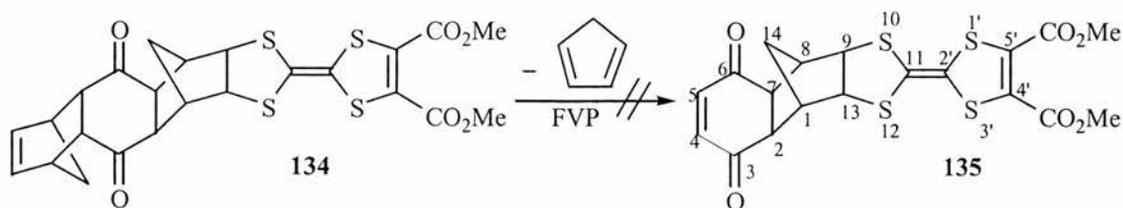
p-Benzoquinone reacted with freshly distilled cyclopentadiene to give a bis Diels Alder adduct **132** in good yield (71%).



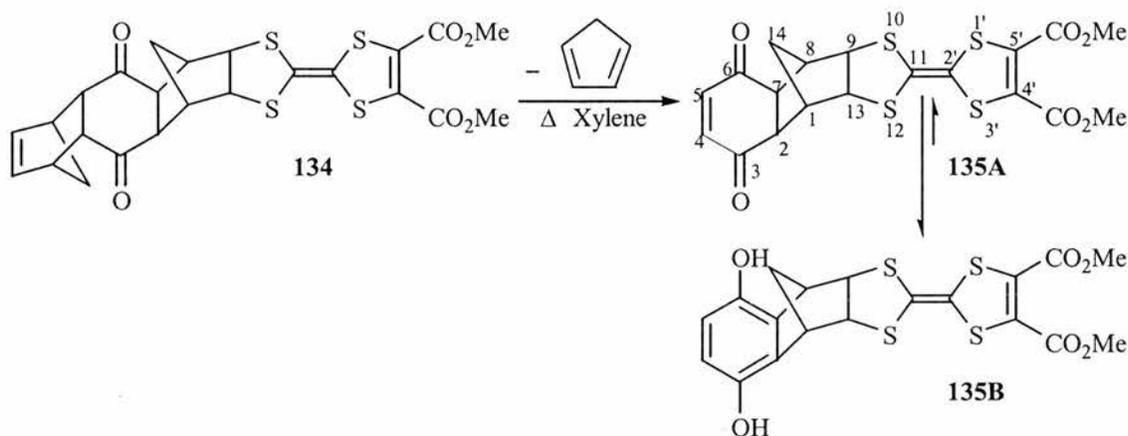
Compound **132** was dissolved in dichloromethane and the adduct **94** and carbon disulfide were added to the solution forming the intermediate **133**. It is interesting that even when double of the amount of the adduct **94** and carbon disulfide were added to **132** in an attempt to form the bis analogue of **133**, formation of a dihydro-TTF on both ends of the molecule did not occur. DMAD was added to the solution which was then allowed to stir for six days forming compound **134** through a cycloaddition reaction between the intermediate and DMAD in low yield (18%).



FVP was initially examined to remove the norbornene part of the molecule from **134** through a retro Diels Alder reaction to give **135**. Unfortunately this reaction did not occur and the starting material **134** remained unchanged. This was unexpected as FVP has been used previously to remove the norbornene portion from **101** to give the tetrathiafulvalene **116** as discussed in Section A part 1 of the Discussion.

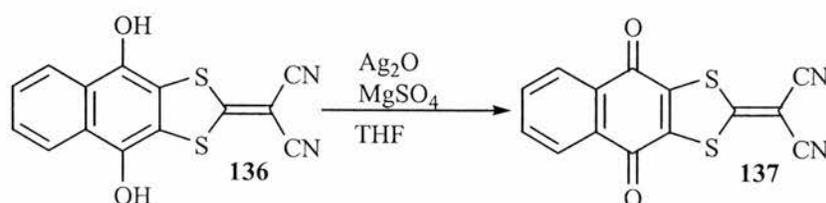


Compound **134** was dissolved in xylene and heated under reflux for 2 days. After chromatography of the crude product the pure product **135** was obtained in moderate yield (45%). The product **135** can exist in two forms, **A** and **B**. From the  $^1\text{H}$  NMR spectrum it was apparent that there was no signal for the C-2 or C-7 positions and instead there was a broad singlet for OH at  $\delta_{\text{H}}$  5.09. This indicated that the product occurred predominately as **135B**. The  $^{13}\text{C}$  NMR spectrum also showed that **135B** was the predominant form with quaternary signals at  $\delta_{\text{C}}$  143.4 (C-3, C-6) and 131.5 (C-2, C-7).

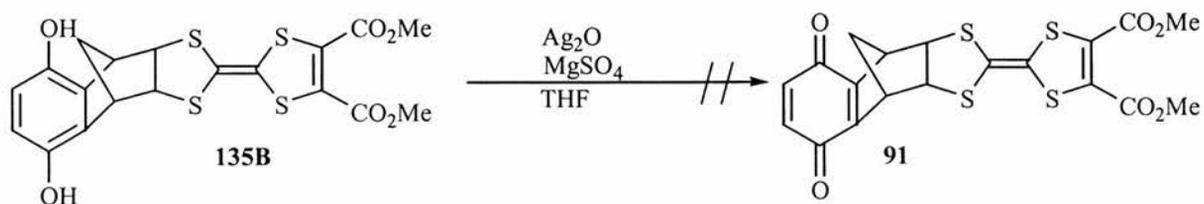


This was fortunate since oxidative removal of the two CH's from **135A** to give **91** would have been difficult whereas oxidation of the hydroquinone of **135B** was expected to be easier. Care had to be taken however to find an oxidation method which would be compatible with the presence of the easily oxidised dihydro-TTF function so methods already used in similar systems were tried.

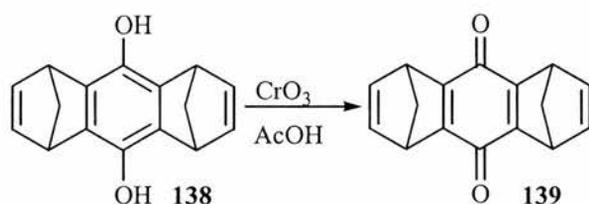
The first of these used silver oxide with magnesium sulfate to absorb the water formed. According to a literature procedure this reaction had worked for the oxidation of **136** into **137**.<sup>104</sup>



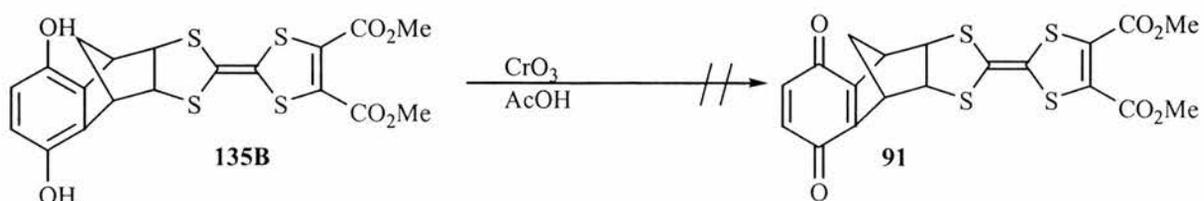
Compound **135B** was dissolved in THF and silver (I) oxide and magnesium sulfate were added to the solution forming a suspension. The suspension was allowed to stir overnight, then filtered, solvent removed and NMR and MS analysis were then carried out on the product. The analysis indicated that the solvent had reacted with the silver oxide to give butyrolactone thus preventing the formation of the desired product **91**.



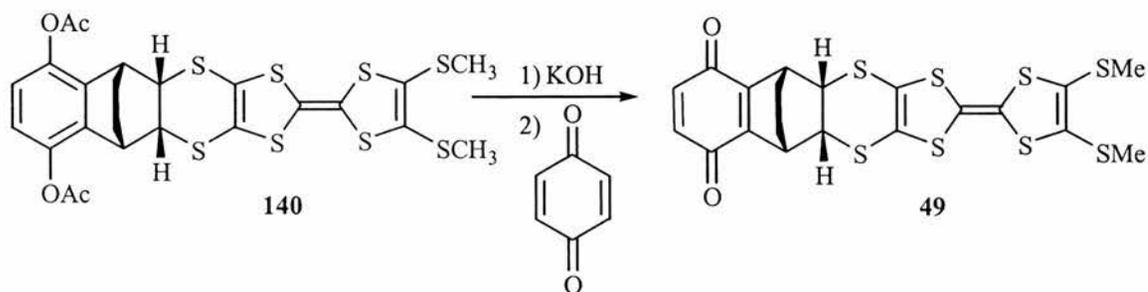
The second procedure, shown below was based on a similar reaction from the literature for the oxidation of **138** to **139**.<sup>93</sup>



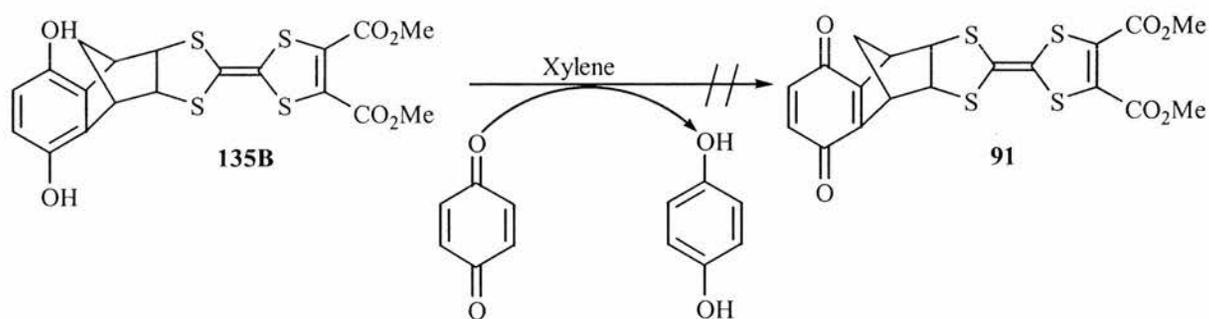
CrO<sub>3</sub> in acetic acid and water was added to a solution of **135B** dissolved in acetic acid in an attempt to produce **91**. However this reaction did not occur and a black oily solid was obtained instead. NMR analysis in d<sub>6</sub>-DMSO indicated that the oxidation had not occurred.



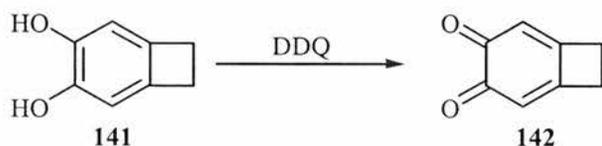
Becker and Khodorkovsky had used p-benzoquinone for the oxidation of **140** to **49** so this reagent was now tried.<sup>45</sup>



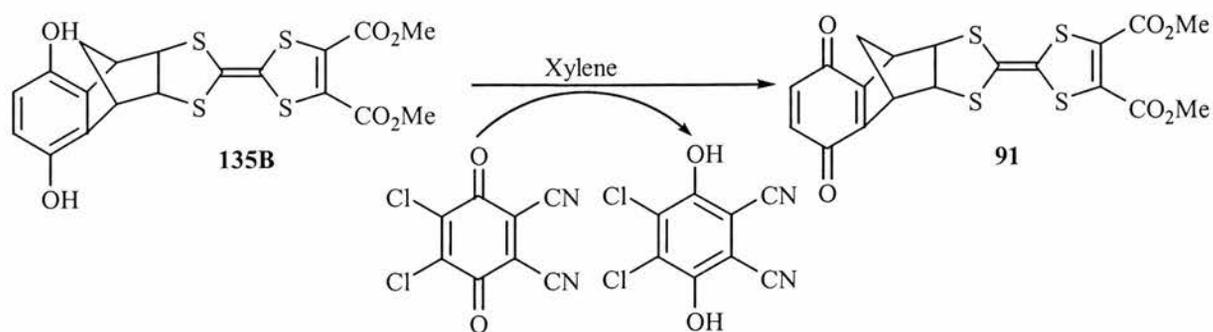
p-Benzoquinone and the compound **135B** were heated under reflux in xylene. If the p-benzoquinone was reduced then the oxidation of **135B** to **91** should occur. Unfortunately NMR analysis of the crude product showed that the starting material had remained unchanged.



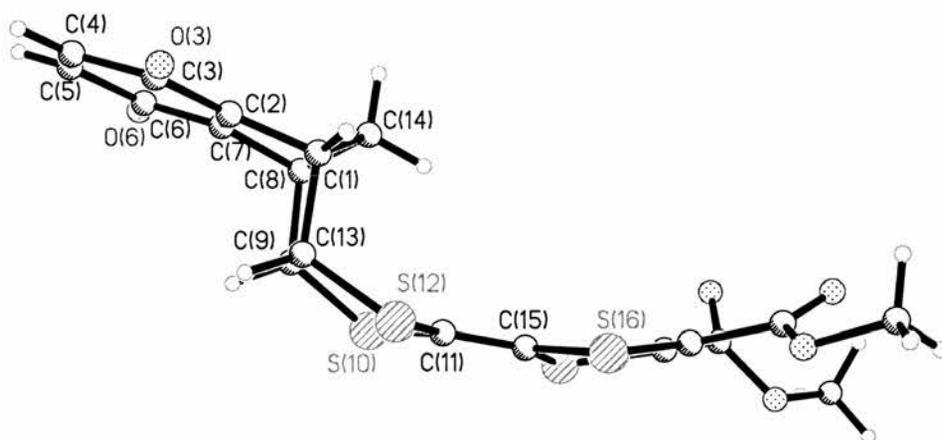
Finally a stronger oxidising agent, DDQ, was chosen instead of p-benzoquinone. This had previously been used for the oxidation of **141** to **142**.<sup>105</sup>



This time the reaction was successful and **135B** was oxidised to the target compound **91** in low yield (34%).



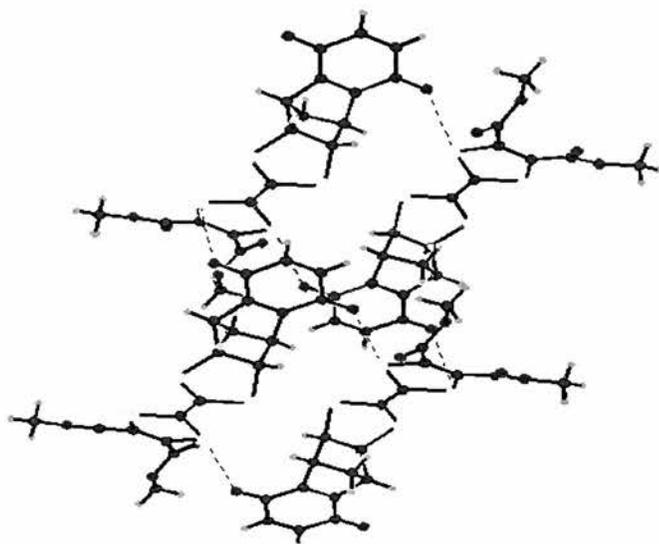
The structure of the target compound **91** was confirmed by obtaining an X-ray structure of the molecule from good quality crystals. The resulting structure is shown in Figure 20.



**Figure 20** X-ray structure of the donor- $\sigma$ -acceptor **91** showing the crystallographic numbering scheme. Selected bond lengths and angles; C(2)-C(3) 1.465(4), C(3)-C(4) 1.479(4), C(4)-C(5) 1.335(4), C(5)-C(6) 1.480 (4), C(6)-C(7) 1.473(4), C(7)-C(2) 1.342(4), S(10)-C(11) 1.757(3), C(11)-S(12) 1.749(3), C(11)-C(15) 1.333(4), C(15)-S(16) 1.758(3), C(15)-S(19) 1.769(3) Å; C(9)-S(10)-C(11) 96.61(12), S(10)-C(11)-S(12) 113.42(14), C(11)-S(12)-C(13) 96.71(12), S(12)-C(13)-C(9) 112.25(16), C(13)-C(9)-S(10) 111.68(17), S(16)-C(15)-C(19) 114.32(14), C(15)-S(19)-C(18) 94.01(12), S(19)-C(18)-C(17) 117.39(19), C(18)-C(17)-S(16) 117.7(2), C(17)-S(16)-C(15) 93.62(12)°.

The donor and acceptor portion of the molecule are aligned almost parallel to each other. The donor portion of **91** is not planar. The sum of the angles of the 1,3-dithiole ring is

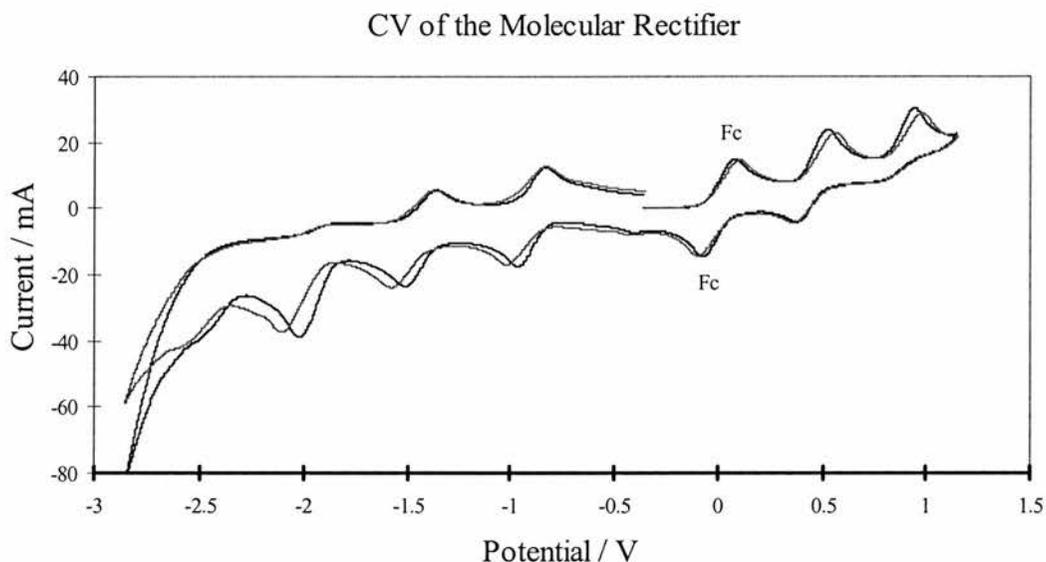
537° indicating that it is almost planar, but the sum of the angles of the 1,3-dithiolane ring is 530° indicating that it is less planar. Interestingly the non-planarity in this case is in the opposite sense from all the norbornane-fused dihydroTTFs previously examined. The dihydro-TTF part is bent up in the exo-direction whereas it is normally bent down in the endo direction. When the bond lengths of the donor portion of **92** were compared with those of the dihydrotetrathiafulvalene **99** they were found to be very similar. The packing diagram shown in Figure 21 showed a quite regular stacking pattern based on intermolecular C=O to S interactions.



**Figure 21** Stacking pattern for compound **91**.

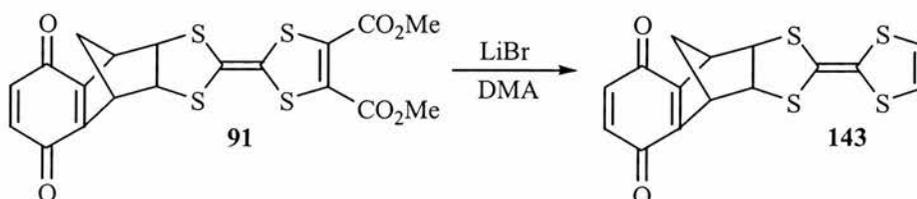
The molecules of compound **91** align themselves in a head to tail fashion within the column forming a staircase type pattern with two columns. The norbornane portion of the molecules in one column points away from norbornane portion of molecules in the other column.

CV measurements were carried out on compound **91**. The cyclic voltammogram, shown in Figure 22, shows two reversible oxidation potentials and two reversible reduction potentials. The relevant potentials are -1.4, -0.8, 0.5 and 0.9 V. The gap of 1.3 V between the first oxidation and reduction values is obviously very much greater than the 0.17 V gap for compound **72** recently reported by Bryce.



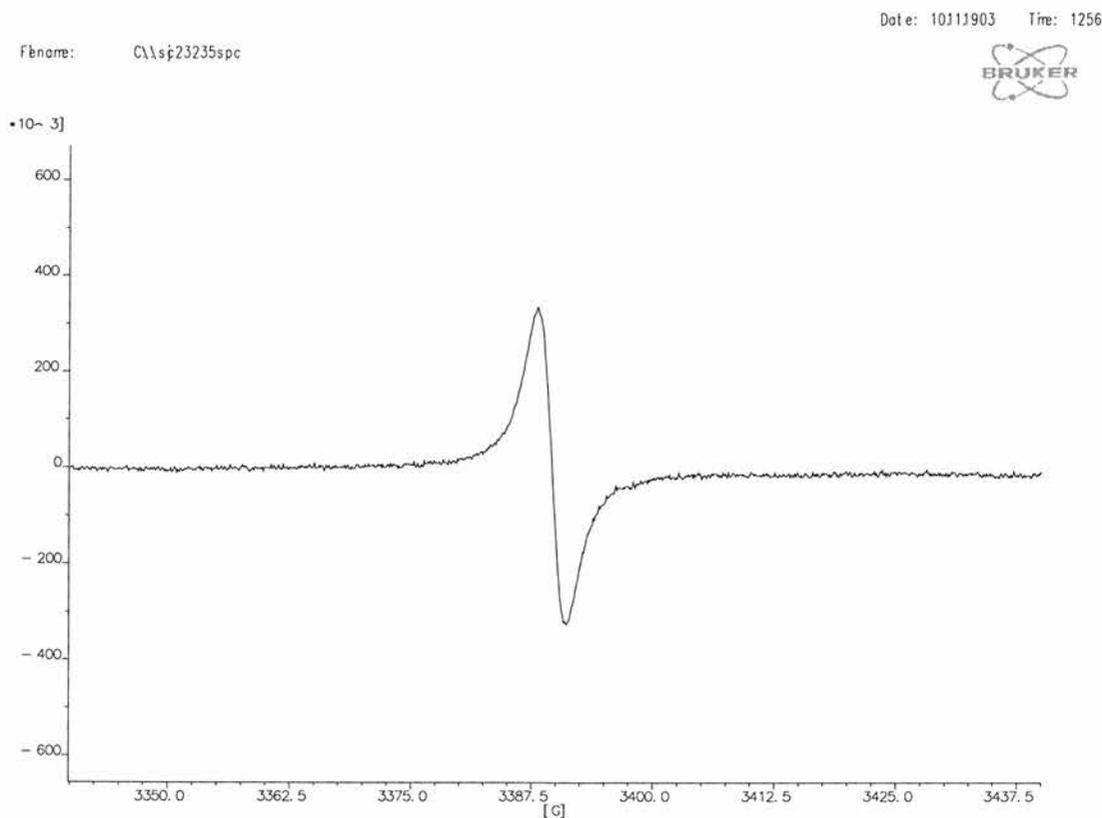
**Figure 22** Cyclic voltammogram of compound **91**

There is also evidence for an irreversible reduction process believed to be due to the ester groups on the donor portion of **91**. These ester groups were removed from **91** using a simple decarboxylation reaction giving the product **143**.



CV measurements could be carried out on **143** to examine if removing the ester groups has removed the irreversible reduction process. However unfortunately the product **143** was only available in very small quantity and was insoluble in any of the solvents normally considered suitable for CV measurements.

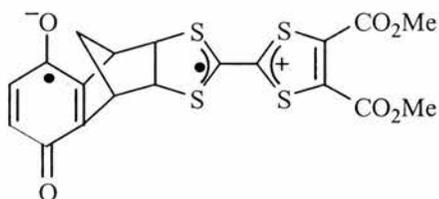
EPR measurements could be used to detect for the presence of radicals in compounds such as **91**. If radicals were detected then this would be further proof that the donor portion of **91** can donate electrons to the acceptor portion of **91** and the radical cation-radical anion form is present at RT even if it is in minute concentration. A 10mM solution of **91** in t-butyl benzene was made up initially. The EPR spectrum did not show the presence of any peaks so another 10mM solution of **91** was made up using acetonitrile as the solvent. The EPR spectrum showed the presence of two peaks as shown in Figure 23. These peaks could be attributed to a 1:1 ratio of TTF radical cation and the benzoquinone radical anion.



**Figure 23** EPR spectrum of **91** carried out in acetonitrile

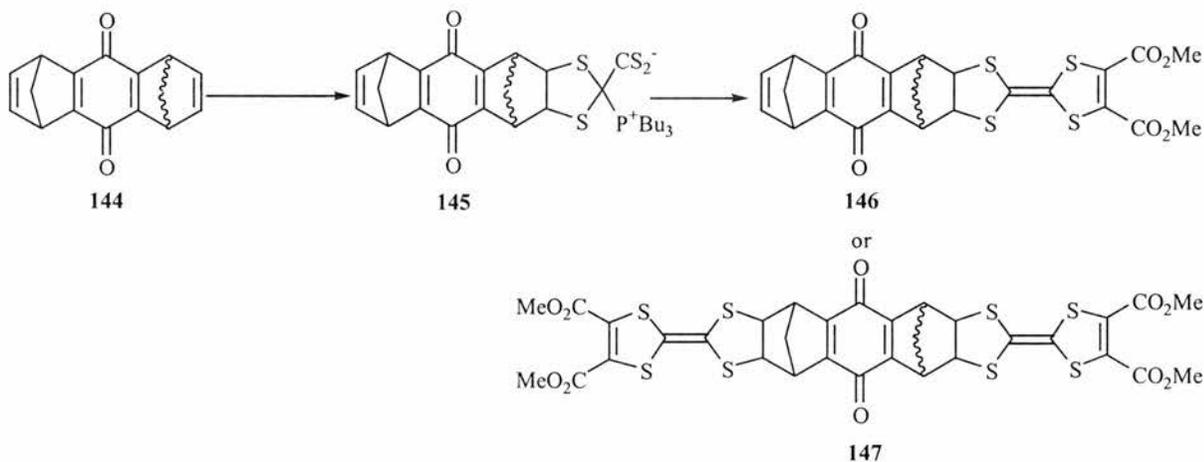
The first peak is easily seen on the spectrum and the second peak is much broader and occurs to the right of the narrow peak, a pattern almost identical to that observed for compound **72** obtained by Bryce and coworkers.<sup>61</sup>

The temperature at which the EPR measurement was carried out was increased. The size of the peaks increased with increasing temperature. This trend has also been observed by Bryce and co-workers in their recent paper.<sup>61</sup> According to the data obtained 0.03% of the compound **91** exists in the biradical state. This means that there is 0.06% of each species present when  $T = 342$  K. This is much lower than the 0.7% of Bryce's compound which existed in the biradical state at  $T = 290$  K. One of the resonance forms for the species responsible for the EPR signal is shown below.



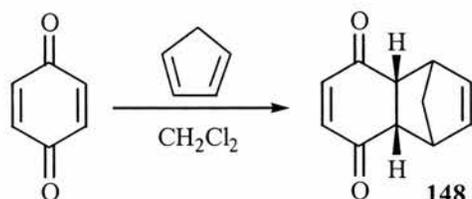
## 2 Attempted formation of a donor- $\sigma$ -acceptor compound using alternative routes

The synthetic plan for the target **146** or **147** is shown below.

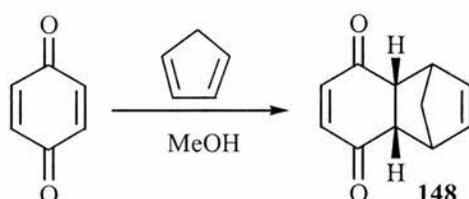


**a Initial attempt to prepare 144**

p-Benzoquinone was dissolved in dichloromethane and freshly distilled cyclopentadiene was added to the solution. A Diels Alder reaction occurred between one of the double bonds on p-benzoquinone and the cyclopentadiene giving the crude product **148** which was then recrystallised giving the pure form of **148** in low yield (20%).<sup>106</sup>

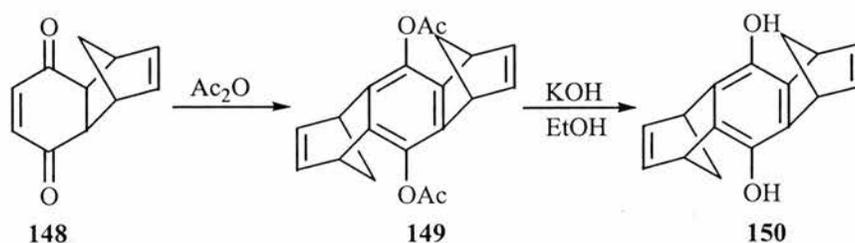


An alternative literature procedure was found. p-Benzoquinone was dissolved in methanol and maintained at 0 °C. Freshly distilled cyclopentadiene was added to the solution which subsequently underwent a Diels Alder reaction to give **148** and crystals precipitated from the solution after some of the solvent had been removed. Changing the solvent increased the yield to 78%.<sup>107</sup>



The starting material **148** was dissolved in acetic anhydride and heated under reflux for two hours. Crystals precipitated from the solution and were redissolved using ethyl acetate. A solid precipitated from the solution which could not be analysed due to its insolubility in common solvents. The solution was filtered and a white solid precipitated from the solution. MS and <sup>1</sup>H NMR analysis indicated that the correct compound, **149**, had

been formed but this was not confirmed using HRMS analysis. The white solid was heated under reflux with potassium hydroxide in ethanol in an attempt to form **150**. The solution was left to stand for three days by which time no crystals had precipitated out of solution. The solution was cooled using an ice bath but this also failed. Water was added slowly to the solution until crystals apparently precipitated from the solution. A black gummy solid began to precipitate from the solution. Attempts to filter off the solution were unsuccessful as the buckner funnel became clogged repeatedly. It was apparent that compound **150** had not formed.

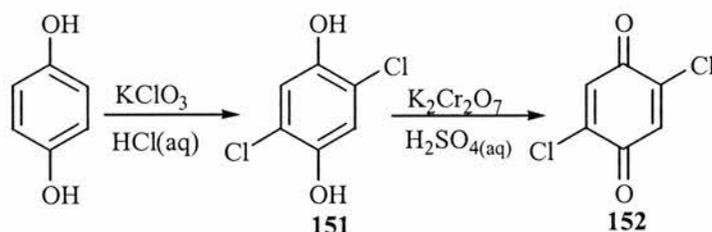


#### b Multi-step preparation and attempted reaction of **144**

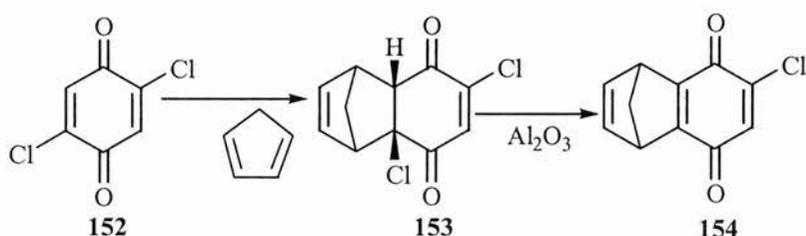
This was a six step synthesis involving the preparation of 2,5-dichloro-1,4-benzoquinone **151** and two subsequent Diels-Alder reactions followed by the removal of HCl over alumina to give **155**.

Hydroquinone was added to a supersaturated solution of hydrochloric acid. Potassium chlorate was added slowly to the mixture because of the vigorous reaction and the generation of chlorine gas. The potassium chlorate was added to chlorinate the hydroquinone. This mixture was allowed to stir overnight. The solid, **151**, was filtered off, washed with water and allowed to air dry. The product, **151**, was dissolved in sulfuric acid and potassium dichromate was added. The potassium dichromate was used to convert the hydroquinone to the fully oxidised form. The solution was stirred for two hours by which time a yellow solid had begun to precipitate out of solution. The solid, **151**, was filtered off and recrystallised.

NMR and mp analysis indicated that the correct product **152** had been formed in low yield (27%).

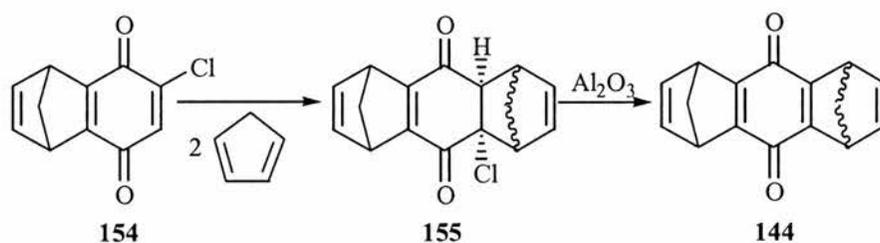


The 2,5-dichloroquinone **152** was dissolved in dichloromethane and freshly distilled cyclopentadiene was added to the solution causing a Diels Alder reaction with **152**. The solvent was removed and the solid was recrystallised. Not all of the solid would dissolve and the solution was filtered. Yellow crystals then precipitated out of solution, which were shown by NMR to be the correct product **153** and were obtained in a low yield (38%). These crystals were dissolved in dichloromethane and columned using alumina to remove HCl from **153** and convert it to the fully oxidised form **154** which was obtained as yellow crystals in excellent yield (93%).

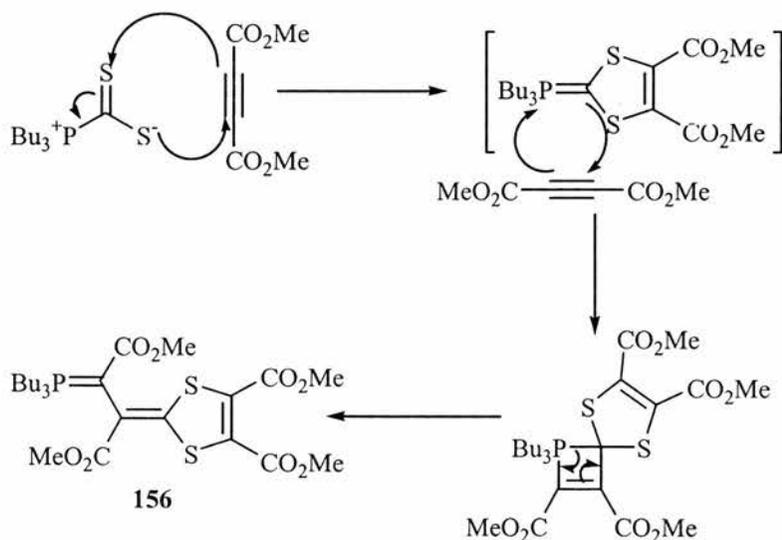


The compound **154** was dissolved in dichloromethane and freshly distilled cyclopentadiene was added to the solution. A Diels Alder reaction occurred within the solution between **154** and cyclopentadiene giving the product **155**. The solvent was removed under reduced pressure and compound **155** was obtained as a bright yellow solid. The NMR

spectrum of the solid was very complicated suggesting that there were different stereoisomers present. The solid was dissolved in dichloromethane and chromatographed using alumina to convert **155** to **144**, with the removal of HCl. An orange solid was obtained after the removal of the solvent. NMR analysis suggested that both stereoisomers were present in **144**.

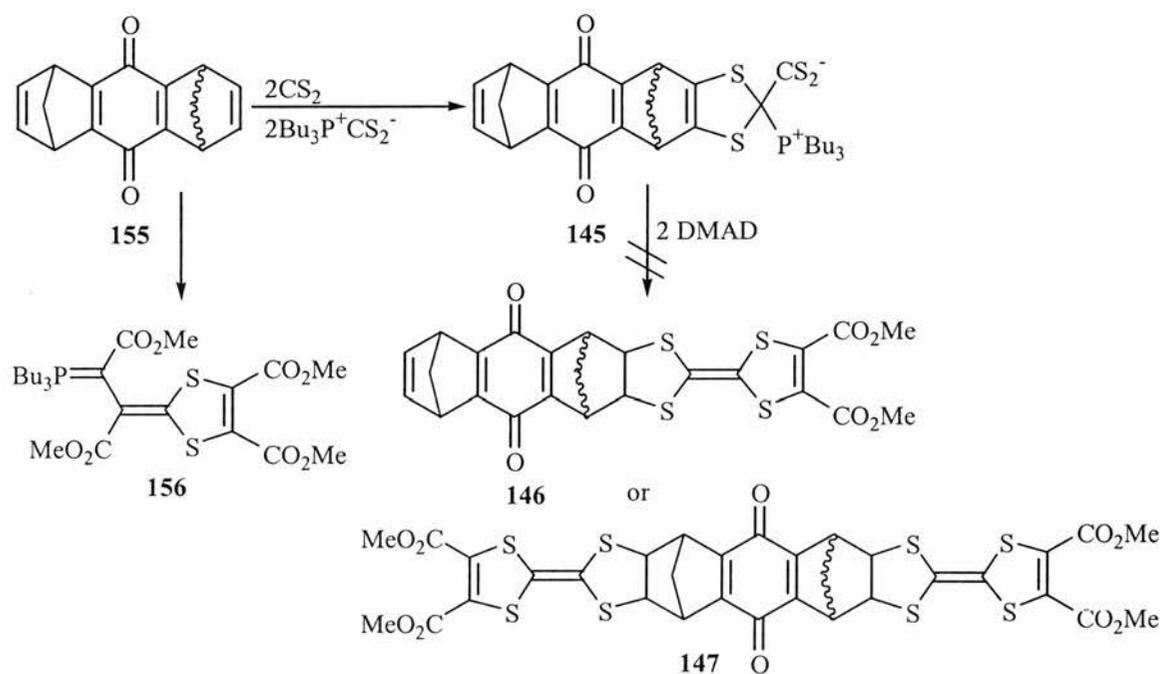


Compound **144** was dissolved in a solution of  $\text{Bu}_3\text{PCS}_2$  in dichloromethane.  $\text{CS}_2$  was added to the mixture which was allowed to stir for four hours. DMAD was added and the solution was allowed to stir overnight. The solvent was removed leaving <sup>a</sup>thick red oil which was shown to be the byproduct **156** as opposed to the desired product **146**.<sup>131</sup>



It was hoped that **144** would undergo a pseudo-1,3-dipolar cycloaddition with  $\text{Bu}_3\text{PCS}_2$  and  $\text{CS}_2$  to give the intermediate **145** which could then react with DMAD to give

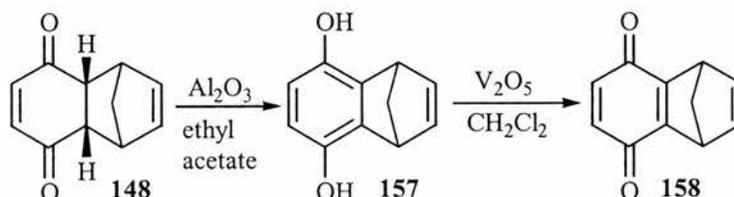
the desired product **146** or the alternative product **147**. It was believed that this reaction would follow the same mechanism as for the formation of the dihydrotetrathiafulvalenes. However the presence of double bonds in the quinone portion of the molecule seems to inhibit the formation of this product. The formation of the byproduct **156** would indicate that the initial intermediate is not formed and this is why the alternative reaction can occur. The double bond on **144** may not be as strained as compared to the compound with an unsaturated quinone portion of the molecule and this could reduce the reactivity of the molecule.



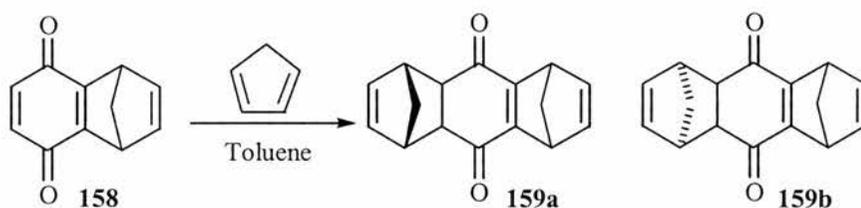
This reaction was then repeated except using acetonitrile as the solvent. The DMAD was added after a longer period in the hope that the intermediate **145** would form. A reaction did occur and NMR analysis of the oil indicated that a product of interest had been formed. The product was columned and NMR analysis showed that  $\text{Bu}_3\text{PS}$  was still present with the compound thus preventing further analysis.

### c Preparation of compound 144 using an alternative route

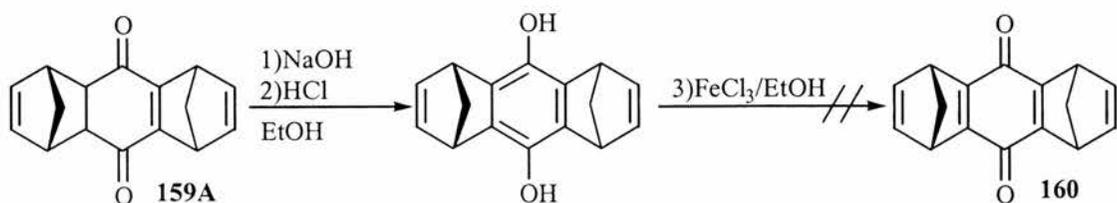
Compound **148** was stirred with alumina in ethyl acetate to convert it to the hydroxyl form **157**. This product could not be recrystallised successfully and the crude product was used for the next step. Using vanadium pentoxide as an oxidising agent **157** was converted to its fully oxidised form **158** in low yield (29%).



A Diels Alder reaction was carried out between cyclopentadiene and **158** which gave the product as a mixture of two isomers **159a,b**. The desired product **159a** was obtained in low yield (5%) through repetitive recrystallisation. The yield is quite low compared to that in the literature (55%).



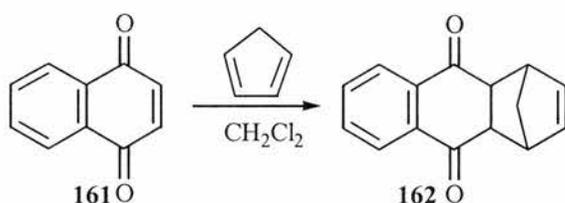
Oxidation to the fully unsaturated form **160** was attempted by following a literature procedure.<sup>104</sup> Base was used to deprotonate **159A**. Acid was then added to convert the compound to the diol.  $\text{FeCl}_3$  was intended to be used as the oxidising agent to convert the diol to **160**. The last step failed to occur. The reaction was repeated but only the first two steps were carried out. NMR analysis was carried out on the diol which showed that it was obtained in a very impure form.



This synthetic scheme for the synthesis of **160** does not appear to be very feasible. The last step did not produce the desired compound **160** and some of the steps in the scheme are very low yielding.

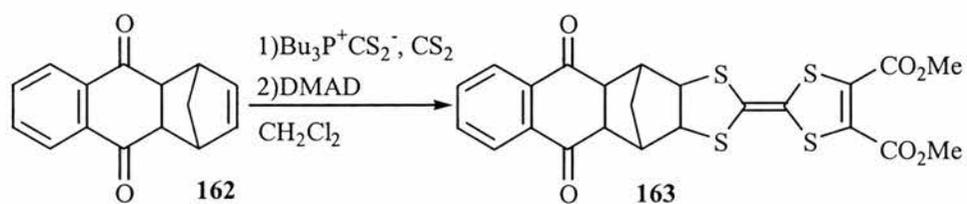
#### d Attempted preparation of compound **163**

Naphthoquinone **161** underwent a Diels Alder reaction with cyclopentadiene to give the dione **162**. This reaction proceeded in good yield (70%). With the successful synthesis of **91** it was hoped that this scheme could be extended using similar starting materials such as **161**. If this was successful then long thio-alkyl chains could be attached to the aromatic portion of the molecule so that they could be attached to a metal electrode thus satisfying the criteria for a molecular rectifier as explained by Aviram and Ratner.<sup>34</sup>



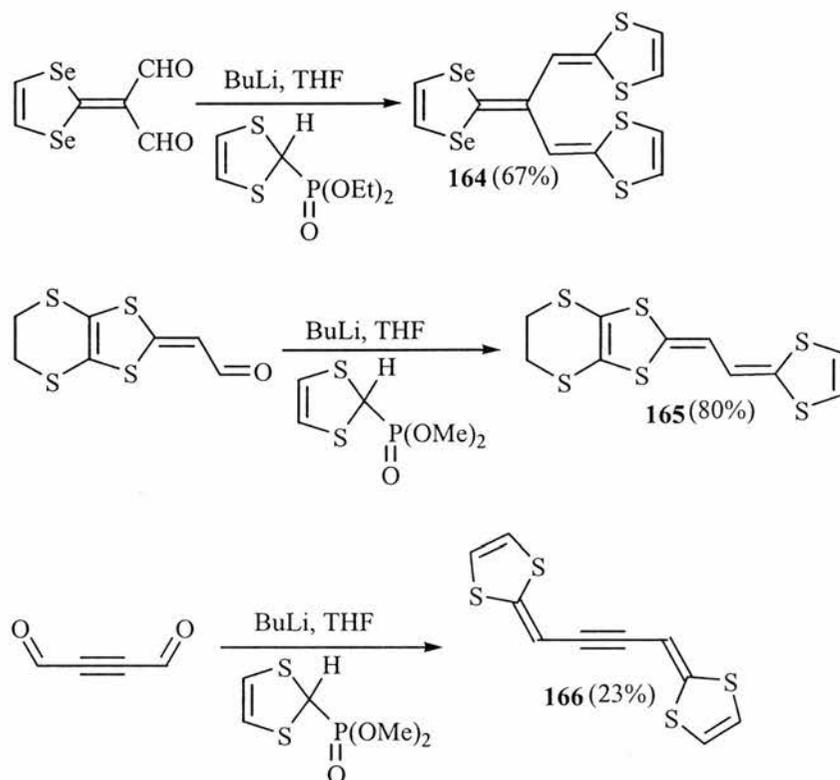
It was hoped that **162** would undergo a pseudo-1,3 dipolar cycloaddition and form the target compound **163**. Unfortunately this did not occur. On examination of the five fractions some of the starting material **162** and  $\text{Bu}_3\text{PO}$  were obtained. This would suggest that the initial reaction did not occur. The highly strained double bond of the norbornene portion of the molecule appears to be affected by what substituent is attached to the other side of the

ring. Comparing molecules **160** and **162** shows the presence of double bonds in the quinone section of the molecule. The behaviour of the quinone may be masked by having substituents attached which may inhibit the reaction from occurring. It would be worthwhile to measure a range of the reduction potentials of benzoquinones with two substituent groups attached one of which would be norbornene before attempting to synthesise target molecules such as **162**.

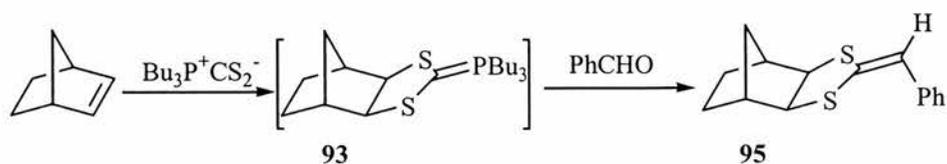


## F A convenient two-step conversion of Aldehydes into 2-Arylmethylene-1,3-Dithioles

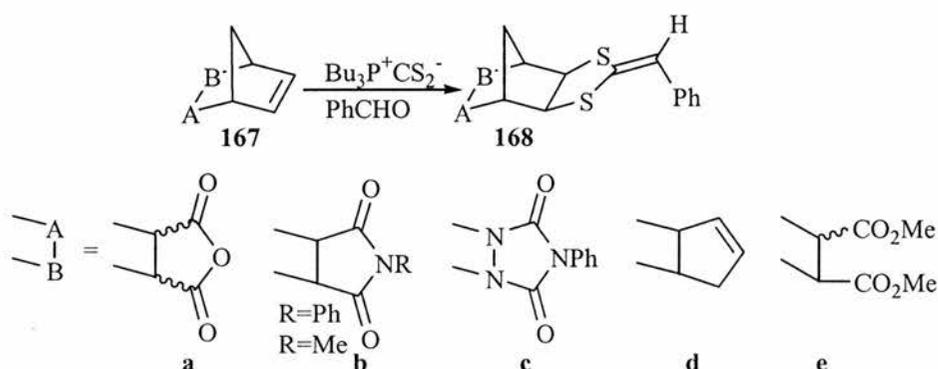
2-Alkylidene-1,3-dithioles (**164-166**) have previously been synthesized by reacting an appropriate aldehyde with an ylide in a Wittig reaction or a phosphonate bearing the 1,3-dithiole-2-ylidene moiety in a Wadsworth-Emmons reaction.<sup>132,133,134</sup>



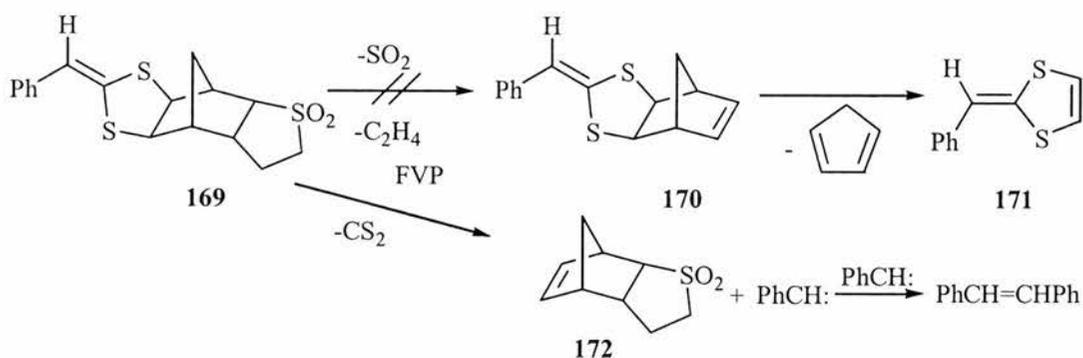
Previous work in the Aitken group showed that the  $\text{Bu}_3\text{P}\cdot\text{CS}_2$  adduct **92** was only reactive towards highly strained double bonds on molecules such as norbornene to give 2-tri-n-butylphosphoranylidene-1,3-dithioles **93** which could then be trapped by an in situ Wittig reaction with an added aldehyde to give **95**.<sup>135</sup>



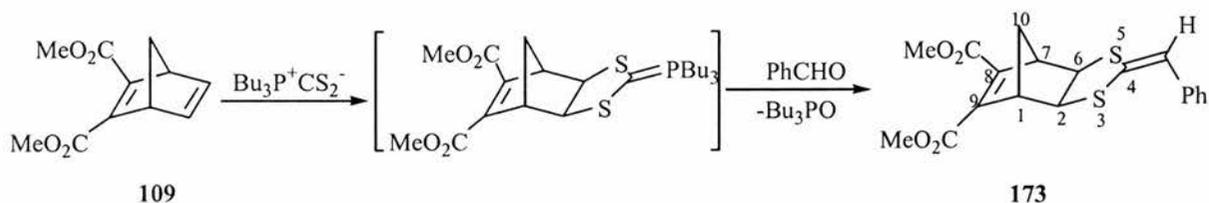
The direct transformation of the double bond of norbornene to the 2-alkylidene-1,3-dithiolane **95** in a one-pot procedure represented a valuable synthetic procedure. The extent of this reaction was examined further with a variety of strained double bond compounds **167a-e** to give the products **168a-e**.<sup>92</sup>



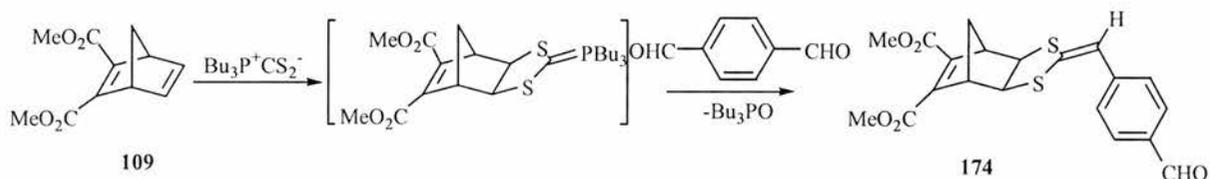
It was hoped that the sulfone compound **169** would undergo extrusion of  $\text{SO}_2$  and ethene to give an intermediate **170** which would then undergo a retro Diels Alder reaction to give the benzylidenedithiole **171**. However the only products obtained were  $\text{CS}_2$ , stilbene and the alkene **172**.<sup>98</sup>



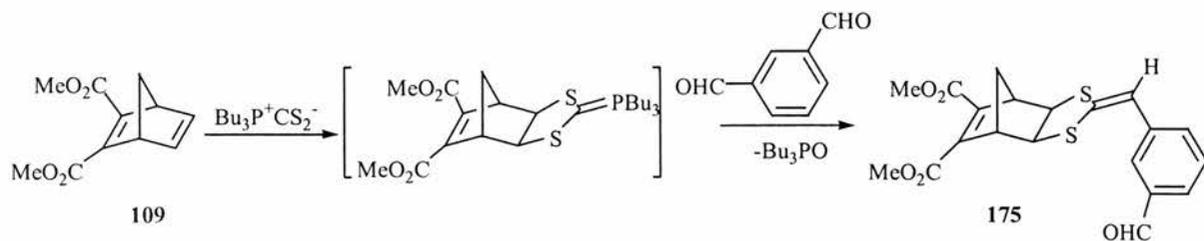
A new strategy was therefore devised using the substituted norbornadiene **109**, readily prepared by Diels Alder reaction of DMAD with cyclopentadiene. It was hoped that the Wittig products derived from this might lose the cyclopentadiene diester in a retro Diels Alder reaction to give the desired dithioles.



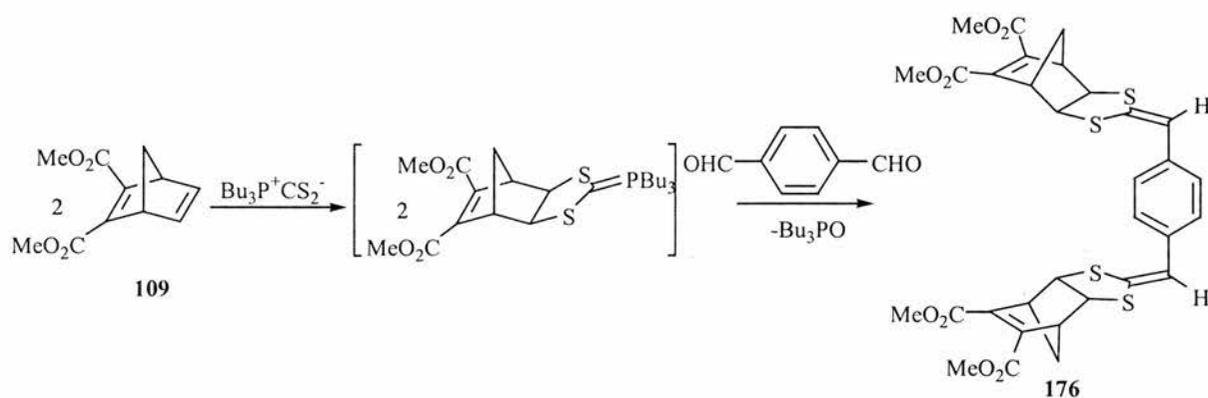
The  $\text{Bu}_3\text{PCS}_2$  adduct was dissolved in dichloromethane. The modified norbornadiene **109** was added to the red coloured solution. This solution was allowed to stir for 30 minutes to allow the intermediate to form. Benzaldehyde was added to the solution which was left stirring overnight. The solvent was removed and the crude product was purified by chromatography giving the pure product **173** in moderate yield (55%). Because the molecule is unsymmetrical separate signals for the C-2 and C-6 positions were observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.



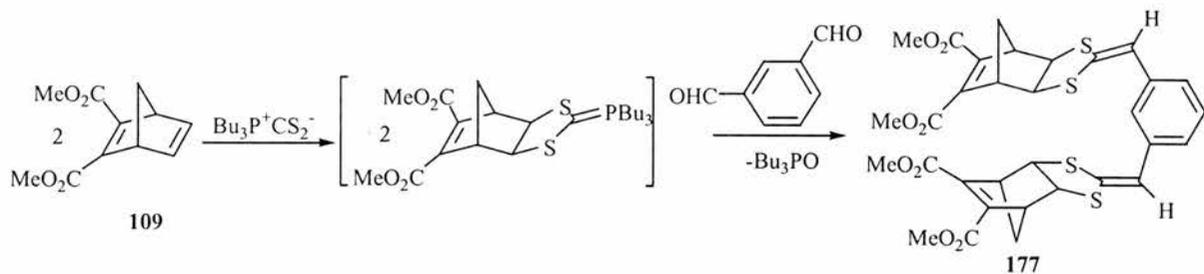
The product **174** was formed again in moderate yield (57%) using the same experimental procedure as for **173**. By adding the terephthalaldehyde in a 1:1 ratio with **109** the Wittig reaction only occurs on one side of the molecule. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra again showed that the molecule was unsymmetrical.



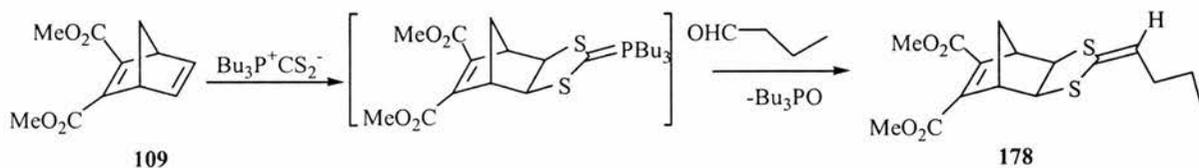
The meta analogue, **175**, of **174** was also synthesised but in a lower yield (41%). The splitting pattern for the aromatic ring is different from **174** because of the meta substitution.



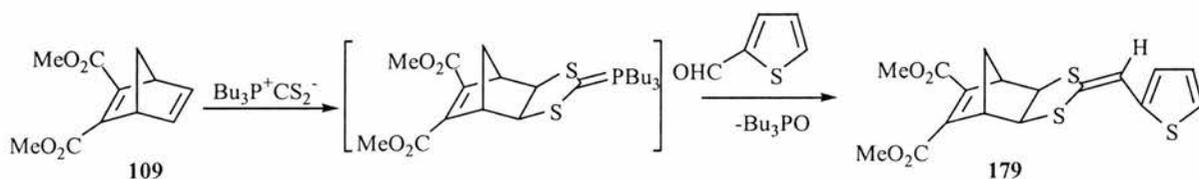
By reacting terephthalaldehyde in a 1:2 ratio with **109** and  $\text{Bu}_3\text{PCS}_2$  **92** the bis product **176** was formed in a very low yield (8%).



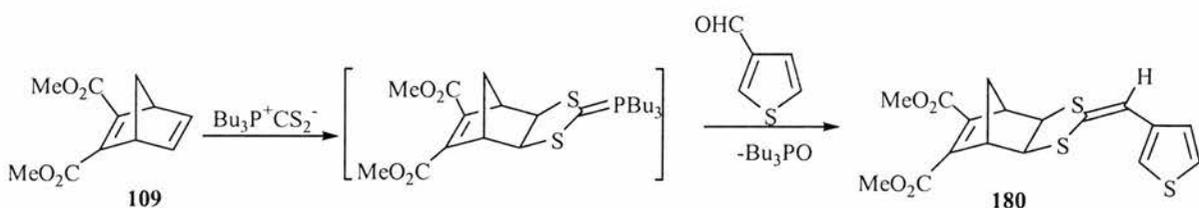
The experimental procedure used to form **176** was also used in the preparation of **177**. The pattern for the aromatic ring in the  $^1\text{H}$  NMR spectrum had again changed from **176** because of the meta-substitution pattern.



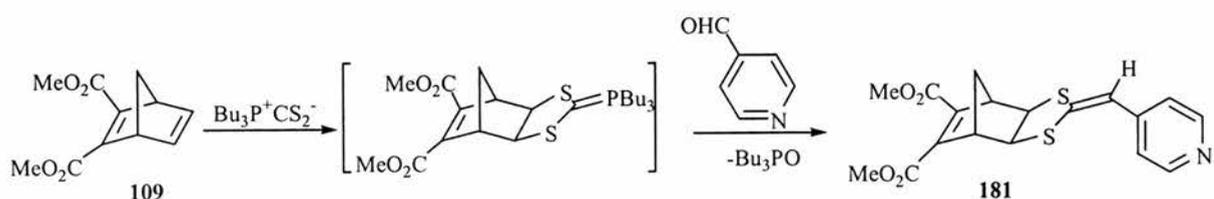
The aldehyde was changed to butyraldehyde and using the same experimental procedure as before compound **178** was synthesised in moderate yield (58%).



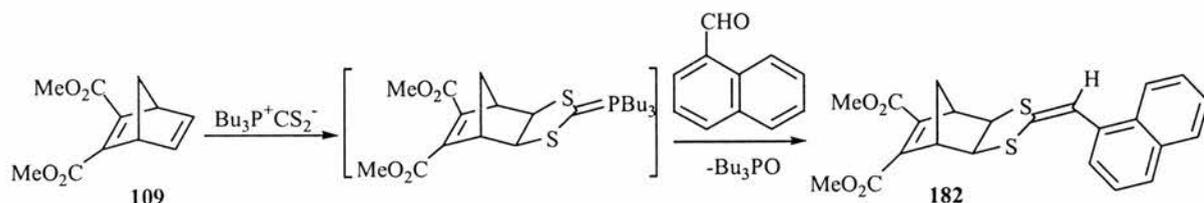
Thiophene-2-carboxaldehyde was used as the aldehyde in the formation of **179**, which was obtained in low yield (18%). The  $^1\text{H}$  NMR spectrum showed an unusual splitting pattern involving long-range coupling between the alkene CH and the protons of the thiophene ring. The splitting pattern was assigned with the help of a simulation programme.



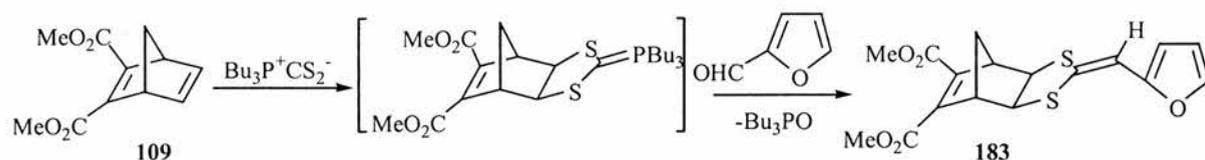
The 3-substituted analogue of **179**, **180**, was synthesised using thiophene-3-carboxaldehyde in similar yield (14%). The  $^1\text{H}$  NMR spectrum again showed long-range coupling.



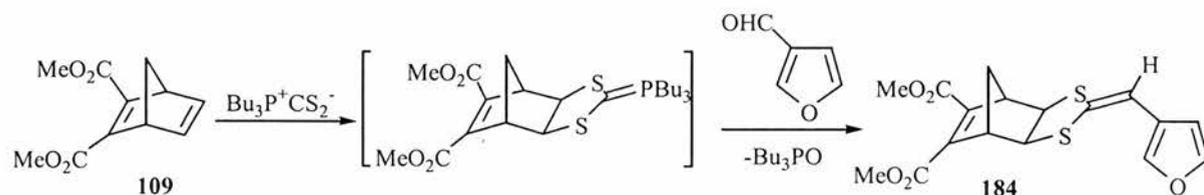
Pyridine-4-carbox aldehyde was reacted with **93** giving the product **181** in low yield (14%).



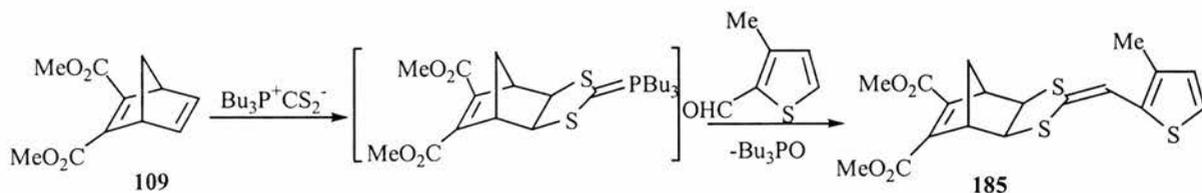
The pure product **182** was obtained in low yield (15%) from the Wittig reaction of **93** and 1-naphthaldehyde.



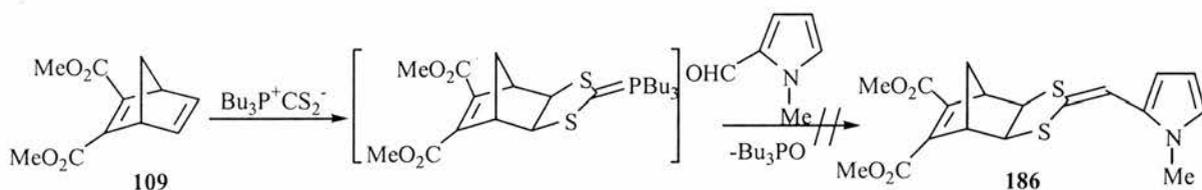
2-Furaldehyde was reacted with the intermediate **93** giving the product **183** in low yield (20%). The signals for the furan ring in **183** were again complicated due to coupling from the methylene hydrogen in the  $^1\text{H}$  NMR spectrum. These patterns were assigned with the help of a simulation programme.



The 3-substituted analogue of **183**, **184** was synthesised in very low yield (6%). The  $^1\text{H}$  NMR spectrum again had a complicated pattern of signals for the furan portion of the spectrum.



A modified thiophene-2-carboxaldehyde was used as an aldehyde in an attempt to synthesise compound **185**. This reaction did work but a side product came off the column in the same fraction as the product. A preparative TLC plate was used in an attempt to separate the two compounds but this proved unsuccessful.

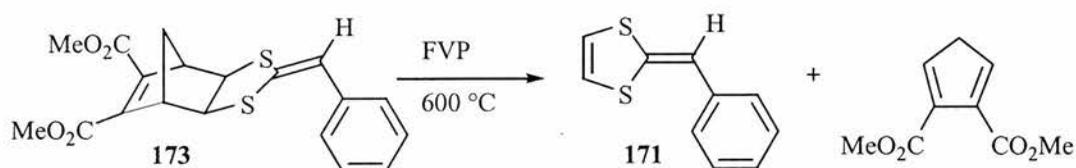


The intermediate **93** was reacted with 1-methylpyrrole-2-carboxaldehyde in an attempt to synthesis **186**. Unfortunately this was unsuccessful and the starting materials were recovered unchanged.

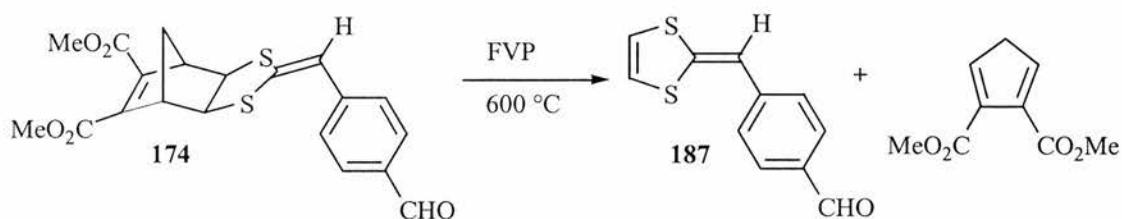
The advantages of this reaction route are that it uses cheap starting materials, **109** and **92** which are easily synthesised. The crude product then only requires chromatography for purification giving the pure product. The only disadvantage to this route is the low yields. The highest yield was 58% and the lowest yield was 6%. This reaction worked well for compounds **173-175** and **178**. Poorer yields were obtained when this reaction was used for compound **176**, **177** and **179-185**.

The next step of the procedure used FVP to convert the Wittig product into the retro Diels Alder product. This is a useful synthetic procedure as it only needs to be set up and left unattended for some time.

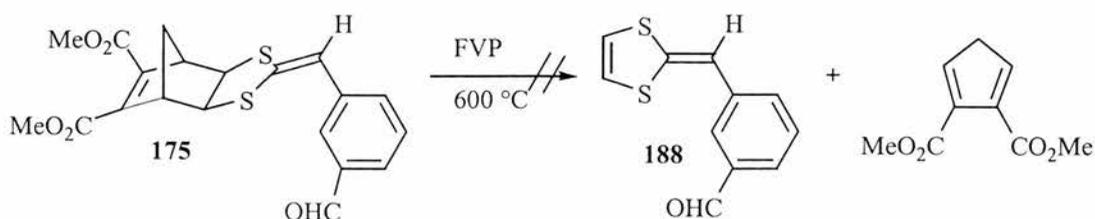
The Wittig product **173** was subjected to FVP at 600 °C which produced a red coloured product **171**. This product was purified using chromatography giving **171** in low yield (17%). An AB pattern of d was obtained for the two hydrogens of the 1,3-dithiole ring, indicating long range coupling of the benzylidene CH.



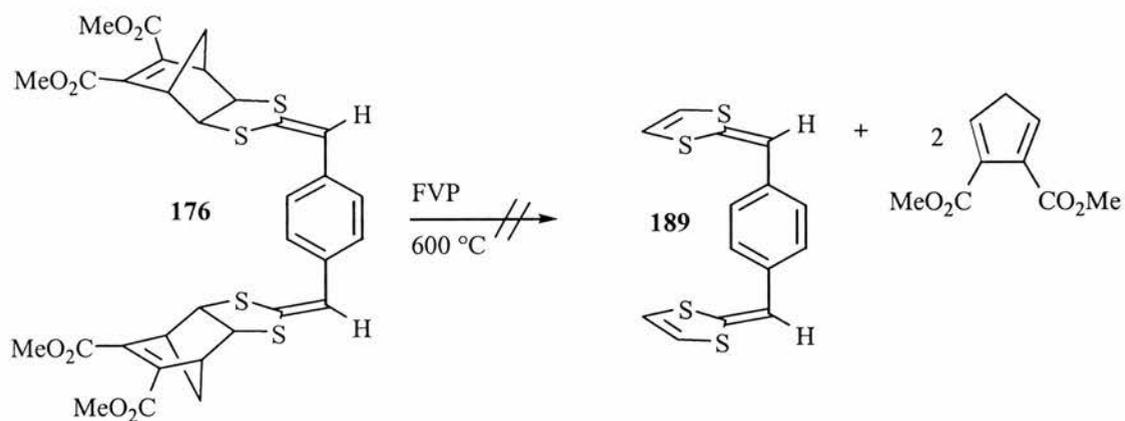
The 1,3-dithiole **187** was similarly synthesised in low yield (19%) through FVP of **174**.



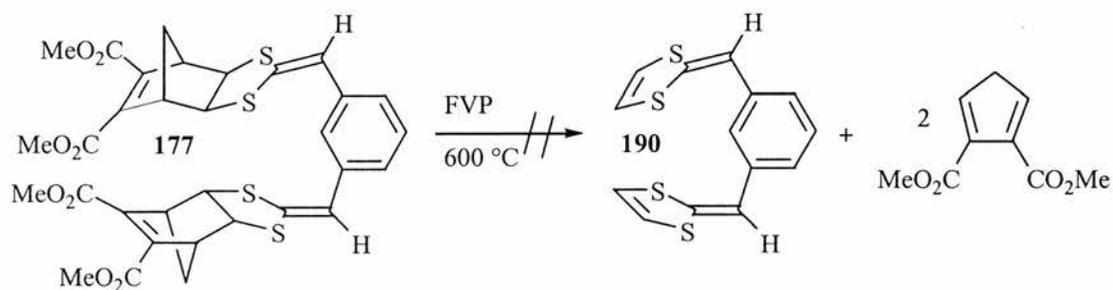
Compound **175** was subjected to FVP in an attempt to form **188** but the reaction did not occur.



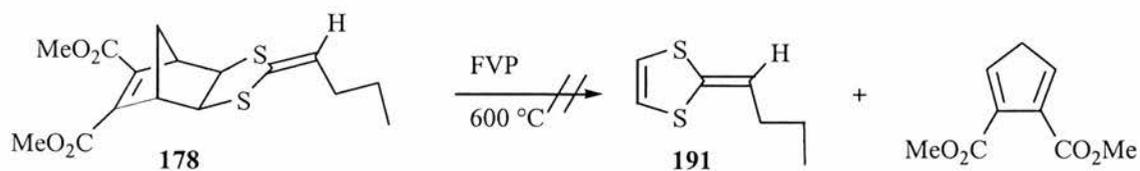
Compound **176** was also subjected to FVP in an attempt to synthesise **189** but again this reaction was unsuccessful.



The FVP also did not work for the synthesis of **190** from **177**.

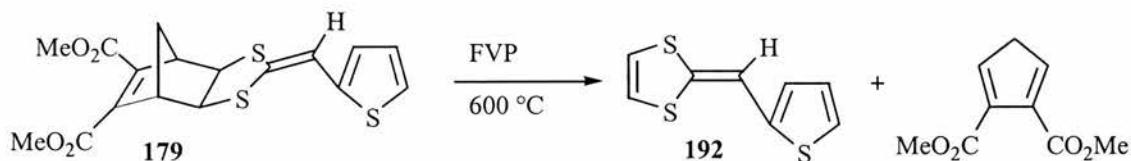


The FVP of the Wittig product **178** did not give the desired product **191**.

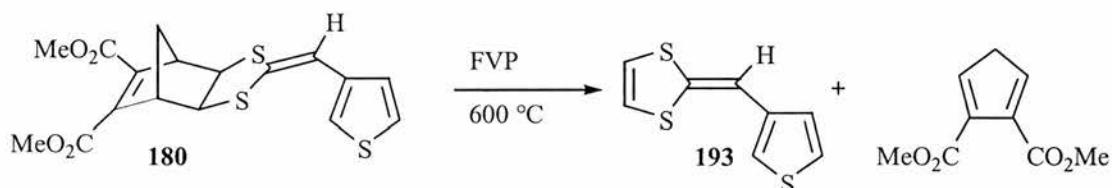


In contrast to these disappointing results, the heterocycle substituted compounds behaved better. The FVP of **179** worked well giving the product **192** in a low yield (17%)

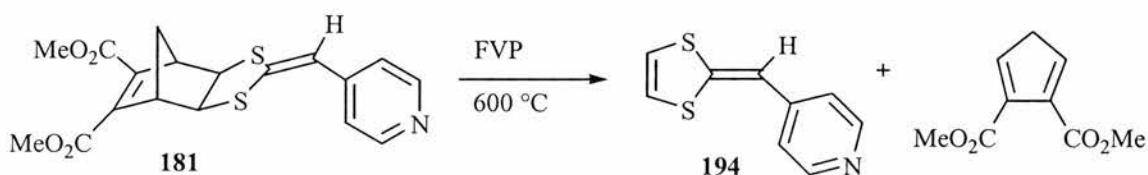
after purification with chromatography. The same complicated pattern of signals was observed for the thiophene ring in the  $^1\text{H}$  NMR spectrum of **192** as was observed for **179**.



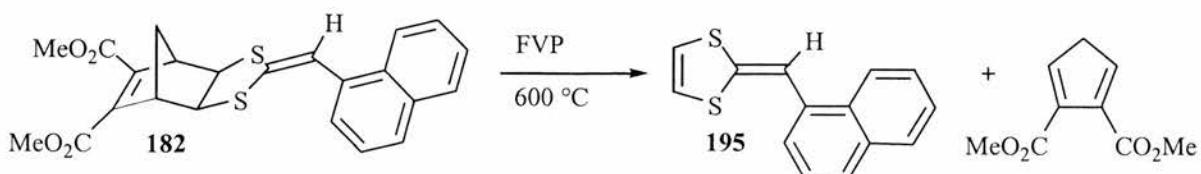
The synthesis of **193** through FVP of **180** worked well and the pure product **193** was obtained in a better yield (24%) than **192**. As before with **192** the same pattern of complicated signals for the thiophene portion of **193** was also observed in the  $^1\text{H}$  NMR spectrum.



The FVP of **181** was successful but gave the product **194** in a very low yield (2%).

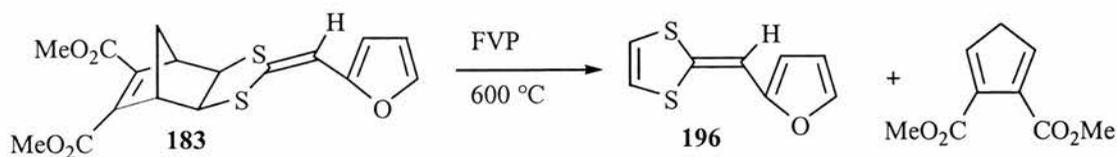


Compound **195** was synthesised in good yield (52%) from the FVP of **182**. This is the highest yield obtained in these experiments for the retro Diels Alder reaction.

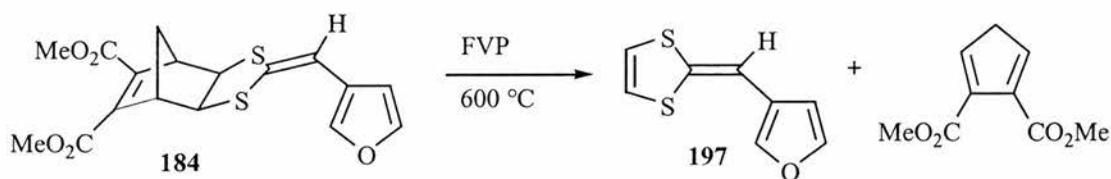


The product **196** was obtained with an unidentified side product from the FVP of **183**.

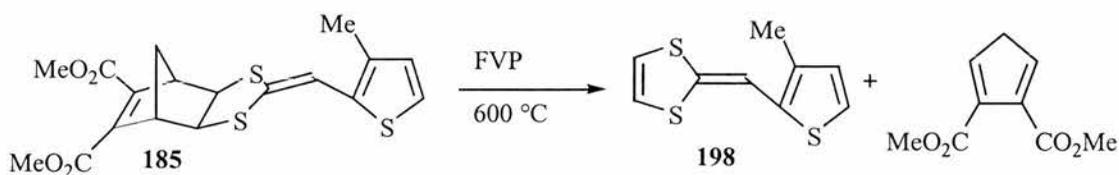
This could not be separated from the product **196**.



FVP of compound **184** also gave the product **197** in an impure form.



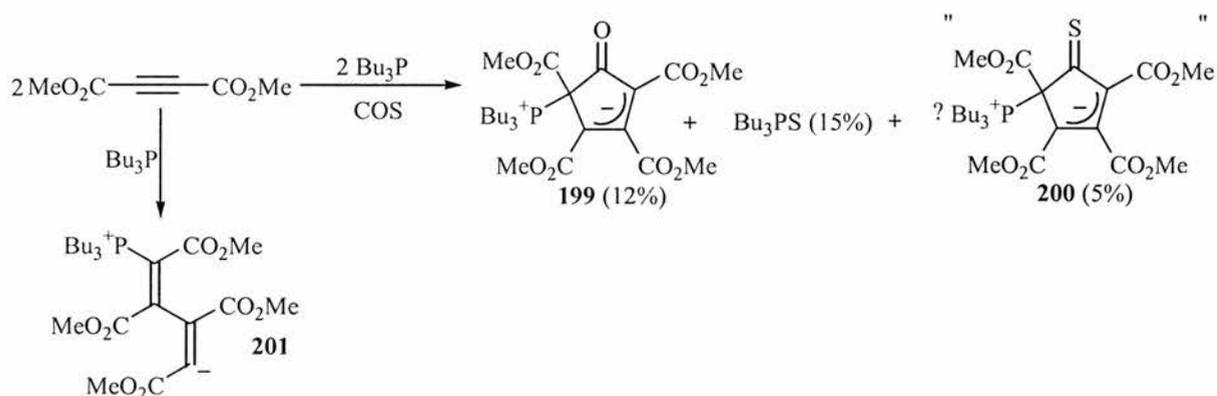
The Wittig product **185** was subjected to FVP at 600 °C which gave the product **198** in an impure form. Further attempts to purify the product were unsuccessful.



It was found that the retro Diels Alder reaction products synthesised began to degrade after a few days. Although a convenient two step synthetic route to 1,3-dithioles has been achieved the yields of the products are too low to make it competitive with existing methods of synthesising 1,3-dithioles.

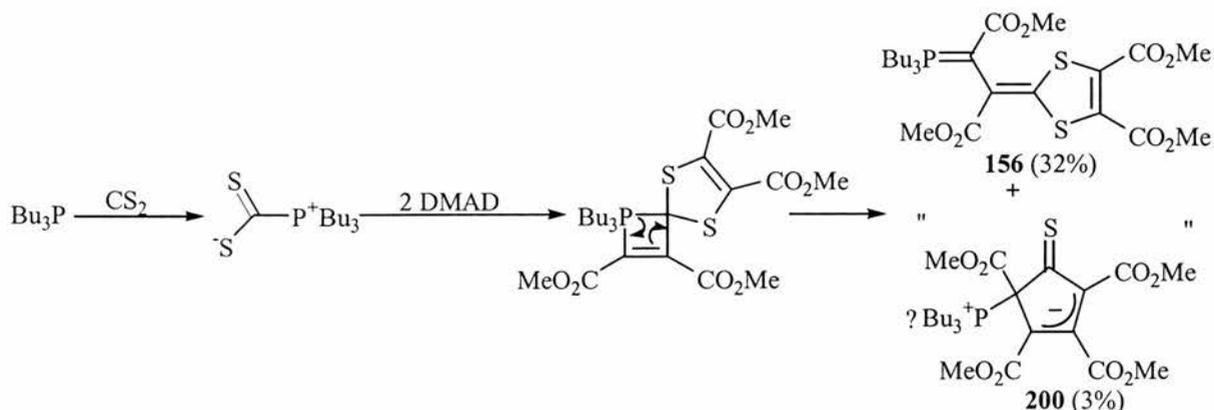
## G Reaction of Bu<sub>3</sub>P with DMAD and various heterocumulenes

Previous work carried out in the group showed that reacting tri-*n*-butylphosphine with DMAD and carbonyl sulphide gave the novel zwitterionic product **199**.<sup>136</sup> An X-ray structure was obtained from good quality crystals of **199** which confirmed the structure. There was a minor product present which was thought to be the thione analogue **200**. Adding Bu<sub>3</sub>P to a solution of COS in dichloromethane did not result in any reaction until DMAD was added and a dark red solution formed indicating that a reaction had occurred. The solution was allowed to warm up to room temperature, the solvent was removed under reduced pressure and the crude product was purified using column chromatography giving the novel zwitterionic product **199**, Bu<sub>3</sub>PS and the minor product thought to be **200**. No X-ray structure of **200** was obtained. The mechanism proposed for the formation of **199** involves initial interaction of Bu<sub>3</sub>P with 2 DMAD to give **201** which then interacts with COS to give the product.

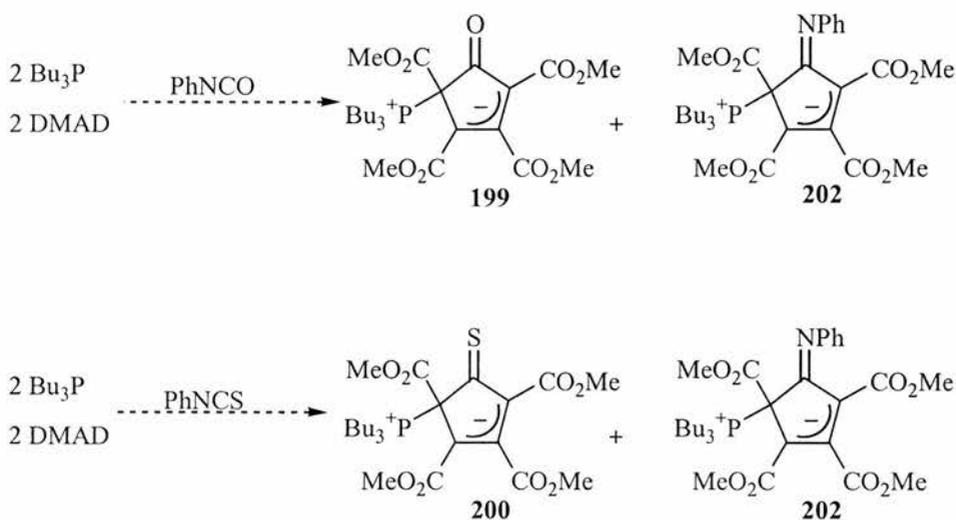


In contrast to this, reacting Bu<sub>3</sub>P and CS<sub>2</sub> together in dichloromethane and then adding DMAD gave the 1:2 adduct **156** since Bu<sub>3</sub>P and CS<sub>2</sub> have combined before DMAD is added.<sup>131</sup> By initially adding Bu<sub>3</sub>P and DMAD together it was hoped that the initial adduct **201** was formed which might then react to give the product thought to be **200**. This did

indeed prove to be the case and by adding the reagents in this order the normal product **156** was accompanied by the product thought to be **200**.<sup>136</sup>

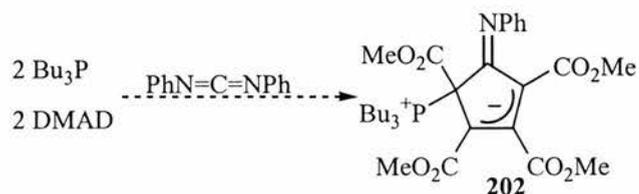


In an attempt to extend this reaction further a variety of different heterocumulenes were used. This was to examine if there were other synthetic routes to compounds **199** and **200** and also to attempt to isolate **200** and obtain an X-ray structure.

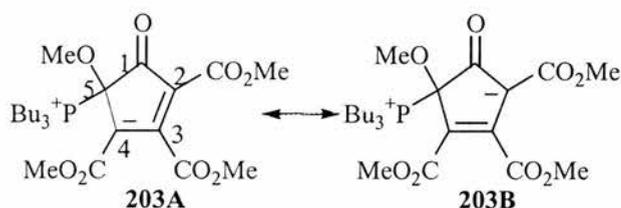


There was no evidence for the formation of compound **202**. Instead the same compound was isolated in each case. The CHN analyses indicated that this was not **199** or **200** but a compound which had almost identical molecular formula. A further reaction was

carried out using a different heterocumulene, diphenylcarbodiimide in an attempt to obtain compound **202**.

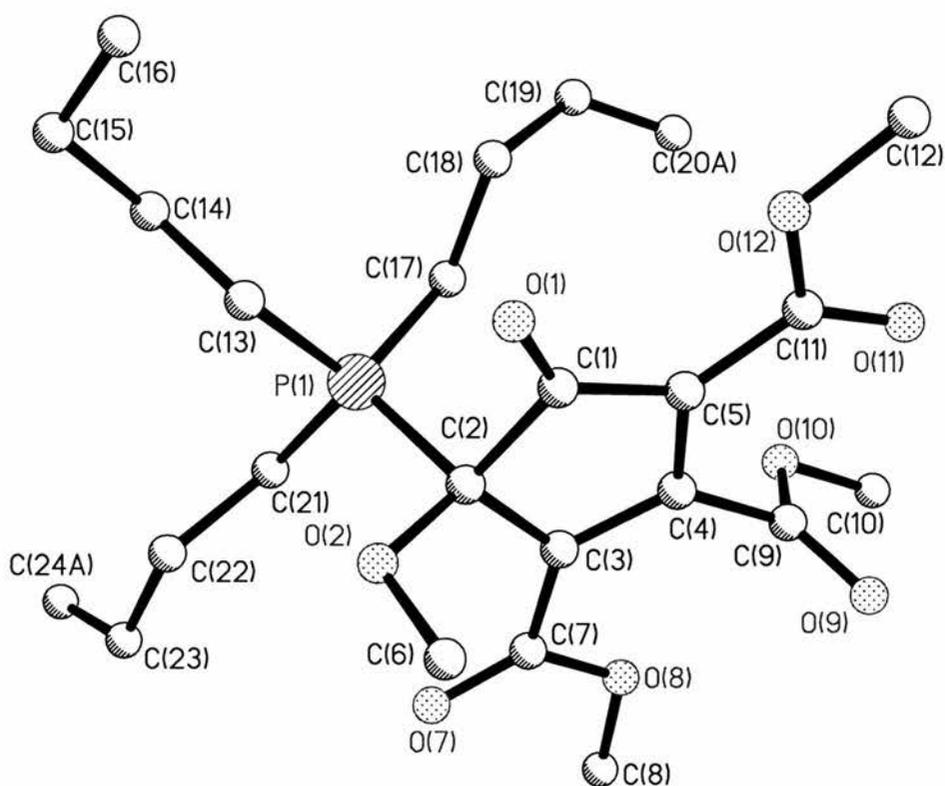


The intended reaction did not occur and a product was isolated which according to the spectroscopic data was identical to the two compounds formed from the reactions using PhNCS and PhNCO. Crystals of high quality were isolated from the second reaction and an X-ray structure was obtained. This indicated that a novel crystalline zwitterionic product **203** had been formed from the reaction of Bu<sub>3</sub>P and DMAD in the presence of heterocumulenes such as PhNCS, PhNCO and diphenylcarbodiimide. The reaction of Bu<sub>3</sub>P and DMAD in the absence of a heterocumulene was carried out and the same product **203** was obtained according to NMR spectroscopic data.



Compound **203** had very similar spectroscopic data to **199**:

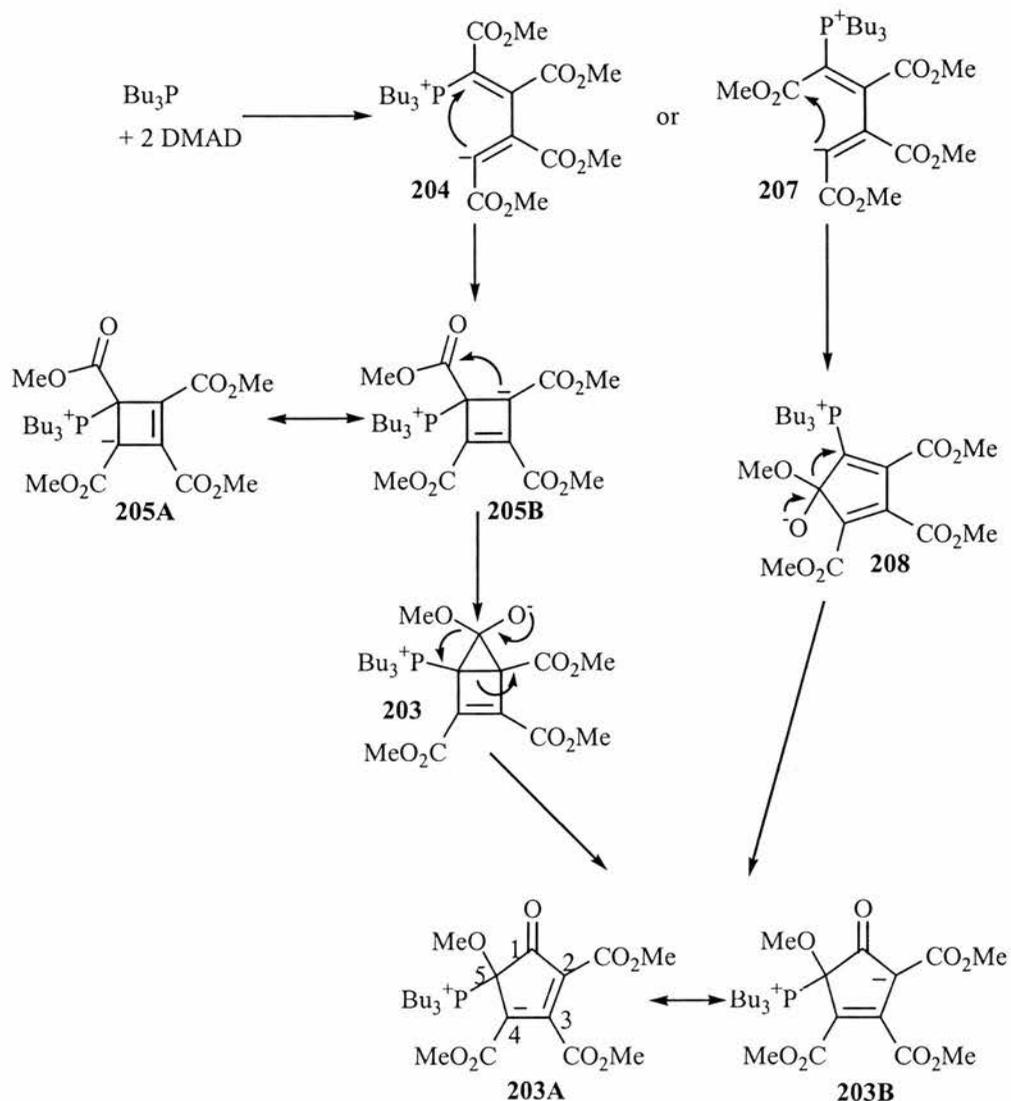
- The <sup>31</sup>P NMR shift is almost identical (**203** δ<sub>p</sub> = 36.1; **199** δ<sub>p</sub> = 36.2 ppm)
- In the <sup>1</sup>H NMR spectrum one of the four OMe signals is shifted to lower frequency from the range δ<sub>H</sub> 4.0-3.7 ppm to δ<sub>H</sub> = 3.25 ppm.



**Figure 24** X-ray structure of the zwitterionic compound **203** showing crystallographic numbering scheme. Selected bond lengths and angles; P(1)-C(2) 1.853(4), P(1)-C(21) 1.796(5), C(1)-C(2) 1.569(5), C(1)-O(1) 1.227(4), C(2)-C(3) 1.522(5), C(3)-C(4) 1.376(5), C(3)-C(7) 1.442(5), C(4)-C(5) 1.418(5), C(4)-C(9), 1.495(9), C(5)-C(1) 1.426(5), C(5)-C(11) 1.433(6) Å; C(1)-C(2)-C(3) 103.0(3), C(2)-C(3)-C(4) 107.2(3), C(3)-C(4)-C(5) 114.0(3), C(4)-C(5)-C(1) 107.9(3), C(5)-C(1)-C(2) 107.0(3)°.

The bond lengths for C(3)-C(4), C(4)-C(5) and C(5)-C(1) are intermediate between those for normal double and single bonds indicating that there is delocalisation. The compound is stabilised by delocalisation. The bond between C(4) and C(9) is much longer than C(3)-C(7) and C(5)-C(11) indicating that only the ester groups on C(3) and C(5) are participating in the delocalisation. The  $^{13}\text{C}$  NMR spectrum also indicates the delocalised

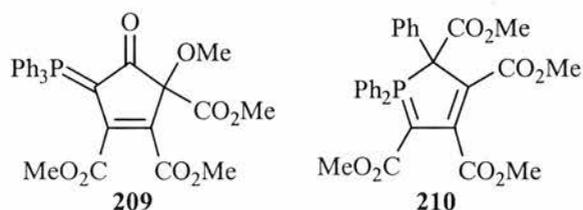
nature of the allyl anion. The chemical shifts for C-2 and C-4 are 93.5 and 101 ppm respectively, but the shift for C-3 is 160 ppm.



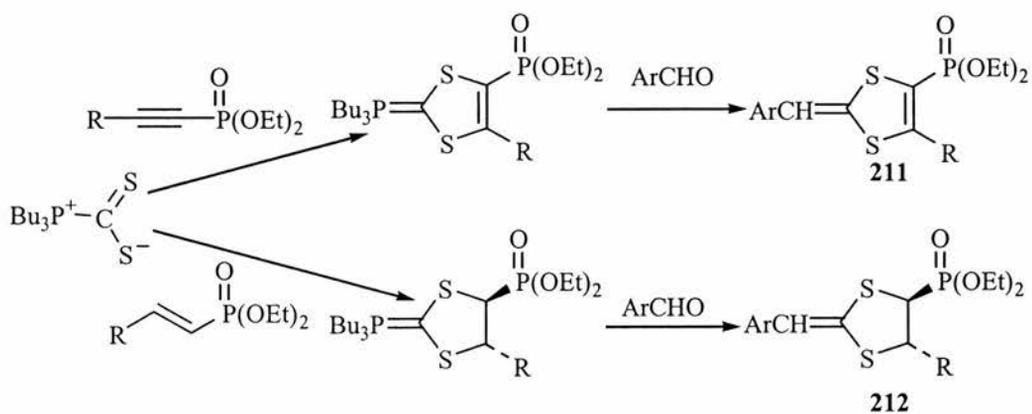
DMAD and  $\text{Bu}_3\text{P}$  are believed to react together to form the intermediate **204** which corresponds to an adduct obtained previously by Horner.<sup>137</sup> Instead of reacting with the heterocumulene this compound may undergo cyclisation to give the resonance stabilised cyclobutenide structure **205**. The strained bicyclo[2.1.0]pentene intermediate **206** is obtained through a further cyclisation which then undergoes a 1,2-shift of the methoxy group to give **203**. Alternatively the isomeric adduct **207** could cyclise directly to give the five-membered

ring intermediate **208** which would then undergo a 1,2-shift of the methoxy group to give **203**.

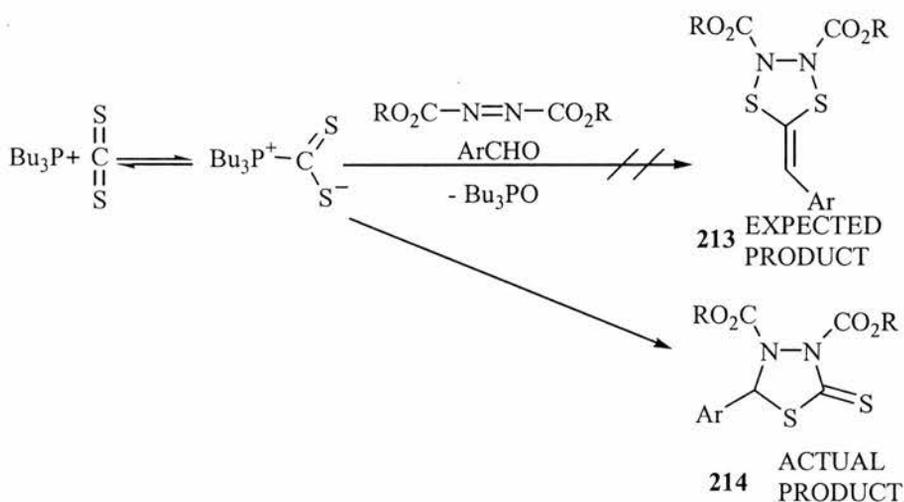
Tebby and co-workers had made a similar analogue **209** to **203** previously by reaction of  $\text{Ph}_3\text{P}$  with DMAD. We synthesised compound **209** to examine if the correct structure had been assigned to the compound or if it was actually the triphenyl analogue of **203**. Compound **209** was prepared according to a literature procedure and the two products **209** and **210** were separated using column chromatography.<sup>114,138</sup> The  $^{13}\text{C}$  NMR spectrum confirmed that the structure for **209** is correct shown by the large P-C coupling ( $J_{\text{p-c}} = 119$  Hz) observed for the doubly bonded ylide carbon as opposed to the smaller value ( $J_{\text{p-c}} = 64$  Hz) for the singly bonded carbon of **203**.<sup>139</sup> In fact it was later discovered that the structure of the tri-*p*-tolylphosphine analogue of **209** had also been confirmed by an X-ray structure determination.<sup>140</sup>



Finally in this section it should be noted that while our work was in progress a series of papers from Chinese workers describing the reaction of  $\text{Bu}_3\text{P}$  and  $\text{CS}_2$  with a range of different dipolarophiles appeared. These included reaction with both acetylenic and vinylic phosphonates followed by trapping in a Wittig reaction to give products **211** and **212** respectively.<sup>141,142</sup>



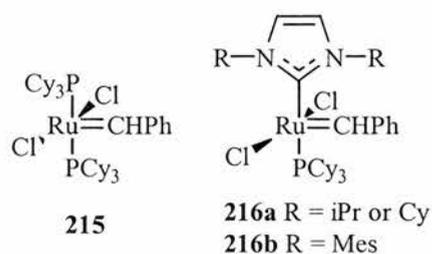
Perhaps most interesting, an attempt to extend this method by using dialkyl azodicarboxylates as the dipolarophiles led not to the expected products **213** but rather to the isomeric products **214** in a mechanism involving the formation of a  $\text{Bu}_3\text{P}$ -azodicarboxylate adduct which then interacts with  $\text{CS}_2$ .<sup>143,144</sup>



## H Ring Opening Metathesis Polymerisation

Ring-opening metathesis polymerisation (ROMP) has been used as an effective method for preparing unsaturated linear polymers from intermolecular metathesis of the propagating species.<sup>145</sup> The most widely used catalysts for ROMP are well defined complexes based on molybdenum and ruthenium. Molybdenum complexes have a very high activity allowing the polymerisation of many electronically deactivated or sterically hindered cyclic olefins but are highly sensitive to air and moisture. The ruthenium complexes are more stable under ambient conditions and tolerate a much wider range of protic and polar functional groups.

In order to improve the properties of the ruthenium catalyst, one of the phosphine ligands was replaced with a more electron donating *N*-heterocyclic carbene ligand giving **216**.<sup>146</sup> This compound had improved metathesis activity, thermal stability and inertness towards oxygen and moisture when compared with **215**.



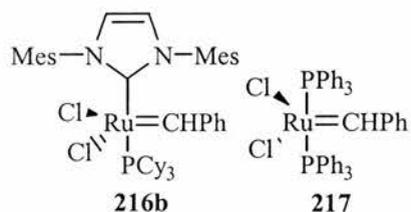
The proportion of *E* double bonds in the polymer backbone gradually increases with time. The molecular weights were regulated by including acyclic alkenes which act as chain transfer agents (CTAs).<sup>145</sup> This technique is very useful when poorly soluble polymers are obtained. When norbornane was used as a monomer and 1,4-diacetoxy-2-butene was included as the CTA a bis(acetoxy) end-terminated polymer was obtained showing excellent agreement between the theoretical and experimental molecular weights. It has previously

been reported that Ru based catalysts give predominately the *E* polymer in the ROMP of norbornane.<sup>147</sup>

No one has reported the preparation of a polytetrathiafulvalene from a tetrathiafulvalene using the ROMP method.<sup>88</sup> A previous worker found that using **215** to catalyse the ROMP of norbornene-fused dihydrotetrathiafulvalenes did not occur due to sulfur poisoning of the catalyst.

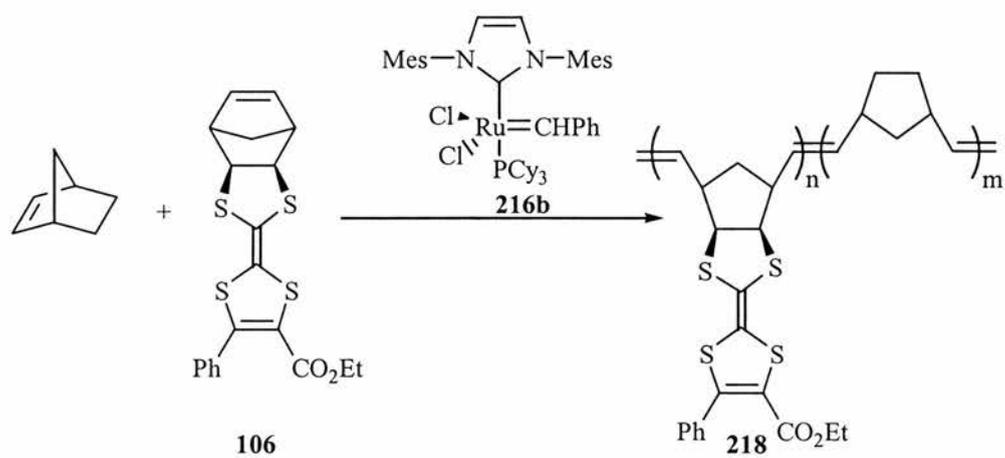
According to a recent publication the Grubbs catalyst **216b** was successfully used in ring closing metathesis reactions of some sulfur containing compounds suggesting that this catalyst does not suffer the same sulfur poisoning as **215**.<sup>148</sup>

The polymerisation of norbornene was successfully carried out using both the catalysts **216b** and **217**. The evidence for this is on the basis of comparison of <sup>1</sup>H-NMR spectra.<sup>115</sup>



The aim of the brief study carried out during the present research was to examine if it was possible to use catalyst **216b** in the polymerisation of norbornene-fused dihydrotetrathiafulvalenes. The catalyst **216b** was used in the ROMP of the norbornene-fused dihydrotetrathiafulvalene **106**. The polymerisation did work but the polymer was very insoluble in common solvents. By incorporating norbornene into the polymer its solubility was increased. It appears that the desired copolymer **218** was formed on the basis of comparison with <sup>13</sup>C and <sup>1</sup>H NMR spectra of polynorbornene.<sup>149</sup> Potentially this would suggest that a route to polymer-supported dihydrotetrathiafulvalenes has been found. In

conclusion further work should be carried out in this promising area to see if this polymerisation could be applied to other norbornene-fused dihydrotetrathiafulvalenes and to examine the properties of the products.



## APPENDIX

- A. X-ray Structural Data for Compounds **99**, **99**(new form), **117**, **91**, **102** and **203**-  
Tables 10-27
- B. Publications During Research Period
1. A new crystalline zwitterionic product from the reaction of tributylphosphane and dimethyl acetylenedicarboxylate, R. A. Aitken, S. J. Costello, A. M. Z. Slawin and N. J. Wilson, *Eur. J. Org. Chem.*, 2003, 623.
  2. Five-Membered ring systems: with O & S(Se, Te) atoms, R. A. Aitken and S. J. Costello, *Prog. Heterocycl. Chem*, 2002, **14**, 222.
  3. Five-Membered ring systems: with O & S(Se, Te) atoms, R. A. Aitken and S. J. Costello, *Prog. Heterocycl. Chem*, 2003, **15**, 249.

**Table 10** Atomic coordinates and U(eq) for **99**

Atom	x	y	z	U(eq)
C(1)	6318(2)	2005(3)	3788(3)	43(1)
C(2)	5634(2)	1151(3)	4043(3)	41(1)
S(3)	4756(1)	2071(1)	4122(1)	49(1)
C(4)	4171(2)	1181(3)	2913(3)	41(1)
S(5)	4657(1)	333(1)	1754(1)	48(1)
C(6)	5576(2)	201(3)	2808(3)	40(1)
C(7)	6240(2)	636(3)	2031(3)	49(1)
C(8)	6999(2)	245(3)	2878(4)	68(1)
C(9)	7050(2)	1215(3)	4084(3)	60(1)
C(10)	6227(2)	2086(3)	2238(3)	49(1)
C(11)	3404(2)	1225(3)	2846(3)	46(1)
S(12)	2924(1)	2146(1)	3985(1)	62(1)
C(13)	2055(2)	1351(3)	3600(4)	60(1)
C(14)	1984(2)	562(3)	2517(4)	59(1)
S(15)	2788(1)	405(1)	1605(1)	56(1)
C(16)	1454(2)	1651(5)	4533(4)	75(1)
O(16)	1173(2)	2712(4)	4599(4)	118(1)
O(17)	1353(2)	708(3)	5337(3)	85(1)
C(17)	802(3)	898(5)	6321(4)	113(2)
C(18)	1270(2)	-96(5)	2016(5)	86(1)
O(18)	656(2)	144(4)	2404(3)	132(1)
O(19)	1386(2)	-913(3)	1031(4)	108(1)
C(19)	716(3)	-1631(7)	403(7)	175(3)
H(1A)	6331	2836	4253	52
H(2A)	5756	674	4896	49
H(6A)	5659	-681	3132	48
H(7A)	6197	365	1073	59
H(8A)	7433	334	2352	81
H(8B)	6976	-631	3201	81
H(9A)	7061	775	4952	72
H(9B)	7504	1750	4093	72
H(10A)	6654	2517	1884	59
H(10B)	5744	2473	1872	59
H(17A)	774	137	6860	169
H(17B)	304	1078	5846	169
H(17C)	963	1606	6906	169
H(19A)	871	-2189	-291	263
H(19B)	334	-1042	1	263
H(19C)	503	-2132	1088	263

**Table 11** Bond lengths (Å) for **99**

Atom	Atom	Distance	Atom	Atom	Distance
C(1)	C(10)	1.520(4)	C(11)	S(12)	1.760(3)
C(1)	C(9)	1.523(4)	C(11)	S(15)	1.760(3)
C(1)	C(2)	1.535(4)	S(12)	C(13)	1.737(4)
C(2)	C(6)	1.564(4)	C(13)	C(14)	1.343(5)
C(2)	S(3)	1.820(3)	C(13)	C(16)	1.503(5)
S(3)	C(4)	1.751(3)	C(14)	C(18)	1.463(5)
C(4)	C(11)	1.336(4)	C(14)	S(15)	1.757(3)
C(4)	S(5)	1.738(3)	C(16)	O(16)	1.216(5)
S(5)	C(6)	1.821(3)	C(16)	O(17)	1.288(5)
C(6)	C(7)	1.529(4)	O(17)	C(17)	1.454(4)
C(7)	C(10)	1.527(4)	C(18)	O(18)	1.206(5)
C(7)	C(8)	1.543(4)	C(18)	O(19)	1.324(5)
C(8)	C(9)	1.556(4)	O(19)	C(19)	1.470(5)

**Table 12** Bond angles (°) for **99**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(10)	C(1)	C(9)	102.4(2)	C(4)	C(11)	S(15)	123.5(2)
C(10)	C(1)	C(2)	101.5(2)	S(12)	C(11)	S(15)	114.16(17)
C(9)	C(1)	C(2)	108.0(2)	C(13)	S(12)	C(11)	93.88(16)
C(1)	C(2)	C(6)	103.0(2)	C(14)	C(13)	C(16)	127.2(3)
C(1)	C(2)	S(3)	112.17(19)	C(14)	C(13)	S(12)	117.9(3)
C(6)	C(2)	S(3)	112.62(18)	C(16)	C(13)	S(12)	114.9(3)
C(4)	S(3)	C(2)	97.10(12)	C(13)	C(14)	C(18)	123.8(4)
C(11)	C(4)	S(5)	123.1(2)	C(13)	C(14)	S(15)	117.1(3)
C(11)	C(4)	S(3)	121.6(2)	C(18)	C(14)	S(15)	119.0(3)
S(5)	C(4)	S(3)	115.19(16)	C(14)	S(15)	C(11)	93.61(15)
C(4)	S(5)	C(6)	97.38(13)	O(16)	C(16)	O(17)	125.4(4)
C(7)	C(6)	C(2)	102.4(2)	O(16)	C(16)	C(13)	122.5(4)
C(7)	C(6)	S(5)	111.31(19)	O(17)	C(16)	C(13)	111.7(3)
C(2)	C(6)	S(5)	111.96(19)	C(16)	O(17)	C(17)	116.8(3)
C(10)	C(7)	C(6)	101.7(2)	O(18)	C(18)	O(19)	125.4(4)
C(10)	C(7)	C(8)	102.3(2)	O(18)	C(18)	C(14)	123.6(5)
C(6)	C(7)	C(8)	107.8(3)	O(19)	C(18)	C(14)	110.9(4)
C(7)	C(8)	C(9)	102.4(2)	C(18)	O(19)	C(19)	117.3(4)
C(1)	C(9)	C(8)	103.3(2)				
C(1)	C(10)	C(7)	94.5(2)				
C(4)	C(11)	S(12)	122.3(2)				

**Table 13** Atomic coordinates and U(eq) for **99** (new form)

Atom	x	y	z	U(eq)
C(1)	4769(3)	3182(1)	3032(2)	22(1)
C(2)	3303(3)	2789(1)	2629(2)	20(1)
S(3)	5173(1)	2327(1)	2910(1)	20(1)
C(4)	3445(3)	2040(1)	3839(2)	17(1)
S(5)	2047(1)	2335(1)	4954(1)	22(1)
C(6)	1716(3)	2801(1)	3771(2)	23(1)
C(7)	2532(4)	3190(1)	4707(2)	31(1)
C(8)	1660(4)	3566(1)	3702(3)	35(1)
C(9)	3158(4)	3555(1)	2526(2)	27(1)
C(10)	5158(4)	3197(1)	4762(2)	31(1)
C(11)	3284(3)	1627(1)	3769(2)	17(1)
S(12)	4694(1)	1315(1)	2683(1)	18(1)
C(13)	2615(3)	917(1)	2500(2)	17(1)
C(14)	1201(3)	930(1)	3446(2)	18(1)
S(15)	1568(1)	1343(1)	4734(1)	20(1)
C(16)	2609(3)	579(1)	1373(2)	18(1)
O(16)	2400(2)	220(1)	1623(2)	23(1)
O(17)	2883(2)	739(1)	77(1)	24(1)
C(17)	2959(4)	442(1)	-1106(2)	33(1)
C(18)	-718(3)	635(1)	3482(2)	20(1)
O(18)	-2033(2)	486(1)	2393(2)	28(1)
O(19)	-788(2)	575(1)	4929(2)	28(1)
C(19)	-2711(4)	323(1)	5141(3)	37(1)
H(1A)	6236	3186	2675	26
H(2A)	2326	2802	1558	24
H(6A)	43	2833	3197	27
H(7A)	2171	3196	5723	37
H(8A)	1926	3824	4303	43
H(8B)	-27	3541	3195	43
H(9A)	2164	3517	1482	32
H(9B)	4074	3813	2564	32
H(10A)	5945	3453	5218	37
H(10B)	6004	2952	5278	37
H(17A)	4446	292	-831	49
H(17B)	2821	587	-2070	49
H(17C)	1662	247	-1215	49
H(19A)	-4173	480	4828	55
H(19B)	-2431	247	6215	55
H(19C)	-2826	73	4522	55

**Table 14** Bond lengths [Å] for **99** (new form)

Atom	Atom	Distance	Atom	Atom	Distance
C(1)	C(10)	1.532(3)	C(10)	H(10A)	0.9900
C(1)	C(2)	1.533(3)	C(10)	H(10B)	0.9900
C(1)	C(9)	1.536(3)	C(11)	S(15)	1.7580(18)
C(1)	H(1A)	1.0000	C(11)	S(12)	1.7620(18)
C(2)	C(6)	1.566(3)	S(12)	C(13)	1.7614(18)
C(2)	S(3)	1.8396(19)	C(13)	C(14)	1.343(3)
C(2)	H(2A)	1.0000	C(13)	C(16)	1.498(2)
S(3)	C(4)	1.7497(18)	C(14)	C(18)	1.489(3)
C(4)	C(11)	1.343(3)	C(14)	S(15)	1.7570(18)
C(4)	S(5)	1.7472(18)	C(16)	O(16)	1.199(2)
S(5)	C(6)	1.834(2)	C(16)	O(17)	1.334(2)
C(6)	C(7)	1.530(3)	O(17)	C(17)	1.452(2)
C(6)-H(6A)		1.0000	C(17)	H(17A)	0.9800
C(7)	C(8)	1.532(3)	C(17)	H(17B)	0.9800
C(7)	C(10)	1.540(3)	C(17)	H(17C)	0.9800
C(7)	H(7A)	1.0000	C(18)	O(18)	1.195(2)
C(8)	C(9)	1.551(3)	C(18)	O(19)	1.340(2)
C(8)	H(8A)	0.9900	O(19)	C(19)	1.451(2)
C(8)	H(8B)	0.9900	C(19)	H(19A)	0.9800
C(9)	H(9A)	0.9900	C(19)	H(19B)	0.9800
C(9)	H(9B)	0.9900	C(19)	H(19C)	0.9800

**Table 15** Bond angles [°] for **99**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(10)	C(1)	C(2)	101.54(15)	C(8)	C(9)	H(9B)	111.1
C(10)	C(1)	C(9)	101.81(16)	C(1)	C(9)	H(9B)	111.1
C(2)	C(1)	C(9)	108.27(16)	H(9A)	C(9)	H(9B)	109.1
C(10)	C(1)	H(1A)	114.6	C(1)	C(10)	C(7)	94.42(16)
C(2)	C(1)	H(1A)	114.6	C(1)	C(10)	H(10A)	112.8
C(9)	C(1)	H(1A)	114.6	C(7)	C(10)	H(10A)	112.8
C(1)	C(2)	C(6)	102.58(15)	C(1)	C(10)	H(10B)	112.8
C(1)	C(2)	S(3)	111.13(13)	C(7)	C(10)	H(10B)	112.8
C(6)	C(2)	S(3)	111.57(12)	H(10A)	C(10)	H(10B)	110.3
C(1)	C(2)	H(2A)	110.4	C(4)	C(11)	S(15)	122.68(14)
C(6)	C(2)	H(2A)	110.4	C(4)	C(11)	S(12)	124.04(14)
S(3)	C(2)	H(2A)	110.4	S(15)	C(11)	S(12)	113.27(10)
C(4)	S(3)	C(2)	95.55(9)	C(13)	S(12)	C(11)	93.19(9)
C(11)	C(4)	S(5)	122.41(14)	C(14)	C(13)	C(16)	124.55(16)
C(11)	C(4)	S(3)	123.45(14)	C(14)	C(13)	S(12)	116.63(14)
S(5)	C(4)	S(3)	114.06(10)	C(16)	C(13)	S(12)	118.75(13)

**Table 15** Bond angles [°] for **99** (continued)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(4)	S(5)	C(6)	96.13(9)	C(13)	C(14)	C(18)	126.44(16)
C(7)	C(6)	C(2)	103.39(16)	C(13)	C(14)	S(15)	117.35(14)
C(7)	C(6)	S(5)	112.36(14)	C(18)	C(14)	S(15)	116.17(13)
C(2)	C(6)	S(5)	112.06(13)	C(14)	S(15)	C(11)	93.16(8)
C(7)	C(6)	H(6A)	109.6	O(16)	C(16)	O(17)	125.92(17)
C(2)	C(6)	H(6A)	109.6	O(16)	C(16)	C(13)	124.20(17)
S(5)	C(6)	H(6A)	109.6	O(17)	C(16)	C(13)	109.88(15)
C(6)	C(7)	C(8)	108.24(19)	C(16)	O(17)	C(17)	115.44(15)
C(6)	C(7)	C(10)	101.74(16)	O(17)	C(17)	H(17A)	109.5
C(8)	C(7)	C(10)	101.11(17)	O(17)	C(17)	H(17B)	109.5
C(6)	C(7)	H(7A)	114.7	H(17A)	C(17)	H(17B)	109.5
C(8)	C(7)	H(7A)	114.7	O(17)	C(17)	H(17C)	109.5
C(10)	C(7)	H(7A)	114.7	H(17A)	C(17)	H(17C)	109.5
C(7)	C(8)	C(9)	103.23(17)	H(17B)	C(17)	H(17C)	109.5
C(7)	C(8)	H(8A)	111.1	O(18)	C(18)	O(19)	125.43(18)
C(9)	C(8)	H(8A)	111.1	O(18)	C(18)	C(14)	125.44(18)
C(7)	C(8)	H(8B)	111.1	O(19)	C(18)	C(14)	109.09(15)
C(9)	C(8)	H(8B)	111.1	C(18)	O(19)	C(19)	115.54(16)
H(8A)	C(8)	H(8B)	109.1	O(19)	C(19)	H(19A)	109.5
C(1)	C(9)	C(8)	103.25(16)	O(19)	C(19)	H(19B)	109.5
C(1)	C(9)	H(9A)	111.1	H(19A)	C(19)	H(19B)	109.5
C(8)	C(9)	H(9A)	111.1	O(19)	C(19)	H(19C)	109.5
H(19A)	C(19)	H(19C)	109.5	H(19B)	C(19)	H(19C)	109.5

**Table 16** Atomic coordinates and U(eq) for **117**

Atom	x	y	z	U(eq)
C(1)	4291(5)	-444(2)	6643(3)	47(1)
C(2)	4729(5)	-76(2)	7946(3)	42(1)
S(3)	5778(1)	839(1)	7740(1)	55(1)
C(4)	4141(5)	1260(2)	8876(3)	42(1)
S(5)	1668(1)	848(1)	9021(1)	53(1)
C(6)	2531(5)	-68(2)	8599(3)	45(1)
C(7)	1098(5)	-419(2)	7562(3)	54(1)
C(8)	1640(6)	-1228(2)	7516(4)	71(1)
C(9)	3836(6)	-1241(2)	6888(4)	67(1)
C(10)	2113(5)	-150(2)	6307(3)	55(1)
S(1')	7142(1)	2304(1)	9254(1)	57(1)
C(2')	4680(5)	1876(2)	9485(3)	43(1)
S(3')	3032(1)	2335(1)	10579(1)	55(1)
C(4')	4986(6)	2928(2)	11105(3)	59(1)
C(5')	6819(6)	2912(2)	10524(3)	60(1)
H(1A)	5364	-354	5982	57
H(2A)	5714	-370	8460	51
H(6A)	2561	-373	9378	54
H(7A)	-408	-310	7646	65
H(8A)	622	-1494	6996	85
H(8B)	1685	-1434	8381	85
H(9A)	4878	-1452	7468	80
H(9B)	3814	-1514	6083	80
H(10A)	1510	-374	5538	66
H(10B)	2088	374	6226	66
H(4'A)	4738	3250	11782	70
H(5'A)	7913	3216	10785	72

**Table 17** Bond lengths (Å) for **117**

Atom	Atom	Distance	Atom	Atom	Distance
C(1)	C(9)	1.518(4)	C(6)	C(7)	1.542(4)
C(1)	C(10)	1.521(4)	C(7)	C(8)	1.529(5)
C(1)	C(2)	1.530(4)	C(7)	C(10)	1.531(4)
C(2)	C(6)	1.550(4)	C(8)	C(9)	1.539(5)
C(2)	S(3)	1.825(3)	S(1')	C(5')	1.737(4)
S(3)	C(4)	1.751(3)	S(1')	C(2')	1.765(3)
C(4)	C(2')	1.341(4)	C(2')	S(3')	1.758(3)
C(4)	S(5)	1.749(3)	S(3')	C(4')	1.736(3)
S(5)	C(6)	1.828(3)	C(4')	C(5')	1.311(4)

**Table 18** Bond angles (°) for **117**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(9)	C(1)	C(10)	102.1(3)	C(8)	C(7)	C(10)	101.2(3)
C(9)	C(1)	C(2)	108.4(3)	C(8)	C(7)	C(6)	107.3(3)
C(10)	C(1)	C(2)	101.7(3)	C(10)	C(7)	C(6)	101.7(3)
C(1)	C(2)	C(6)	103.1(2)	C(7)	C(8)	C(9)	103.4(3)
C(1)	C(2)	S(3)	111.8(2)	C(1)	C(9)	C(8)	103.2(3)
C(6)	C(2)	S(3)	111.8(2)	C(1)	C(10)	C(7)	94.5(2)
C(4)	S(3)	C(2)	96.54(15)	C(5')	S(1')	C(2')	94.42(17)
C(2')	C(4)	S(3)	122.6(2)	C(4)	C(2')	S(3')	123.8(2)
C(2')	C(4)	S(5)	123.6(3)	C(4)	C(2')	S(1')	122.5(3)
S(3)	C(4)	S(5)	113.53(19)	S(3')	C(2')	S(1')	113.69(19)
C(4)	S(5)	C(6)	96.38(15)	C(4')	S(3')	C(2')	94.46(17)
C(7)	C(6)	C(2)	102.8(3)	C(5')	C(4')	S(3')	118.4(3)
C(7)	C(6)	S(5)	112.1(2)	C(4')	C(5')	S(1')	117.9(3)
C(2)	C(6)	S(5)	112.5(2)				

**Table 19** Atomic coordinates and U(eq) for **102**

Atom	x	y	z	U(eq)
C(1)	17280(19)	17899(16)	15691(12)	69(6)
C(2)	17520(20)	16801(18)	15432(15)	90(7)
S(3)	16073(5)	16140(4)	14833(3)	71(2)
C(4)	16459(14)	15798(15)	14029(10)	49(4)
S(5)	17886(6)	16396(4)	14030(3)	75(2)
C(6)	18391(16)	16983(12)	14982(12)	60(5)
C(7)	18735(14)	18126(11)	15037(9)	40(4)
C(8)	19475(15)	18481(12)	15842(9)	44(4)
C(9)	18570(20)	18261(13)	16263(13)	80(8)
C(10)	17530(20)	18556(15)	15088(14)	87(8)
C(11)	15810(20)	15194(13)	13494(14)	82(8)
S(12)	14304(5)	14679(4)	13497(3)	69(2)
C(13)	13960(20)	13957(14)	12606(10)	60(6)
C(14)	14826(14)	13971(17)	12323(9)	55(5)
S(15)	16187(5)	14781(5)	12711(3)	77(2)
C(16)	12779(19)	13329(18)	12381(15)	77(8)
O(16)	12116(15)	13383(12)	12805(8)	87(5)
O(17)	12536(16)	12810(12)	11804(9)	87(5)
C(17)	11330(20)	12166(18)	11538(13)	96(8)
C(18)	14601(15)	13545(18)	11573(12)	56(5)
O(18)	14258(16)	14001(11)	11066(10)	87(5)

**Table 19** Atomic coordinates and U(eq) for **102** (continued)

Atom	x	y	z	U(eq)
O(19)	15030(14)	12639(11)	11511(7)	76(4)
C(19)	14890(20)	12025(19)	10787(12)	91(8)
S(21)	20057(5)	19858(4)	15948(3)	65(2)
C(22)	19705(17)	20186(12)	16747(10)	45(5)
S(23)	18299(5)	19520(4)	16758(3)	63(1)
C(24)	20230(20)	20861(17)	17280(13)	72(6)
S(25)	19810(5)	21149(5)	18057(3)	76(2)
C(26)	21170(20)	21892(16)	18588(15)	90(9)
C(27)	21960(20)	22077(19)	18221(13)	88(7)
S(28)	21644(5)	21572(5)	17295(3)	73(2)
C(29)	21193(18)	22349(15)	19282(12)	61(5)
O(29)	21439(16)	21799(11)	19759(8)	92(5)
O(30)	21007(13)	23295(11)	19385(10)	87(5)
C(30)	21030(20)	23780(20)	20049(14)	102(9)
C(31)	23148(19)	22657(15)	18574(16)	70(7)
O(31)	23454(16)	23033(14)	19188(9)	101(6)
O(32)	23750(13)	22818(11)	18086(9)	86(5)
C(32)	24911(19)	23361(18)	18437(12)	80(7)
C(41)	12891(19)	17185(16)	15588(11)	69(6)
C(42)	12675(17)	16513(16)	14897(13)	69(6)
S(43)	11191(5)	15706(4)	14664(3)	66(2)
C(44)	10730(20)	16010(20)	13816(11)	89(8)
S(45)	11174(5)	17277(4)	13672(3)	59(1)
C(46)	12640(20)	17400(20)	14361(15)	105(9)
C(47)	12888(15)	18418(11)	14830(8)	37(4)
C(48)	14200(20)	18481(15)	15291(11)	83(7)
C(49)	14226(17)	17619(13)	15838(10)	55(5)
C(50)	12270(20)	18166(19)	15359(13)	96(8)
C(51)	9930(20)	15387(15)	13251(14)	74(7)
S(52)	9387(5)	14123(4)	13394(3)	65(2)
C(53)	8729(17)	13712(15)	12454(13)	67(6)
C(54)	8721(16)	14445(16)	12050(12)	70(6)
S(55)	9256(6)	15730(4)	12416(3)	74(2)
C(56)	8240(16)	12610(20)	12239(12)	76(8)
O(56)	7947(16)	12320(10)	11596(10)	97(5)
O(57)	8246(13)	12097(14)	12757(9)	90(5)
C(57)	7630(30)	11020(17)	12461(12)	146(15)
C(58)	8210(40)	14250(20)	11215(16)	111(11)
O(58)	8879(14)	14194(13)	10859(8)	88(5)
O(59)	7090(20)	14412(12)	11027(8)	87(5)
C(59)	6539(19)	14313(15)	10240(12)	75(6)
S(61)	14741(5)	19758(4)	15766(3)	75(2)
C(62)	15207(19)	19492(14)	16635(12)	62(6)
S(63)	14707(5)	18160(4)	16747(3)	70(2)
C(64)	15710(20)	20171(16)	17166(13)	74(6)

**Table 19** Atomic coordinates and U(eq) for **102** (continued)

Atom	x	y	z	U(eq)
S(65)	16058(6)	19767(4)	18055(3)	83(2)
C(66)	16900(20)	21010(20)	18504(15)	97(9)
C(67)	16923(18)	21749(15)	18092(12)	62(5)
S(68)	16250(6)	21410(4)	17135(4)	84(2)
C(69)	17300(30)	21080(20)	19301(17)	104(8)
O(69)	16624(16)	21327(18)	19650(10)	130(7)
O(70)	18365(19)	20795(12)	19504(8)	98(6)
C(70)	18840(20)	20829(19)	20321(14)	107(8)
C(71)	17700(20)	22781(18)	18395(16)	82(6)
O(71)	18065(16)	22913(11)	19015(9)	92(5)
O(72)	17527(15)	23321(12)	17907(9)	98(6)
C(72)	18132(18)	24325(15)	18211(14)	82(8)
H(1A)	16532	17998	15840	82
H(2A)	17879	16396	15839	108
H(6A)	19141	16653	15211	72
H(7A)	19078	18368	14659	48
H(8A)	20161	18032	15983	53
H(9A)	18831	17722	16594	96
H(10A)	16890	18401	14630	105
H(10B)	17626	19319	15243	105
H(17A)	11309	11611	11844	145
H(17B)	11210	11851	11045	145
H(17C)	10680	12621	11555	145
H(19A)	14406	11362	10749	137
H(19B)	15679	11880	10734	137
H(19C)	14478	12435	10409	137
H(30A)	20336	23509	20187	153
H(30B)	21009	24538	20032	153
H(30C)	21774	23640	20401	153
H(32A)	24831	23916	18798	121
H(32B)	25232	23669	18083	121
H(32C)	25461	22865	18670	121
H(41A)	12606	16851	15958	83
H(42A)	13351	16060	14901	82
H(46A)	13295	17315	14124	126
H(47A)	12636	19050	14586	45
H(48A)	14719	18277	14978	100
H(49A)	14750	17057	15749	66
H(50A)	11396	18014	15142	115
H(50B)	12425	18732	15762	115
H(57A)	6845	11088	12121	219
H(57B)	7508	10652	12854	219
H(57C)	8125	10623	12217	219
H(59A)	6669	14983	10064	112
H(59B)	5674	14122	10129	112

**Table 19** Atomic coordinates and U(eq) for **102** (continued)

Atom	x	y	z	U(eq)
H(59C)	6912	13769	10008	112
H(70A)	18740	21519	20548	161
H(70B)	19695	20703	20452	161
H(70C)	18391	20287	20483	161
H(72A)	17624	24728	18445	123
H(72B)	18295	24701	17832	123
H(72C)	18893	24235	18564	123

**Table 20** Bond lengths (Å) for **102**

Atom	Atom	Distance	Atom	Atom	Distance
C(1)	C(2)	1.509(3)	C(41)	C(42)	1.48(3)
C(1)	C(14)	1.537(4)	C(41)	C(49)	1.55(3)
C(1)	C(13)	1.561(3)	C(41)	C(50)	1.53(3)
C(2)	C(7)	1.342(4)	C(41)	H(41A)	1.0000
C(2)	C(3)	1.465(4)	C(42)	C(46)	1.62(3)
C(3)	O(3)	1.224(3)	C(42)	S(43)	1.884(19)
C(3)	C(4)	1.479(4)	C(42)	H(42A)	1.0000
C(4)	C(5)	1.335(4)	S(43)	C(44)	1.69(2)
C(5)	C(6)	1.480(4)	C(44)	C(51)	1.38(3)
C(6)	O(6)	1.226(3)	C(44)	S(45)	1.76(3)
C(6)	C(7)	1.473(4)	S(45)	C(46)	1.85(3)
C(7)	C(8)	1.513(3)	C(46)	C(47)	1.48(3)
C(6)	H(6A)	1.0000	C(46)	H(46A)	1.0000
C(7)	C(10)	1.55(3)	C(47)	C(50)	1.46(3)
C(7)	C(8)	1.58(2)	C(47)	C(48)	1.53(3)
C(7)	H(7A)	1.0000	C(47)	H(47A)	1.0000
C(8)	C(9)	1.54(2)	C(48)	C(49)	1.61(3)
C(8)	S(21)	1.836(16)	C(48)	S(61)	1.80(2)
C(8)	H(8A)	1.0000	C(48)	H(48A)	1.0000
C(9)	S(23)	1.887(15)	C(49)	S(63)	1.77(2)
C(9)	H(9A)	1.0000	C(49)	H(49A)	1.0000
C(10)	H(10A)	0.9900	C(50)	H(50A)	0.9900
C(10)	H(10B)	0.9900	C(50)	H(50B)	0.9900
C(11)	S(15)	1.75(3)	C(51)	S(55)	1.72(3)
C(11)	S(12)	1.84(2)	C(51)	S(52)	1.79(2)
S(12)	C(13)	1.822(19)	S(52)	C(53)	1.80(3)
C(13)	C(14)	1.28(2)	C(53)	C(54)	1.29(2)
C(13)	C(16)	1.48(3)	C(53)	C(56)	1.48(3)
C(14)	C(18)	1.46(3)	C(54)	C(58)	1.57(4)
C(14)	S(15)	1.78(2)	C(54)	S(55)	1.75(2)
C(16)	O(17)	1.21(3)	C(56)	O(56)	1.22(2)

**Table 20** Bond lengths (Å) for **102** (continued)

Atom	Atom	Distance	Atom	Atom	Distance
C(16)	O(16)	1.28(3)	C(56)	O(57)	1.26(3)
O(17)	C(17)	1.52(2)	O(57)	C(57)	1.51(3)
C(17)	H(17A)	0.9800	C(57)	H(57A)	0.9805
C(17)	H(17B)	0.9800	C(57)	H(57B)	0.9805
C(17)	H(17C)	0.9800	C(57)	H(57C)	0.9805
C(18)	O(18)	1.19(2)	C(58)	O(58)	1.18(3)
C(18)	O(19)	1.30(2)	C(58)	O(59)	1.29(4)
O(19)	C(19)	1.52(2)	O(59)	C(59)	1.48(2)
C(19)	H(19A)	0.9800	C(59)	H(59A)	0.9800
C(19)	H(19B)	0.9800	C(59)	H(59B)	0.9800
C(19)	H(19C)	0.9800	C(59)	H(59C)	0.9800
S(21)	C(22)	1.741(16)	S(61)	C(62)	1.71(2)
C(22)	C(24)	1.27(3)	C(62)	C(64)	1.27(3)
C(22)	S(23)	1.813(19)	C(62)	S(63)	1.837(19)
C(24)	S(25)	1.73(2)	C(64)	S(68)	1.70(2)
C(24)	S(28)	1.83(2)	C(64)	S(65)	1.81(2)
S(25)	C(26)	1.80(3)	S(65)	C(66)	1.84(2)
C(26)	C(27)	1.34(3)	C(66)	C(67)	1.31(3)
C(26)	C(29)	1.42(3)	C(66)	C(69)	1.49(4)
C(27)	C(31)	1.48(3)	C(67)	C(71)	1.53(3)
C(27)	S(28)	1.79(2)	C(67)	S(68)	1.82(2)
C(29)	O(29)	1.21(2)	C(69)	O(69)	1.20(3)
C(29)	O(30)	1.25(2)	C(69)	O(70)	1.28(3)
O(30)	C(30)	1.38(3)	O(70)	C(70)	1.54(3)
C(30)	H(30A)	0.9800	C(70)	H(70A)	0.9800
C(30)	H(30B)	0.9800	C(70)	H(70B)	0.9800
C(30)	H(30C)	0.9800	C(70)	H(70C)	0.9800
C(31)	O(31)	1.20(3)	C(71)	O(71)	1.16(3)
C(31)	O(32)	1.36(3)	C(71)	O(72)	1.22(3)
O(32)	C(32)	1.44(2)	O(72)	C(72)	1.43(3)
C(32)	H(32A)	0.9800	C(72)	H(72A)	0.9800
C(32)	H(32B)	0.9800	C(72)	H(72B)	0.9800
C(32)	H(32C)	0.9800	C(72)	H(72C)	0.9800

**Table 21** Bond angles (°) for **102**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(2)	C(1)	C(10)	101.8(18)	C(42)	C(41)	C(49)	108.5(17)
C(2)	C(1)	C(9)	99.4(17)	C(42)	C(41)	C(50)	102.4(18)
C(10)	C(1)	C(9)	94.6(15)	C(49)	C(41)	C(50)	101.0(17)
C(2)	C(1)	H(1A)	118.9	C(42)	C(41)	H(41A)	114.5
C(10)	C(1)	H(1A)	118.8	C(49)	C(41)	H(41A)	114.5

**Table 21** Bond angles (°) for **102** (continued)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(9)	C(1)	H(1A)	118.8	C(50)	C(41)	H(41A)	114.5
C(6)	C(2)	C(1)	104.0(18)	C(41)	C(42)	C(46)	100.2(19)
C(6)	C(2)	S(3)	109.0(17)	C(41)	C(42)	S(43)	111.1(14)
C(1)	C(2)	S(3)	107.6(15)	C(46)	C(42)	S(43)	111.2(16)
C(6)	C(2)	H(2A)	112.1	C(41)	C(42)	H(42A)	111.3
C(1)	C(2)	H(2A)	111.8	C(46)	C(42)	H(42A)	111.2
S(3)	C(2)	H(2A)	112.0	S(43)	C(42)	H(42A)	111.4
C(4)	S(3)	C(2)	101.7(10)	C(44)	S(43)	C(42)	94.9(11)
C(11)	C(4)	S(3)	125.0(17)	C(51)	C(44)	S(43)	125(2)
C(11)	C(4)	S(5)	121.6(17)	C(51)	C(44)	S(45)	118.0(16)
S(3)	C(4)	S(5)	113.4(11)	S(43)	C(44)	S(45)	116.8(15)
C(4)	S(5)	C(6)	98.2(9)	C(44)	S(45)	C(46)	96.2(11)
C(7)	C(6)	C(2)	109.7(15)	C(47)	C(46)	C(42)	105(2)
C(7)	C(6)	S(5)	110.8(14)	C(47)	C(46)	S(45)	113.6(17)
C(2)	C(6)	S(5)	116.4(15)	C(42)	C(46)	S(45)	109.9(17)
C(7)	C(6)	H(6A)	106.3	C(47)	C(46)	H(46A)	109.3
C(2)	C(6)	H(6A)	106.6	C(42)	C(46)	H(46A)	109.3
S(5)	C(6)	H(6A)	106.4	S(45)	C(46)	H(46A)	109.4
C(6)	C(7)	C(10)	99.1(14)	C(50)	C(47)	C(46)	99.8(17)
C(6)	C(7)	C(8)	106.7(14)	C(50)	C(47)	C(48)	99.9(16)
C(10)	C(7)	C(8)	96.8(14)	C(46)	C(47)	C(48)	107.6(16)
C(6)	C(7)	H(7A)	117.1	C(50)	C(47)	H(47A)	115.9
C(10)	C(7)	H(7A)	116.9	C(46)	C(47)	H(47A)	115.7
C(8)	C(7)	H(7A)	117.1	C(48)	C(47)	H(47A)	115.7
C(9)	C(8)	C(7)	103.5(15)	C(47)	C(48)	C(49)	105.1(16)
C(9)	C(8)	S(21)	114.5(11)	C(47)	C(48)	S(61)	113.6(14)
C(7)	C(8)	S(21)	110.0(11)	C(49)	C(48)	S(61)	111.1(13)
C(9)	C(8)	H(8A)	109.7	C(47)	C(48)	H(48A)	109.0
C(7)	C(8)	H(8A)	109.4	C(49)	C(48)	H(48A)	109.0
S(21)	C(8)	H(8A)	109.5	S(61)	C(48)	H(48A)	108.9
C(8)	C(9)	C(1)	107.8(17)	C(41)	C(49)	C(48)	99.9(16)
C(8)	C(9)	S(23)	110.1(12)	C(41)	C(49)	S(63)	113.3(13)
C(1)	C(9)	S(23)	104.0(14)	C(48)	C(49)	S(63)	113.2(12)
C(8)	C(9)	H(9A)	111.6	C(41)	C(49)	H(49A)	110.0
C(1)	C(9)	H(9A)	111.6	C(48)	C(49)	H(49A)	110.0
S(23)	C(9)	H(9A)	111.6	S(63)	C(49)	H(49A)	110.0
C(7)	C(10)	C(1)	99.6(15)	C(47)	C(50)	C(41)	99.2(19)
C(7)	C(10)	H(10A)	111.9	C(47)	C(50)	H(50A)	111.9
C(1)	C(10)	H(10A)	112.0	C(41)	C(50)	H(50A)	112.0
C(7)	C(10)	H(10B)	111.9	C(47)	C(50)	H(50B)	111.9
C(1)	C(10)	H(10B)	111.7	C(41)	C(50)	H(50B)	112.0
H(10A)	C(10)	H(10B)	109.6	H(50A)	C(50)	H(50B)	109.6
C(4)	C(11)	S(15)	126.6(18)	C(44)	C(51)	S(55)	126.9(16)
C(4)	C(11)	S(12)	120(2)	C(44)	C(51)	S(52)	119.1(19)
S(15)	C(11)	S(12)	113.8(12)	S(55)	C(51)	S(52)	113.8(16)
C(13)	S(12)	C(11)	94.5(11)	C(51)	S(52)	C(53)	93.6(11)

**Table 21** Bond angles (°) for **102** (continued)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(14)	C(13)	C(16)	131(2)	C(54)	C(53)	C(56)	128(2)
C(14)	C(13)	S(12)	114.5(17)	C(54)	C(53)	S(52)	114.4(18)
C(16)	C(13)	S(12)	114.1(17)	C(56)	C(53)	S(52)	117.4(15)
C(13)	C(14)	C(18)	119.1(18)	C(53)	C(54)	C(58)	123(2)
C(13)	C(14)	S(15)	122.4(16)	C(53)	C(54)	S(55)	121.1(19)
C(18)	C(14)	S(15)	116.3(13)	C(58)	C(54)	S(55)	116.3(15)
C(11)	S(15)	C(14)	94.3(9)	C(51)	S(55)	C(54)	93.8(10)
O(17)	C(16)	O(16)	126(2)	O(56)	C(56)	O(57)	130(2)
O(17)	C(16)	C(13)	116(2)	O(56)	C(56)	C(53)	115(3)
O(16)	C(16)	C(13)	118(2)	O(57)	C(56)	C(53)	114.0(18)
C(16)	O(17)	C(17)	118(2)	C(56)	O(57)	C(57)	108.2(18)
O(17)	C(17)	H(17A)	109.4	O(57)	C(57)	H(57A)	109.6
O(17)	C(17)	H(17B)	109.5	O(57)	C(57)	H(57B)	109.4
H(17A)	C(17)	H(17B)	109.5	H(57A)	C(57)	H(57B)	109.4
O(17)	C(17)	H(17C)	109.6	O(57)	C(57)	H(57C)	109.6
H(17A)	C(17)	H(17C)	109.5	H(57A)	C(57)	H(57C)	109.4
H(17B)	C(17)	H(17C)	109.5	H(57B)	C(57)	H(57C)	109.4
O(18)	C(18)	O(19)	121(2)	O(58)	C(58)	O(59)	128(3)
O(18)	C(18)	C(14)	127(2)	O(58)	C(58)	C(54)	120(3)
O(19)	C(18)	C(14)	111.7(18)	O(59)	C(58)	C(54)	110(2)
C(18)	O(19)	C(19)	121.8(16)	C(58)	O(59)	C(59)	114(2)
O(19)	C(19)	H(19A)	109.4	O(59)	C(59)	H(59A)	109.6
O(19)	C(19)	H(19B)	109.6	O(59)	C(59)	H(59B)	109.4
H(19A)	C(19)	H(19B)	109.5	H(59A)	C(59)	H(59B)	109.5
O(19)	C(19)	H(19C)	109.4	O(59)	C(59)	H(59C)	109.3
H(19A)	C(19)	H(19C)	109.5	H(59A)	C(59)	H(59C)	109.5
H(19B)	C(19)	H(19C)	109.5	H(59B)	C(59)	H(59C)	109.5
C(22)	S(21)	C(8)	94.8(8)	C(62)	S(61)	C(48)	102.1(10)
C(24)	C(22)	S(21)	130.2(16)	C(64)	C(62)	S(61)	124.4(16)
C(24)	C(22)	S(23)	117.3(14)	C(64)	C(62)	S(63)	122.1(17)
S(21)	C(22)	S(23)	112.3(11)	S(61)	C(62)	S(63)	112.9(13)
C(22)	S(23)	C(9)	93.8(8)	C(49)	S(63)	C(62)	99.2(10)
C(22)	C(24)	S(25)	127.4(18)	C(62)	C(64)	S(68)	126.7(18)
C(22)	C(24)	S(28)	119.3(16)	C(62)	C(64)	S(65)	118.4(16)
S(25)	C(24)	S(28)	113.1(14)	S(68)	C(64)	S(65)	114.5(15)
C(24)	S(25)	C(26)	98.4(11)	C(64)	S(65)	C(66)	95.0(13)
C(27)	C(26)	C(29)	128(2)	C(67)	C(66)	C(69)	129(2)
C(27)	C(26)	S(25)	114(2)	C(67)	C(66)	S(65)	116(2)
C(29)	C(26)	S(25)	117.4(13)	C(69)	C(66)	S(65)	115(2)
C(26)	C(27)	C(31)	121(3)	C(66)	C(67)	C(71)	120(2)
C(26)	C(27)	S(28)	121(2)	C(66)	C(67)	S(68)	117.3(17)
C(31)	C(27)	S(28)	118(2)	C(71)	C(67)	S(68)	121.4(17)
C(27)	S(28)	C(24)	93.4(12)	C(64)	S(68)	C(67)	97.2(11)
O(29)	C(29)	O(30)	123(2)	O(69)	C(69)	O(70)	130(3)
O(29)	C(29)	C(26)	117.0(19)	O(69)	C(69)	C(66)	121(3)

**Table 21** Bond angles (°) for **102** (continued)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(30)	C(29)	C(26)	120(2)	O(70)	C(69)	C(66)	109(2)
C(29)	O(30)	C(30)	122(2)	C(69)	O(70)	C(70)	113(2)
O(30)	C(30)	H(30A)	109.3	O(70)	C(70)	H(70A)	109.3
O(30)	C(30)	H(30B)	109.7	O(70)	C(70)	H(70B)	109.7
H(30A)	C(30)	H(30B)	109.5	H(70A)	C(70)	H(70B)	109.5
O(30)	C(30)	H(30C)	109.4	O(70)	C(70)	H(70C)	109.4
H(30A)	C(30)	H(30C)	109.5	H(70A)	C(70)	H(70C)	109.5
H(30B)	C(30)	H(30C)	109.5	H(70B)	C(70)	H(70C)	109.5
O(31)	C(31)	O(32)	125(2)	O(71)	C(71)	O(72)	137(3)
O(31)	C(31)	C(27)	124(2)	O(71)	C(71)	C(67)	115(2)
O(32)	C(31)	C(27)	110(2)	O(72)	C(71)	C(67)	106(2)
C(31)	O(32)	C(32)	109.9(19)	C(71)	O(72)	C(72)	106(2)
O(32)	C(32)	H(32A)	109.4	O(72)	C(72)	H(72A)	109.3
O(32)	C(32)	H(32B)	109.7	O(72)	C(72)	H(72B)	109.5
H(32A)	C(32)	H(32B)	109.5	H(72A)	C(72)	H(72B)	109.5
O(32)	C(32)	H(32C)	109.3	O(72)	C(72)	H(72C)	109.6
H(32A)	C(32)	H(32C)	109.5	H(72A)	C(72)	H(72C)	109.5
H(32B)	C(32)	H(32C)	109.5	H(72B)	C(72)	H(72C)	109.5

**Table 22** Atomic coordinates and U(eq) for **91**

Atom	x	y	z	U(eq)
C(1)	13907(3)	1670(2)	7220(2)	21(1)
C(2)	14854(3)	1652(2)	6390(2)	20(1)
C(3)	16061(3)	2140(2)	6366(2)	22(1)
O(3)	16537(2)	2611(1)	7135(2)	32(1)
C(4)	16664(3)	2038(2)	5344(2)	24(1)
C(5)	16140(3)	1526(2)	4052(2)	25(1)
C(6)	14922(3)	1033(2)	4527(2)	23(1)
O(6)	14478(2)	555(1)	3757(2)	32(1)
C(7)	14312(3)	1143(1)	5538(2)	21(1)
C(8)	12989(3)	816(2)	5791(2)	21(1)
C(9)	11887(3)	1478(2)	5498(2)	22(1)
S(10)	10103(1)	1187(1)	5592(1)	26(1)
C(11)	10201(3)	1520(1)	6962(2)	20(1)
S(12)	11309(1)	2309(1)	7365(1)	28(1)
C(13)	12529(2)	2075(2)	6488(2)	22(1)
C(14)	13429(3)	838(2)	7150(2)	22(1)
C(15)	9420(3)	1233(1)	7635(2)	20(1)
S(16)	9466(1)	1568(1)	9058(1)	22(1)
C(17)	8068(2)	765(1)	9418(2)	19(1)
C(18)	8027(2)	276(1)	8539(2)	19(1)
S(19)	8205(1)	484(1)	7132(1)	20(1)

**Table 22** Atomic coordinates and U(eq) for **91** (continued)

Atom	x	y	z	U(eq)
C(20)	8600(2)	629(2)	10668(2)	19(1)
O(20)	8443(2)	15(1)	11061(2)	25(1)
O(21)	8813(2)	1271(1)	11288(2)	23(1)
C(21)	8968(3)	1179(2)	12547(2)	27(1)
C(22)	7284(2)	-445(2)	8686(2)	20(1)
O(22)	7678(2)	-1056(1)	8479(2)	31(1)
O(23)	6128(2)	-299(1)	9049(2)	23(1)
C(23)	5378(3)	-961(2)	9288(3)	38(1)
H(1A)	14343	1874	8023	26
H(4A)	17442	2345	5284	28
H(5A)	16565	1477	3863	30
H(8A)	12660	316	5419	25
H(9A)	11860	1694	4703	27
H(13A)	12790	2545	6119	26
H(14A)	14217	486	7530	27
H(14B)	12620	752	7496	27
H(21A)	9115	1675	12935	41
H(21B)	9788	853	12889	41
H(21C)	8105	946	12668	41
H(23A)	4548	-803	9550	57
H(23B)	6013	-1263	9910	57
H(23C)	5065	-1264	8565	57

**Table 23** Bond lengths (Å) for **91**

Atom	Atom	Distance	Atom	Atom	Distance
C(1)	C(2)	1.509(3)	C(17)	C(20)	1.486(4)
C(1)	C(14)	1.537(4)	C(18)	C(22)	1.498(4)
C(1)	C(13)	1.561(3)	C(18)	S(19)	1.741(3)
C(2)	C(7)	1.342(4)	C(20)	O(20)	1.204(3)
C(2)	C(3)	1.465(4)	C(20)	O(21)	1.333(3)
C(3)	O(3)	1.224(3)	O(21)	C(21)	1.451(3)
C(3)	C(4)	1.479(4)	C(22)	O(22)	1.193(3)
C(4)	C(5)	1.335(4)	C(22)	O(23)	1.332(3)
C(5)	C(6)	1.480(4)	O(23)	C(23)	1.446(3)
C(6)	O(6)	1.226(3)	S(16)	C(17)	1.754(3)
C(6)	C(7)	1.473(4)	C(17)	C(18)	1.347(3)
C(7)	C(8)	1.513(3)	C(15)	S(19)	1.769(3)
C(8)	C(14)	1.534(4)	C(15)	S(16)	1.758(3)
C(8)	C(9)	1.563(4)	S(12)	C(13)	1.815(2)
C(9)	C(13)	1.569(4)	C(11)	S(12)	1.749(3)
C(9)	S(10)	1.824(4)	C(11)	C(15)	1.333(4)
S(10)	C(11)	1.757(3)			

**Table 24** Bond angles (°) for **91**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(2)	C(1)	C(14)	100.0(2)	S(16)	C(15)	S(19)	114.32(14)
C(2)	C(1)	C(13)	103.97(19)	C(17)	S(16)	C(15)	93.62(12)
C(14)	C(1)	C(13)	101.77(19)	C(18)	C(17)	C(20)	122.5(2)
C(7)	C(2)	C(3)	122.6(2)	C(18)	C(17)	S(16)	117.7(2)
C(7)	C(2)	C(1)	107.8(2)	C(20)	C(17)	S(16)	119.73(19)
C(3)	C(2)	C(1)	129.2(2)	C(17)	C(18)	C(22)	125.1(2)
O(3)	C(3)	C(2)	122.4(2)	C(17)	C(18)	S(19)	117.39(19)
O(3)	C(3)	C(4)	121.5(2)	C(22)	C(18)	S(19)	117.49(18)
C(2)	C(3)	C(4)	116.0(2)	C(18)	S(19)	C(15)	94.01(12)
C(5)	C(4)	C(3)	121.6(2)	O(20)	C(20)	O(21)	125.1(2)
C(4)	C(5)	C(6)	122.4(3)	O(20)	C(20)	C(17)	123.9(2)
O(6)	C(6)	C(7)	122.9(2)	O(21)	C(20)	C(17)	111.0(2)
O(6)	C(6)	C(5)	121.2(3)	C(20)	O(21)	C(21)	114.7(2)
C(7)	C(6)	C(5)	115.9(2)	O(22)	C(22)	O(23)	125.9(2)
C(2)	C(7)	C(6)	121.5(2)	O(22)	C(22)	C(18)	123.7(2)
C(2)	C(7)	C(8)	107.3(2)	O(23)	C(22)	C(18)	110.4(2)
C(6)	C(7)	C(8)	130.9(2)	C(22)	O(23)	C(23)	114.8(2)
C(7)	C(8)	C(14)	100.15(19)	C(1)	C(13)	S(12)	113.11(17)
C(7)	C(8)	C(9)	104.1(2)	C(9)	C(13)	S(12)	112.25(16)
C(14)	C(8)	C(9)	101.2(2)	C(8)	C(14)	C(1)	94.4(2)
C(8)	C(9)	C(13)	103.00(19)	C(11)	C(15)	S(16)	123.9(2)
C(8)	C(9)	S(10)	112.88(17)	C(11)	C(15)	S(19)	121.7(2)
C(13)	C(9)	S(10)	111.68(17)	S(12)	C(11)	S(10)	113.42(14)
C(11)	S(10)	C(9)	96.61(12)	C(11)	S(12)	C(13)	96.71(12)
C(15)	C(11)	S(12)	123.5(2)	C(1)	C(13)	C(9)	102.3(2)
C(15)	C(11)	S(10)	122.8(2)	O(19)	C(19)	H(19C)	109.5
C(23)	C(9)	C(1)	130.9(2)	O(19)	C(18)	C(14)	111.0(2)
C(1)	C(10)	C(7)	94.41(19)	C(18)	O(19)	C(19)	114.7(2)
O(20)	C(20)	C(8)	122.4(2)	O(19)	C(19)	H(19A)	109.5
O(20)	C(20)	C(21)	121.5(2)	O(19)	C(19)	H(19B)	109.5
C(8)	C(20)	C(21)	116.1(2)	H(19A)	C(19)	H(19B)	109.5
C(22)	C(21)	C(20)	121.5(2)	H(19A)	C(19)	H(19C)	109.5
C(22)	C(21)	H(21A)	119.2	H(19B)	C(19)	H(19C)	109.5
C(20)	C(21)	H(21A)	119.2				

**Table 25** Atomic coordinates and U(eq) for **203**

Atom	x	y	z	U(eq)
P(1)	2285(1)	6073(1)	4480(1)	56(1)
O(1)	5353(4)	6274(1)	6932(3)	67(1)
C(1)	5390(5)	6253(1)	5603(4)	50(1)
C(2)	4423(4)	5937(1)	4642(4)	46(1)
O(2)	4488(3)	5584(1)	5344(3)	53(1)
C(3)	5007(5)	5973(1)	3165(4)	49(1)
C(4)	5953(5)	6291(1)	3239(4)	48(1)
C(5)	6171(5)	6473(1)	4633(4)	48(1)
C(6)	6059(6)	5427(1)	5660(5)	69(1)
C(7)	4657(5)	5708(1)	1964(5)	55(1)
O(7)	3936(4)	5415(1)	1985(3)	78(1)
O(8)	5259(4)	5822(1)	773(3)	74(1)
C(8)	4989(7)	5580(1)	-518(5)	88(2)
C(9)	6733(6)	6433(1)	1998(5)	53(1)
O(9)	8053(4)	6349(1)	1835(3)	81(1)
O(10)	5752(4)	6658(1)	1124(3)	65(1)
C(10)	6388(7)	6798(1)	-159(5)	92(2)
C(11)	7076(5)	6813(1)	4972(5)	58(1)
O(11)	7775(5)	6979(1)	4119(4)	95(1)
O(12)	7106(4)	6930(1)	6360(3)	75(1)
C(12)	7987(8)	7268(1)	6812(6)	107(2)
C(13)	1780(5)	6033(1)	6306(5)	64(1)
C(14)	74(6)	6139(2)	6438(6)	85(2)
C(15)	-244(8)	6115(2)	8015(7)	120(2)
C(16)	722(10)	6365(2)	9045(8)	162(3)
C(17)	2016(6)	6541(1)	3747(6)	83(2)
C(18)	2391(8)	6864(2)	4800(8)	113(2)
C(19)	2195(14)	7245(3)	3883(18)	207(5)
C(20A)	3130(30)	7350(7)	3060(30)	240(13)
C(19)	2195(14)	7245(3)	3883(18)	207(5)
C(20B)	2500(30)	7564(6)	4600(30)	262(14)
C(21)	1012(6)	5772(1)	3216(5)	73(1)
C(22)	806(7)	5374(2)	3694(6)	99(2)
C(23)	11(13)	5106(3)	2430(11)	171(3)
C(24A)	-1510(20)	5121(7)	1950(30)	170(11)
C(23)	11(13)	5106(3)	2430(11)	171(3)
C(24B)	-1050(40)	5264(8)	1750(40)	310(30)
H(6A)	6015	5188	6140	103
H(6B)	6747	5595	6299	103
H(6C)	6473	5394	4756	103
H(8A)	5467	5691	-1295	132
H(8B)	3856	5550	-846	132
H(8C)	5464	5338	-269	132
H(10A)	5608	6958	-733	139
H(10B)	6622	6589	-753	139

**Table 25** Atomic coordinates and U(eq) for **203** (continued)

Atom	x	y	z	U(eq)
H(10C)	7353	6938	166	139
H(12A)	7913	7323	7823	161
H(12B)	7544	7474	6197	161
H(12C)	9093	7234	6717	161
H(13A)	1966	5775	6638	77
H(13B)	2505	6192	6970	77
H(14A)	-659	5972	5820	102
H(14B)	-136	6394	6075	102
H(15A)	-1367	6172	8017	144
H(15B)	-57	5858	8361	144
H(16A)	465	6328	10016	244
H(16B)	504	6622	8745	244
H(16C)	1837	6312	9059	244
H(17A)	2678	6567	2984	100
H(17B)	907	6565	3269	100
H(18A)	3480	6842	5330	136
H(18B)	1664	6863	5516	136
H(19A)	1137	7236	3281	248
H(19B)	2166	7446	4595	248
H(20A)	2749	7583	2589	360
H(20B)	3179	7162	2312	360
H(20C)	4177	7387	3622	360
H(19C)	2891	7230	3143	248
H(19D)	1101	7256	3358	248
H(20D)	2312	7770	3910	393
H(20E)	3597	7567	5077	393
H(20F)	1806	7589	5322	393
H(21A)	-42	5888	3007	87
H(21B)	1435	5766	2296	87
H(22A)	154	5374	4470	119
H(22B)	1851	5273	4110	119
H(23A)	551	5148	1589	206
H(23B)	257	4850	2760	206
H(24A)	-1784	4939	1173	256
H(24B)	-1787	5369	1576	256
H(24C)	-2082	5065	2743	256
H(23C)	784	5037	1804	206
H(23D)	-365	4878	2844	206
H(24D)	-1557	5106	967	468
H(24E)	-660	5489	1346	468
H(24F)	-1804	5331	2382	468

**Table 26** Bond lengths (Å) for **203**

Atom	Atom	Distance	Atom	Atom	Distance
P(1)	C(13)	1.802(4)	C(9)	O(10)	1.322(5)
P(1)	C(17)	1.789(5)	O(10)	C(10)	1.460(5)
P(1)	C(21)	1.796(5)	C(11)	O(11)	1.208(5)
P(1)	C(2)	1.853(4)	C(11)	O(12)	1.335(5)
O(1)	C(1)	1.227(4)	O(12)	C(12)	1.438(5)
C(1)	C(5)	1.426(5)	C(13)	C(14)	1.513(6)
C(1)	C(2)	1.569(5)	C(14)	C(15)	1.517(7)
C(2)	O(2)	1.407(4)	C(15)	C(16)	1.446(9)
C(2)	C(3)	1.522(5)	C(17)	C(18)	1.501(7)
O(2)	C(6)	1.423(5)	C(18)	C(19)	1.585(10)
C(3)	C(4)	1.376(5)	C(18)	C(19)	1.585(10)
C(3)	C(7)	1.442(5)	C(19)	C(20A)	1.24(2)
C(4)	C(5)	1.418(5)	C(19)	C(20B)	1.31(2)
C(4)	C(9)	1.495(5)	C(21)	C(22)	1.500(6)
C(5)	C(11)	1.433(6)	C(22)	C(23)	1.562(9)
C(7)	O(7)	1.206(5)	C(22)	C(23)	1.562(9)
C(7)	O(8)	1.341(5)	C(23)	C(24A)	1.29(2)
O(8)	C(8)	1.452(5)	C(23)	C(24B)	1.15(2)
C(9)	O(9)	1.187(4)			

**Table 27** Bond angles (°) for **203**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(13)	P(1)	C(17)	112.8(2)	O(7)	C(7)	C(3)	126.1(4)
C(13)	P(1)	C(21)	110.2(2)	O(8)	C(7)	C(3)	111.6(4)
C(17)	P(1)	C(21)	106.4(2)	C(7)	O(8)	C(8)	117.1(3)
C(13)	P(1)	C(2)	106.39(18)	O(9)	C(9)	O(10)	125.6(4)
C(17)	P(1)	C(2)	109.5(2)	O(9)	C(9)	C(4)	123.6(4)
C(21)	P(1)	C(2)	111.6(2)	O(10)	C(9)	C(4)	110.8(4)
O(1)	C(1)	C(5)	132.6(4)	C(9)	O(10)	C(10)	114.6(4)
O(1)	C(1)	C(2)	120.4(4)	O(11)	C(11)	O(12)	122.1(4)
C(5)	C(1)	C(2)	107.0(3)	O(11)	C(11)	C(5)	124.7(4)
O(2)	C(2)	C(3)	119.2(3)	O(12)	C(11)	C(5)	113.2(4)
O(2)	C(2)	C(1)	113.7(3)	C(11)	O(12)	C(12)	117.5(4)
C(3)	C(2)	C(1)	103.0(3)	C(14)	C(13)	P(1)	115.4(3)
O(2)	C(2)	P(1)	103.5(2)	C(13)	C(14)	C(15)	112.6(4)
C(3)	C(2)	P(1)	111.2(3)	C(16)	C(15)	C(14)	114.8(6)
C(1)	C(2)	P(1)	105.6(3)	C(18)	C(17)	P(1)	117.8(4)
C(2)	O(2)	C(6)	113.9(3)	C(17)	C(18)	C(19)	108.5(7)
C(4)	C(3)	C(7)	128.0(4)	C(17)	C(18)	C(19)	108.5(7)
C(4)	C(3)	C(2)	107.2(3)	C(19)	C(18)	C(19)	0.0(4)

**Table 27** Bond angles (°) for **203** (continued)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(7)	C(3)	C(2)	124.8(4)	C(20A)	C(19)	C(18)	124.2(17)
C(3)	C(4)	C(5)	114.0(3)	C(20B)	C(19)	C(18)	118(2)
C(3)	C(4)	C(9)	124.3(4)	C(22)	C(21)	P(1)	117.3(3)
C(5)	C(4)	C(9)	121.6(4)	C(21)	C(22)	C(23)	114.4(6)
C(4)	C(5)	C(1)	107.9(3)	C(21)	C(22)	C(23)	114.4(6)
C(4)	C(5)	C(11)	124.4(4)	C(23)	C(22)	C(23)	0.0(8)
C(1)	C(5)	C(11)	127.6(4)	C(24A)	C(23)	C(22)	120.7(12)
O(7)	C(7)	O(8)	122.3(4)	C(24B)	C(23)	C(22)	108(2)

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