SOLID-STATE ^{13}C N.M.R. OF DIARYLIDE PIGMENTS

BY

KENNETH S. CAMERON

A THESIS SUBMITTED FOR THE
DEGREE OF MASTER OF SCIENCE AT
ST.ANDREWS UNIVERSITY

ACKNOWLEDGEMENTS

I would like to thank Dr. Riddell for offering me the chance to do this M.Sc. in the first place and for all his encouragement and help over the past year. To Ciba-Geigy there is thanks for the funding and to Dr. Fraser for looking after me when I was working at Paisley and for his input during this time and his visits to St.Andrews. Also at Ciba-Geigy thanks to Ian MacCormack for running the X-ray powder diffraction patterns. Many thanks to Dr. Arumagum for helping to run most of the solid-state ^{13}C N.M.R. spectra and latterly to Melanja Smith who has taken over from him. I would also like to thank my colleagues for their help and for not complaining too much about all the yellow equipment that has resulted from making the various compounds for this thesis.

CONTENTS

1 INTRODUCTION

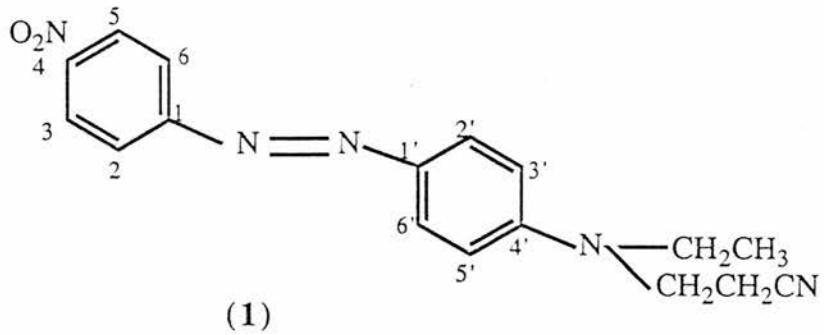
1.1 Literature Survey on the Solid-State N.M.R. of Pigments

A literature survey was carried out to establish what solid-state N.M.R. work had been done on pigments, especially diarylide pigments. The survey ultimately proved disappointing in terms of information about the diarylide yellow pigments. Most of the solid-state N.M.R. research work that has been done on pigments has involved the aryl- and phenyl-azo naphthols which are the basic structure of C.I. pigment red 57. There has been some solid-state NMR involving these structures mainly looking into the enol-azo keto-hydrazo tautomerism, which is also possible in the diarylide pigments.

1.11 J. Chem. Soc. Perkin Trans. 2, 1981, 1031.

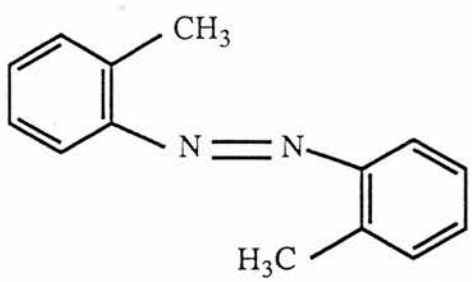
High-Resolution ^{13}C Nuclear Magnetic Resonance Spectra of Some Solid trans-Azobenzene and Dyestuff Species.
By Chippendale and Mathias; Harris, Packer and Say.

The ^{13}C NMR spectra of Disperse Orange 25 (1), shows clear differences when obtained in the solid-state compared to solution, especially in the aromatic carbon region.



(1)

The paper proceeds to examine a series of di-substituted 4,4'-trans-azobenzene [$RC_6H_4N{=}NC_6H_4R$] reference compounds. Six R groups were used H, OH, COCl, CO_2H, $NHCOCH_3$ and CH_3. The main difference in the solid and solution state chemical shifts is that in the solid-state C (2) and C(6) are split but in solution they are equivalent. This indicates there is free rotation in solution of the C-N bonds but not in the solid. The case of 2,2'-dimethylazobenzene (2) was examined since for steric reasons it is likely to exist in the conformation shown in solution as well as in the solid.



(2)

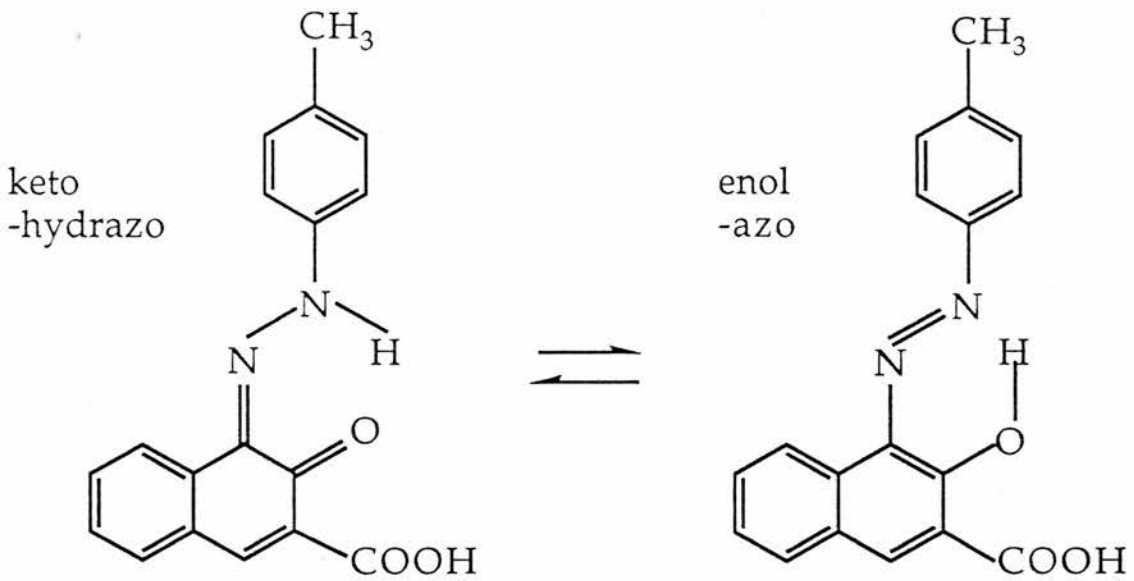
The solid-state and solution chemical shifts were found experimentally to be identical within experimental error. This confirms that in the other compounds it is the free rotation about the C-N bonds that causes the differences between the solid and solution state spectra.

1.12 J.Chem. Soc. Perkin Trans. 2, 1987, 1383

Investigation of the Structure of an Insoluble Pigment by Means of Nuclear Magnetic Resonance

By Harris, Jonsen and Packer; Campbell

The paper deals with the monohydrated calcium salt CIPR 57:1. The main objectives being to see if it prefers the keto-hydrazo or enol-azo form and to determine the nature of the calcium ion interaction with the organic molecule.



(1) Free acid of CIPR 57:1

From Jonsen's Ph.D thesis it is known the carbonyl and hydroxy-substituted aromatic carbons are at δ c.a. 182 ppm and 152 ppm respectively. The phenyl ring can also be fully assigned from data in Jonsen's thesis. The naphthalene ring can be assigned using

substituent chemical shift (SCS) parameters. For the hydrazo form these were calculated from solution-state ^{13}C N.M.R. The azo SCS parameters were calculated from solid-state ^{13}C N.M.R. in paper (1.1). The SCS parameters allow the calculation of ^{13}C chemical shifts for the two conformations.

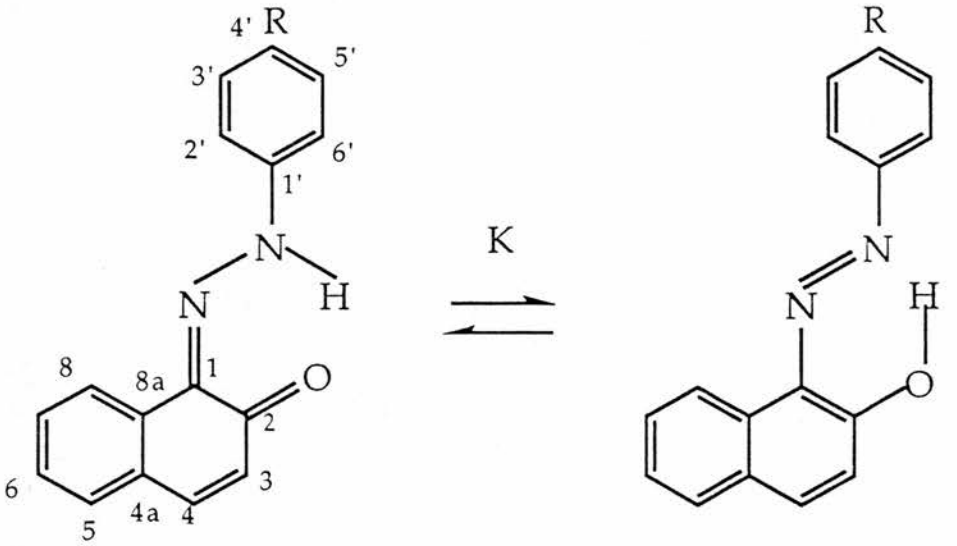
To aid in the interpretation of the NMR data a series of model compounds were synthesised. These included: (a) isotopic labelling of nitrogens; (b) Ca^{2+} replaced by Cd^{2+}; (c) sodium salts of the acid dyestuff 1; (d) chemically modified pigments e.g. sulpho or carboxyl groups removed. There were 13 models in total and all the carbons were tentatively assigned using the SCS parameters.

By doing ^{15}N NMR with dipolar dephasing (N.Q.S.) the N-H nitrogen was easily identifiable since it was phased out of the spectrum leaving only the doubly bonded N in the spectrum. The ^{113}Cd NMR proves that there is only one site for the metal ion. It is divalently attached to two oxygens and so it must be coordinated to both the carboxyl and sulphonate groups.

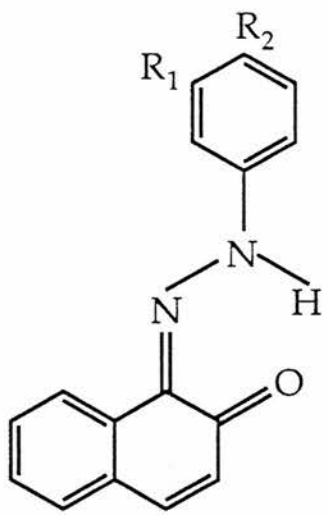
1.13 J. Am. Chem. Soc., 1989, 5525

^{13}C N.M.R. and X-ray Structure Determination of 1-(Arylazo)-2-naphthols. Intramolecular Proton Transfer between Nitrogen and Oxygen Atoms in the Solid State.
By Olivieri, Wilson, Paul and Curtin

This paper studies the same molecule as (1.2) except with different ring substituents (1-7).



R		
H	1a	1b
OMe	2a	2b
OEt	3a	3b
NMe_2	4a	4b



	R_1	R_2
5	NO_2	Me
6	NO_2	Cl
7	H	NO_2

Structures 5, 6, and 7 are shown in the keto-hydrazo form because it is known that electron-withdrawing groups push the equilibrium towards the hydrazone structure and conversely electron-donating groups favour the enol-azo form.

The equilibrium constant, K was calculated by solution ^{13}C NMR at different temperatures. K was determined by using the fact that C (2) has a chemical shift of 180 ppm in the hydrazone and in the azo it is 147 ppm and so the observed position between these values allowed the relative amounts of each to be determined.

The solid-state ^{13}C NMR measurements of 1 gives C (2) at 174.1 ppm showing that in the solid there is still a fast proton exchange going on. The hydrazone form is favoured in 1 when the temperature is lowered (table 1).

T	δ C (2)	
293	174.1	**Table 1**
213	176.2	
173	177.8	

Compounds 2-4 have equilibria increasingly more towards the azo structure.

The assignment of chemical shifts to the carbons was done by direct comparison to solution-state data. The only difficulty being with the splitting of the C (2'), C (6') and C (3'), C (5') pairs in the solid state because the phenyl ring is no longer free to rotate.

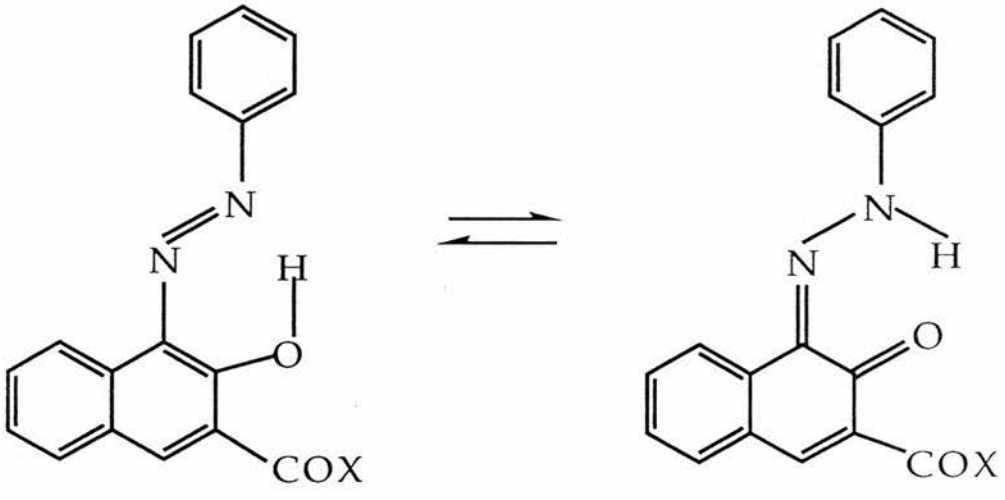
X-ray crystallography shows that there are no intermolecular interactions present that would permit proton transfer between molecules, ruling out intermolecular exchange as an explanation for the NMR results.

1.14 Collect. Czech. Chem. Commun., 1990, 193

N.M.R. Studies of 1-Phenylazo-3-substituted-2-naphthols in solution and in the solid-state.

By Lycka, Necas, Jirman, Straka and Schneider.

The compounds are very similar to those in papers (1.2) and (1.3):

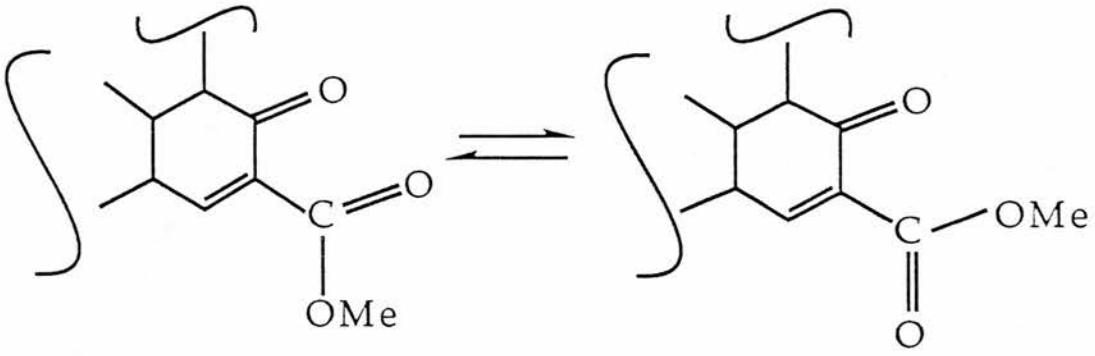


1, X=OH
2, X=OCH_3

3, X=NH— 

Solution ^{1}H and ^{15}N NMR shows that 1 and 3 are in the hydrazone form. This structured is favoured because of the hydrogen bonding of the COOH in 1 and of CONH in 3 to the carbonyl group. Compound 2, however, gives two nitrogen peaks in the solid. These are split by 18.4 ppm, much more than the 3.4-5.8 for hydrazo-azo tautomerism. The ^{13}C CP/MAS NMR spectrum is composed of two sets of signals thus indicating two conformers for 2. The biggest

splitting of chemical shifts is of the OCH_3 group, thus the two conformers differ by a rotation about the C-$COOCH_3$ (see below).



1.15 Dyes and Pigments 17 (1991) 41-55

Azo Pigments and their Intermediates. A CP MAS ^{13}C-N.M.R. Study of the Tetrazotised Products of 1,5-Diamino-4,8-dihydroxyanthraquinone.
Law, Kaplan and Tarnawskyj.

The paper looks at forming azo pigments from isomeric diaminoanthraquinone (1). Azo pigments have the common structural characteristic of an azo chromophore connecting two carbons, where at least one is aromatic. The diaminoanthraquinones are commercially available are non-toxic and are inexpensive. The synthesis (fig.1) and structure of the tetrazotised products of (1) are characterised.

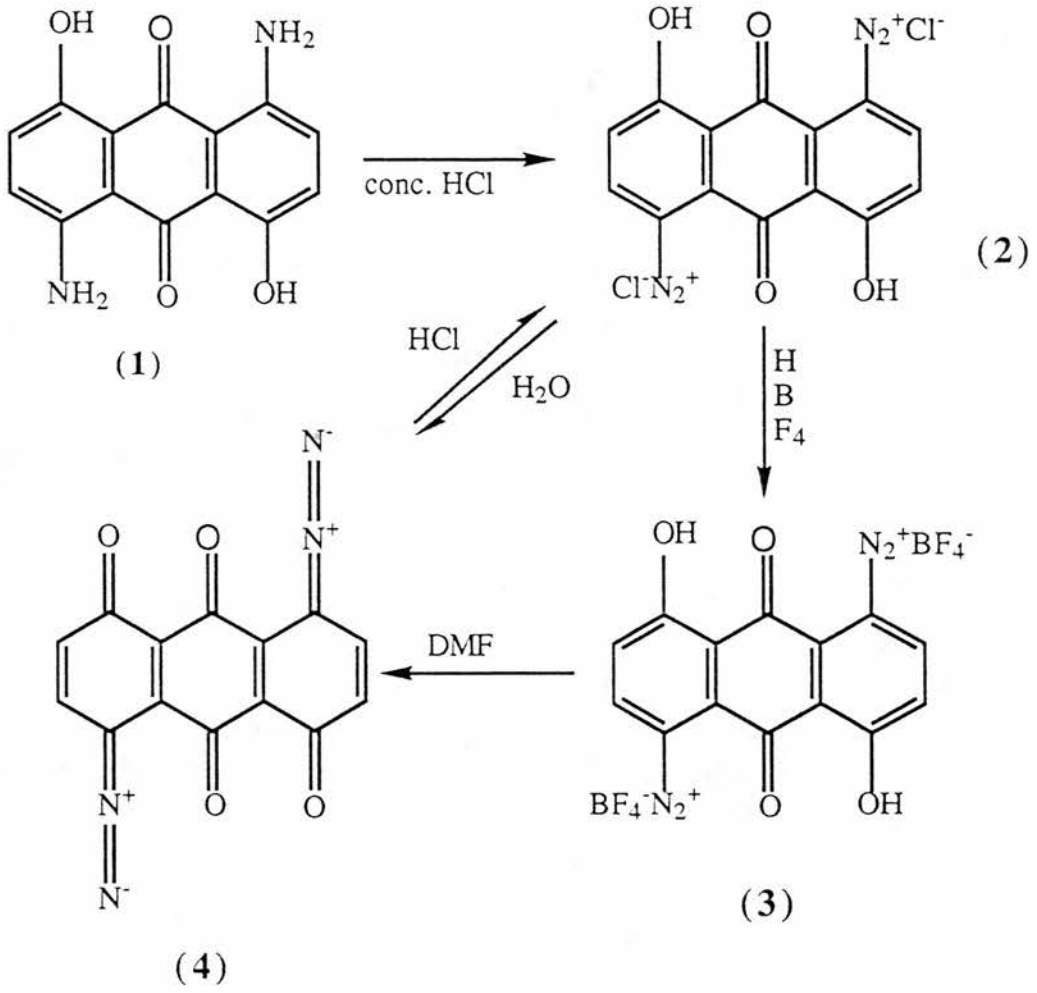


fig.1

The conversion is initially followed by Infra-Red, with the N-H, C=O, =N=N and -N=N all easily identifiable. Deprotonation of compounds 2, 3, or 4 is not known, but for *p*-aminophenol it is well documented (fig.2).

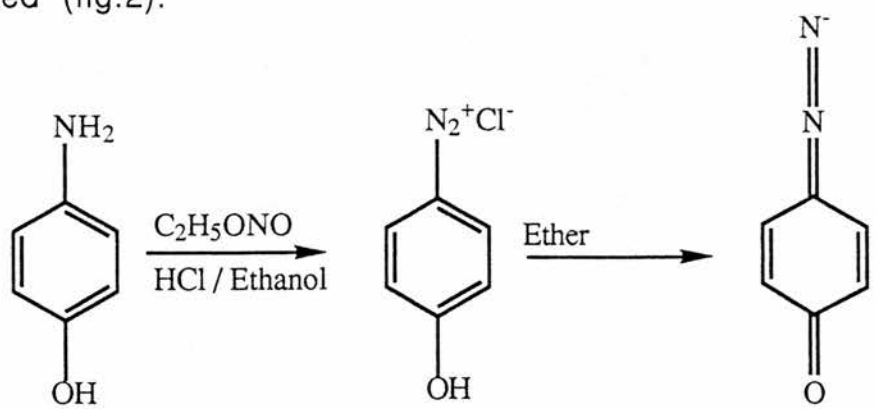


fig.2

The diazonium group is a very powerful electron withdrawing group known, therefore, deprotonation in DMF is reasonable.

Solution ^{1}H NMR gives identical spectra for 3 and 4 and as such the compounds must be identical in the deuterium-chloride solution used to do ^{1}H NMR.

The solid-state MAS ^{13}C N.M.R. 50.3 MHz spectra show that carbons 1 and 5 (fig. 3) are split due to the quadrupolar ^{14}N. Carbons 4, 8 and 9, 10 are distinguished by the decrease in intensity of the 4,8 peak in the NQS spectrum because they are spatially nearer to hydrogens and therefore more easily dephased.

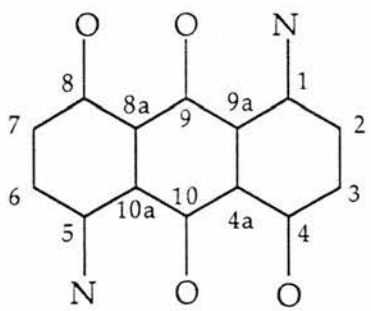


fig.3

The higher frequency resonance at 82.7 ppm (table 1) must be 1 and 5 because of the strong shielding by the electrons in the diazo resonance.

Table 1: solid-state ^{13}C chemical shifts of 1,3 and 4.

C No.	1	3	4
1,5	147.2+150.2	101.3	82.7
2,6	128.3	145.9	136.6
3,7	128.3	126.1	132.2
4,8	156.6	170.8	176.8
9,10	185.9	182.4	178.2
4a,8a	114.4	117.9	123.2
9a,10a	108.3	138.6	142.5

Carbons 1 and 5 expected to be at between 20 and 67 ppm, therefore, the shielding must be reduced by the resonance stabilisation of the negative charge of the para C=O group (fig. 4).

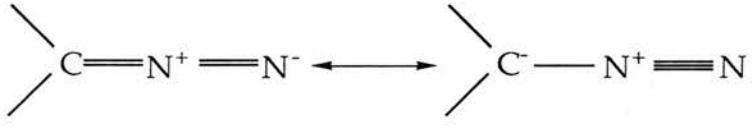


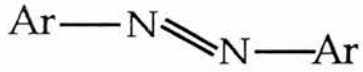
fig.4

The objective was to synthesise bisazo pigments from 1, but 3 deprotonates to insoluble 5 in water and organic solvents. Therefore, coupling at alkaline or neutral pH is ruled out. 3 is soluble in concentrated HCL and coupling can occur if a very reactive coupling component is used. The coupling of 3 with N,N-dimethylaniline did not give any pigment even if the pH was raised slightly with NaOH (pH ~1-2) this resulted in 4 precipating out. and the pH was about 1-2. Therefore, the facile deprotonation of 3 to 4 appears to be a limiting factor for pigment synthesis.

1.2 PIGMENTS

A definition of a pigment is that of a colourant in powder form which is insoluble in and essentially physically and chemically unaffected by its application medium. By contrast a dye is a colourant that is soluble at some stage in the application medium. Therefore, certain compounds can act as a pigment in one application medium and as a dye in another. That means in terms of chemical structure a particular compound could be regarded as both a pigment and a dyestuff.

Almost all classical organic pigments (CP's) are azo pigments with the general formula:



One of the most important groups of azo pigments are the azoacetoacetanilides. The monoazoacetoacetanilides or Hansa yellows (fig.1.1 and Table 1.1) as they are called, were very important in the early part of this century.[1,2]

When a new pigment is made it is given a colour index (C.I.) number and in the case of yellow pigments their full title is C.I. pigment yellow (P.Y.) X. This is just a short hand so that it is easy to refer to the different pigments. An orange pigment is also examined, these are similarly named and are abbreviated to P.O. X.

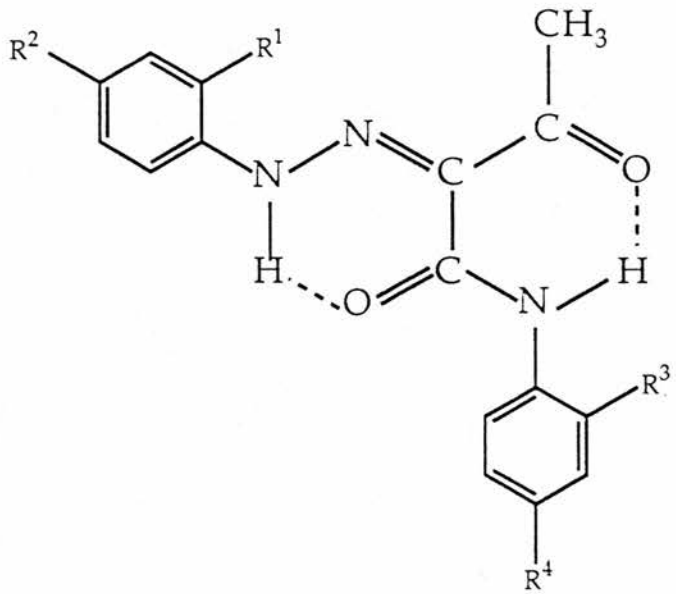


fig.1.1

Table 1.1: substituents of some common Hansa yellow pigments.

C.I. Number	R-1	R-2	R-3	R-4
PY 1	NO_2	CH_3	H	H
PY 3	NO_2	Cl	Cl	H
PY 4	H	NO_2	H	H
PY 5	NO_2	H	H	H
PY 6	NO_2	Cl	H	H
PY65	NO_2	OCH_3	OCH_3	H
PY73	NO_2	Cl	OCH_3	H
PY 74	$0CH_3$	NO_2	OCH_3	H
PY 98	NO_2	Cl	CH_3	Cl

The diarylide yellow pigments or disazoacetoacetanilides (fig.1.2) have largely replaced them due to their improved pigment properties.

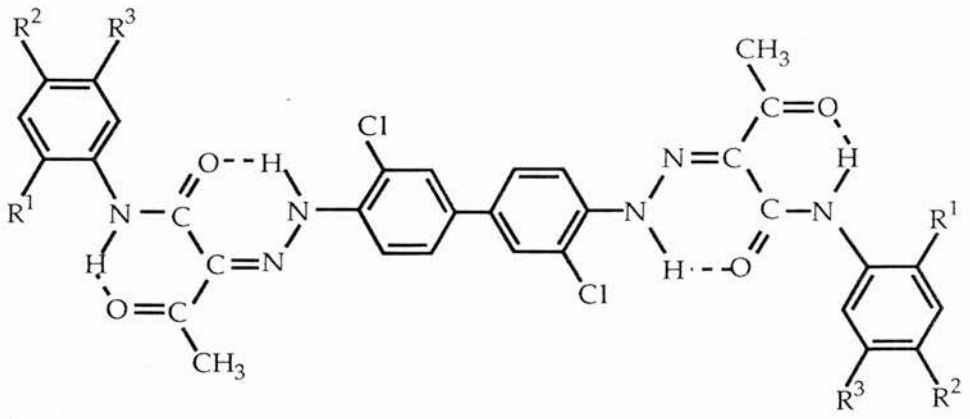


fig.1.2

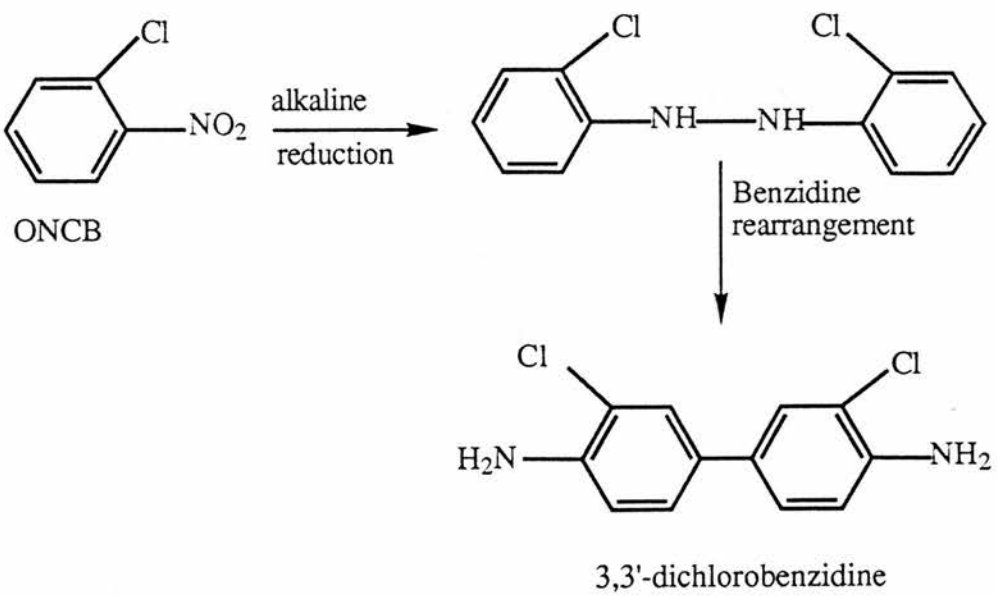
The properties which are important in pigment technology are tinctorial (colour) strength, fastness to light and solvents, shade, transparency as well as heat stability and the economics of production. The particle size of a pigment is very important, and is generally in the range 0.02 to 0.7 μ. The wavelength of visible light is 0.4 to 0.7μ, therefore, the way light interacts with these particles is of critical importance. The disazo pigments are superior to the monoazos in terms of tinctorial strength, transparency, fastness to solvents and heat stability. This makes them suitable for use in printing inks and in the colouration of plastics and elastomers. The disazo pigments therefore, dominate the production of organic yellow pigments. In the United States in 1980-81 diarylide yellows accounted for 80% of the market in major products and of the seven diarylide yellow pigments analysed (Chapter 3) P.Y.12 has by far the largest share of the market (Table 1.2) and P.O.16 has 25% of the orange market.[2]

Table 1.2: usage of diarylide yellow pigments in the U.S. as of 1980-81.

C.I. Number	R-1	R-2	R-3	Usage (millions of lbs)
PY 12	H	H	H	11
PY 13	CH_3	CH_3	H	0.4
PY 14	CH_3	H	H	3.5
PY 17	OCH_3	H	H	0.7
PY 55	H	CH_3	H	-
PY 63	Cl	H	H	-
PY 83	OCH_3	Cl	OCH_3	0.8

1.21 Reaction Schemes[2]

The diazotisation reaction involves the reaction of a tetrazo compound with two moles of a coupling component which contain an activated methylene group. The 3,3'-dichlorobenzidine is prepared from *ortho*-nitro-chlorobenzene (ONCB) (fig.1.3) which is then converted to the tetrazo.



ONCB

3,3'-dichlorobenzidine

fig.1.3

The acetoacetanilides are prepared from benzene (fig.1.4):

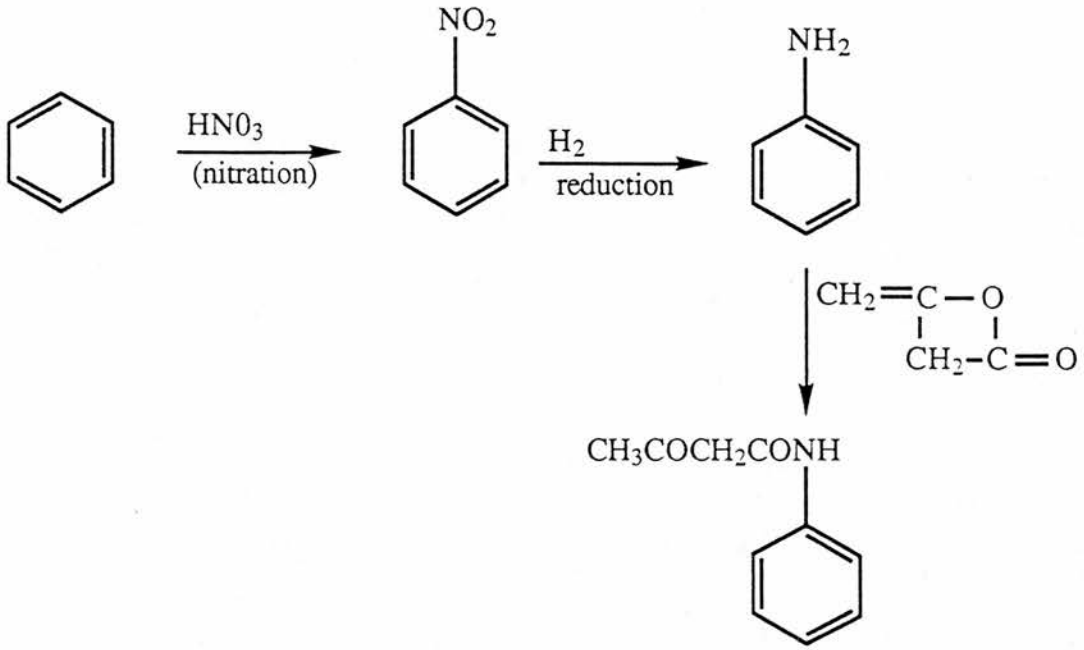


fig.1.4

The raw materials are obtained from the coal and petroleum industry, with the supply of ONCB crucial for DCB based pigments i.e. diarylide yellow pigments. The coupling components rely on the availability of benzene or aniline. For P.Y.14, toluene and *o*-toluidine and for P.Y.13, xylene and 2,4-xylidine are also important raw materials in determining costs. Acetoacetanilide (AAA) is much used and so can be produced most efficiently and gives P.Y.12 the lowest cost.

The coupling reaction involves the tetrazo form of the DCB. The conversion of aniline to the diazo compound shows the reaction scheme in fig.1.5.

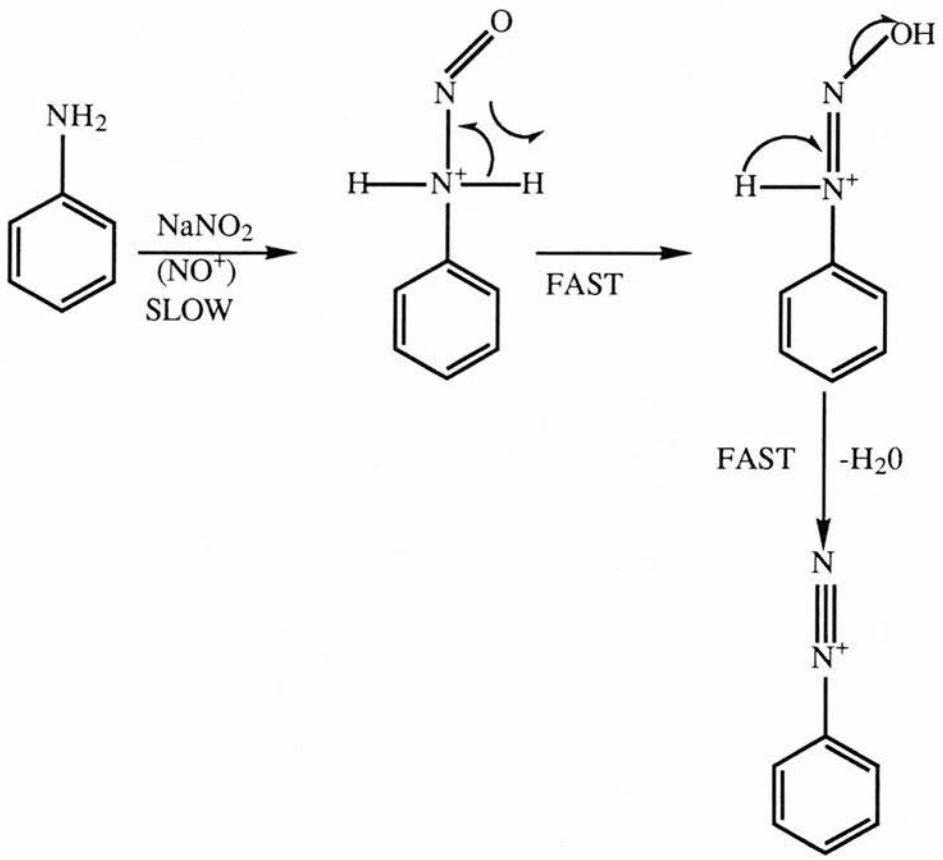


fig.1.5

The reaction of the tetrazo and the coupling component is affected by a number of different factors.[2]

(a) temperature: increase the temperature and the rate increases, but if the temperature is too high then the diazo decomposes and so a compromise temperature is reached. The temperature used is 16°C which allows a steady rate with little chance of diazo decomposition.

(b) pH: if the pH is too high then the reaction is slowed by the formation of $ON\text{-}NO_2$. If the pH is too low then the reaction is slowed by the protonation of the amine. A buffer of $NaCOOCH_3$ and CH_3CO_2H is used to help control the pH.

(c) **concentration:** the rate increases with higher concentration but, the addition of the DCB tetrazo is carried out slowly so that there is no excess of the tetrazo at any time at this elevated pH, since it could start to decompose. The coupling component is also used in 3-5 % excess to ensure the complete use of the tetrazo and so avoiding decomposition.

The complexity and size of the pigments that had to be analysed meant that the first compounds that were examined in this work were the coupling components and then the monoazo compounds. The monoazo compounds analysed are not actually pigments, but are half disazos i.e. one half of a standard Colour Index pigment yellow. This, therefore, made it much easier to assign the spectra of the diarylide yellow pigments.

1.3 Introduction to Solid-State CP MAS ^{13}C N.M.R.[5,6]

Solid-state ^{13}C nuclear magnetic resonance (N.M.R.) is a relatively new technique and differs from solution N.M.R. in a number of ways. In particular the following differences between molecules in the solid and in solution are important:

(a) in solids the molecules are held in a matrix and are surrounded by other similar molecules instead of being surrounded by solvent molecules.
(b) in an unspun sample the molecules are held steady with respect to the magnetic field unlike the solution-state.

(c) the same molecules can be inequivalent in the solid-state because of the crystallographic space group which determines the number of molecules in the asymmetric unit and therefore the number of N.M.R. resonances.
(d) for solids there is no averaging of the chemical shift anisotropy (CSA) because the molecules are not tumbling as in the solution-state.

These factors give rise to interactions in solid-state N.M.R. that are averaged out in solution by molecular tumbling. They can cause problems in obtaining good high resolution spectra, but the extra interactions potentially provide more information on the environment of the molecules than is possible in solution.

The main problems that affect the quality of spectra in the solid-state are CSA, dipolar coupling and long relaxation times.

1.31 Chemical Shift Anisotropy

The theory of CSA can be explained by looking at a simple molecule like CO_2 (fig.1.6). The field experienced by the central carbon nucleus depends on its orientation of the molecule with respect to the magnetic field B_0.

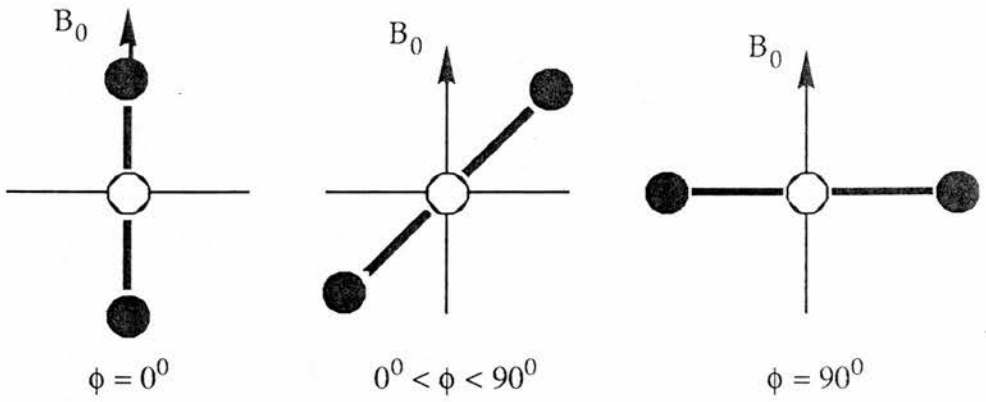


fig.1.6

It is clear from fig.1.6 that when $\phi = 0^o$ the central carbon experiences a different magnetic field from the case when $0^o < \phi < 90^o$ and also when $\phi = 90^o$ and so this gives rise to a range of chemical shifts. There are more ways that the molecules can be arranged when $\phi = 90^o$, therefore there is greater intensity of the spectrum when $\phi = 90^o$ (perpendicular) than for $\phi = 0^o$ (parallel) as shown in fig.1.7.

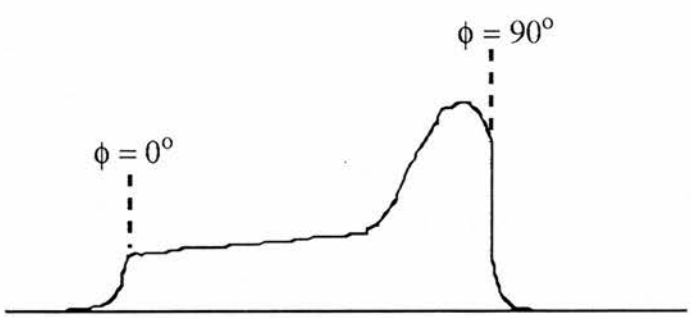
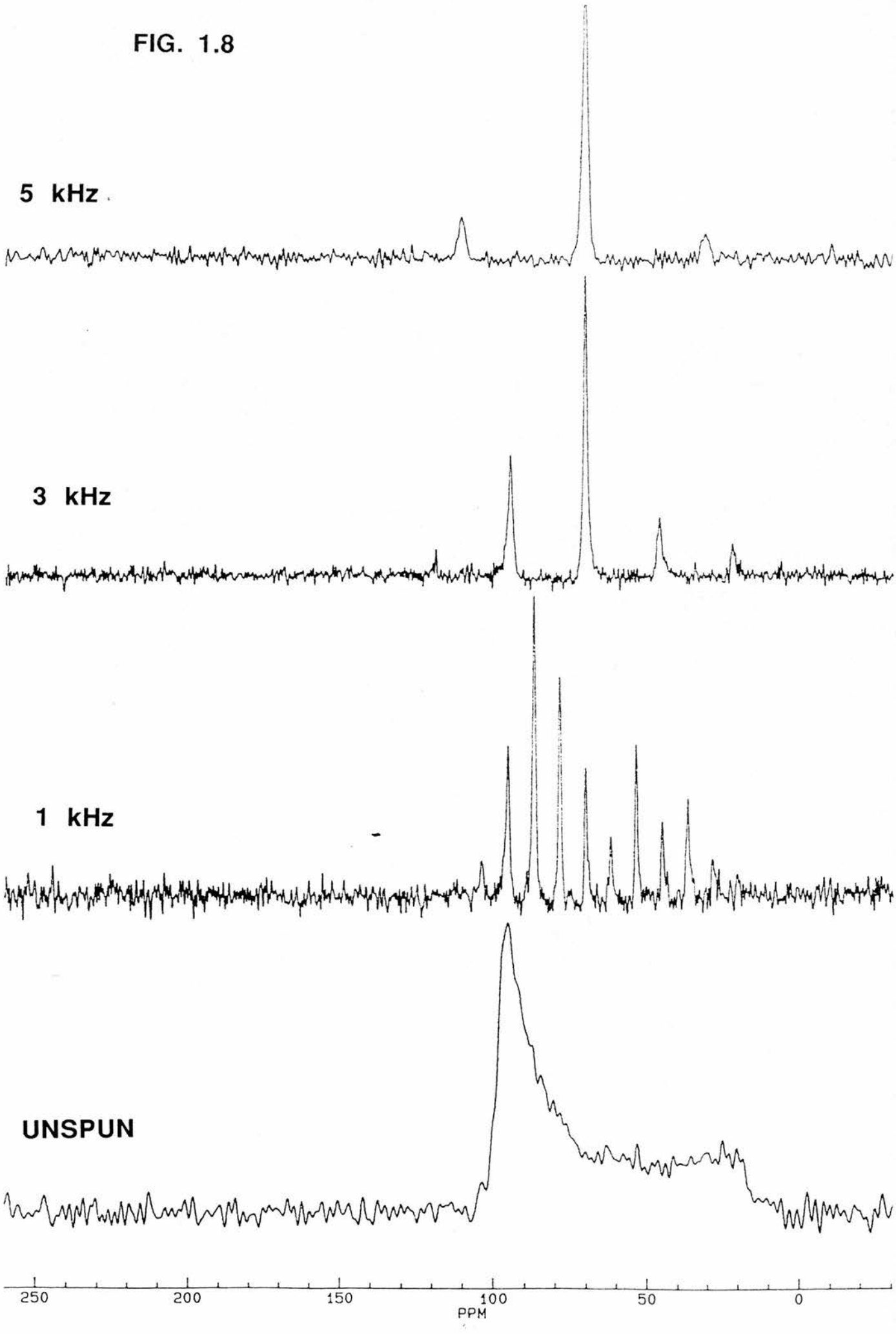


fig.1.7

This has been demonstrated in ferrocene (fig.1.8) by Dr K.D.M. Harris at St.Andrews. Thanks to him for allowing the use of the spectra.

FIG. 1.8



1.32 Dipolar Interactions

These can occur between isolated pairs of nuclei and for I = 1/2 nuclei i.e. ^{1}H, ^{13}C the through space coupling $J \propto [k(3\cos^2\phi-1)]/r^3$.

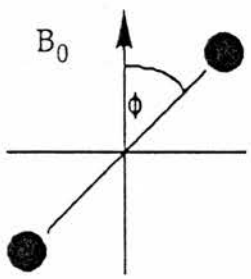


fig.1.9

Because ^{1}H is an abundant spin (100%) and ^{13}C is a rare spin (1%) $^{1}H/^{13}C$ interactions are important but $^{13}C/^{13}C$ interactions can be neglected. Dipolar interaction give rise to the so called "Pake pattern" (fig.1.10) where each spin affects the other and results in a spectrum of an axially symmetrical molecule. For a many spin system i.e. a real compound the linewidths are many kHz (fig.1.10).

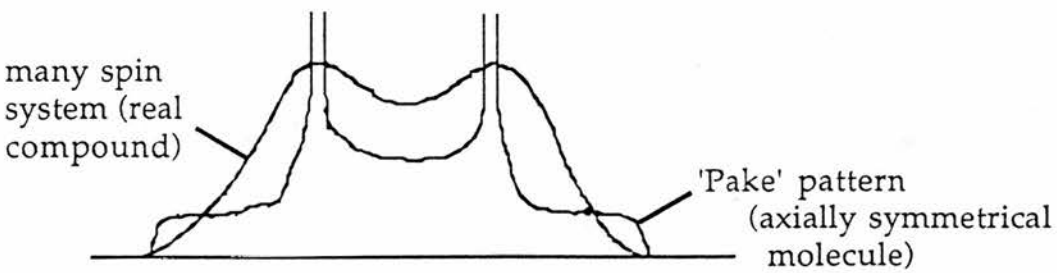


fig.1.10

$^{1}H/^{13}C$ dipolar interactions are largely removed by high power decoupling at the ^{1}H frequency. Band width of the decoupler must exceed line width of ^{1}H spectrum, therefore, need high power.

The magic angle can be used to reduce these interactions. The magic angle (ϕ_m) is the angle between opposing vertices of a cube (fig.1.11) and is the angle at which $3\cos^2\phi - 1 = 0$.

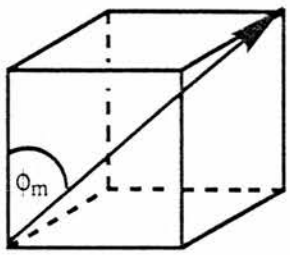


fig.1.11

The sample is spun about the magic angle the average AB vector (fig.1.12) lies at ϕ_m to H_0 and therefore terms involving $(3\cos^2\phi - 1)$ vanish.

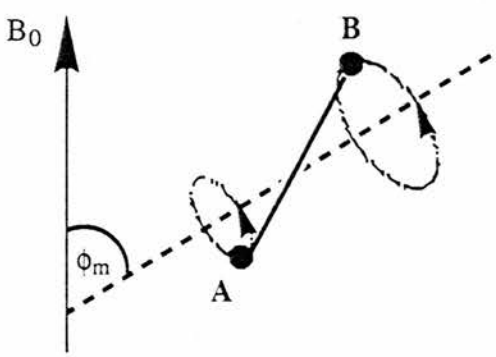


fig.1.12

Narrow lines are generated but, they have side bands on them occurring at integral multiples of the spinning speed which reflect the CSA pattern (fig.1.8). This is the reason why the compounds are run at different spinning speeds since the spinning side bands move out the faster you spin the sample and so are easily identifiable. The spinning speed has to be in the several kHz range, because to average out the CSA it must be rapid compared to the linewidths.

Therefore, the complete removal of spinning side bands requires the spinning speed to be greater than the CSA (in Hz).

1.33 Cross Polarisation

The conventional solution-state pulse sequence for ^{13}C N.M.R. can be used for solids but, the ^{13}C relaxation time (T_1) for ^{13}C is in general very long and therefore, a long inter pulse interval is needed. In cross polarisation from ^{1}H to ^{13}C it is the relaxation time of the ^{1}H that is important. The pulse sequence for cross polarisation (fig.1.13) has a decoupling and spin locking on the ^{1}H channel and a contact time and free induction decay on the ^{13}C channel.

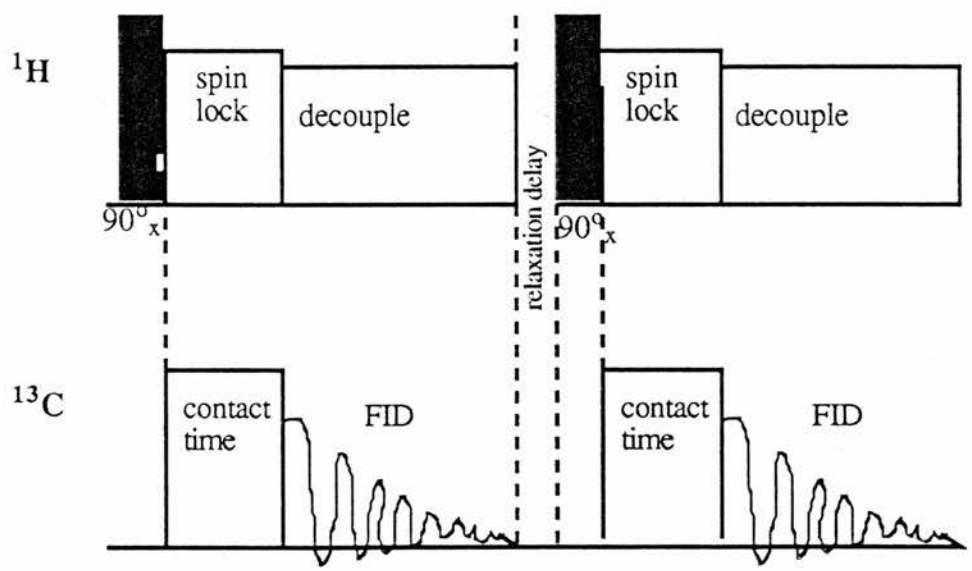


Fig.1.13

This can be shown in the rotating frame of reference (fig.1.14).

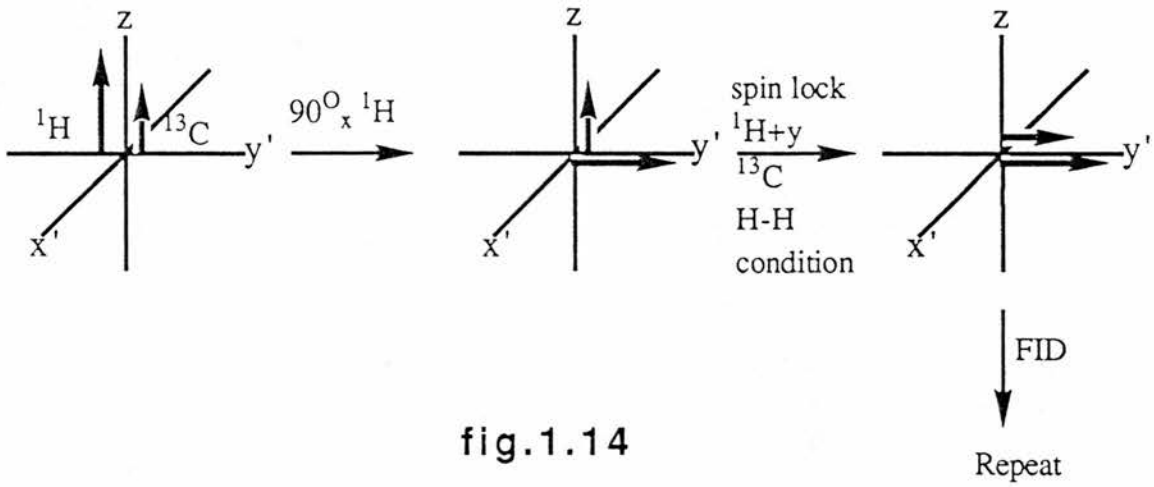


fig.1.14

The cross polarisation only works if the Hartmann-Hahn condition (eq.1) is met.

$$\omega_H = \gamma_H H_H = \gamma_C H_C = \omega_C \qquad \textbf{eq.1}$$

H_H is the field for irradiating ^{1}H

H_C is the field for irradiating ^{13}C

γ are the gyromagnetic ratios of the given nucleus which relates the moment μ with the angular moment I.

Each nucleus has a different gyromagnetic ratio and so in any given magnetic field the precession frequency is different. In order to transfer magnetisation from the ^{1}H to the ^{13}C the two nuclei must be precessing at the same angular velocity. To satisfy the Hartmann-Hahn condition the applied radiofrequency fields H_H and H_C must be different. The cross polarisation enhances the ^{13}C magnetisation because the signal intensity depends on γ_H and γ_H/γ_C = 3.

2 EXPERIMENTAL

2.1 Synthesis of a Diarylide Yellow Pigment

A solution of NaOH (13 g, 0.325 moles) in water (455 ml) is added to a 5 l beaker equipped with a pH meter and a thermometer. The coupling component (0.3 moles) is then added to the NaOH solution and stirred until it dissolves, usually after 15-20 minutes. Glacial acetic acid (23.4 g, 0.39 moles) is added to water (83 ml) and this is put into a dropping funnel. The coupling component solution is at pH 12.5 at 22°C. The coupling component is carefully re-precipitated by addition of the glacial acetic acid solution until pH 6 is reached. The solution requires rapid stirring during re-precipitation and is furthered stirred for 15 minutes at pH 6. The DCB tetrazo solution (361.1 g) is put in a 1 l beaker and immersed in ice. The excess nitrite is taken out of the tetrazo solution by the addition of a little sulphamic acid, this is checked with starch/KI paper. The coupling is best done using a pump and slowly adding the tetrazo to the coupling component suspension which is kept at 16°C. This is the way that the coupling is done at the Ciba-Geigy laboratories in Paisley while at St.Andrews the DCB tetrazo was taken from the beaker in 10-20 ml aliquots and added to a dropping funnel. This allowed the slow addition of the DCB tetrazo and also meant it was kept cold. The DCB tetrazo solution was prepared in Paisley and kept at St.Andrews at 4°C in a fridge. The pH is allowed to fall from 6 to 4.8 where it is held by the addition of successive amounts of NaOH (23.5 g, 0.59 moles) in water (175 ml). During coupling excess of DCB tetrazo is checked for with some alkaline H-acid solution. Coupling should take about an hour and at the end

excess coupling component is checked for with DCB tetrazo. If it is detected more DCB is added until no more coupling component is detected. The suspension is stirred for 90 minutes and the temperature is allowed to increase to room temperature. The pH is increased to 6 with some dilute NaOH solution and the reaction mixture is then heated to 95°C for 30 minutes after which time ice is added to cool the suspension to 70°C. The suspension is then washed free of salt with water and dried overnight in the oven at 60°C.

2.2 Synthesis of Pure Asymmetric Pigments[7]

This reaction is quantitative and requires the use of the DCB tetrazo solution supplied by Ciba-Geigy. It is known to contain about 10% of actual DCB tetrazo, therefore a gravimetric analysis was carried out as follows, before the synthesis of an asymmetric pigment was undertaken.

2.21 Gravimetric analysis of DCB tetrazo

The method used was the standard synthesis of a diarylide yellow pigment except using 20% excess of the coupling component. The coupling component used was AAMX, therefore the quantities used were:

mass of DCB tetrazo solution = 15 g (ca. 0.0054 moles)
mass of AAMX = 2.6 g (0.013 moles)

The pigment was washed with water as usual and then dried to a constant weight in the oven.

results:

mass of P.Y.13 = 3.98 g

no. of moles of P.Y.13 = 3.98/685

$= 5.81 \times 10^{-3}$ moles

therefore, since the molecular weight of DCB tetrazo is 277 g. The actual mass of DCB tetrazo in 15 g is;

$$5.81 \times 10^{-3} \times 277 = 1.61 \text{ g}$$

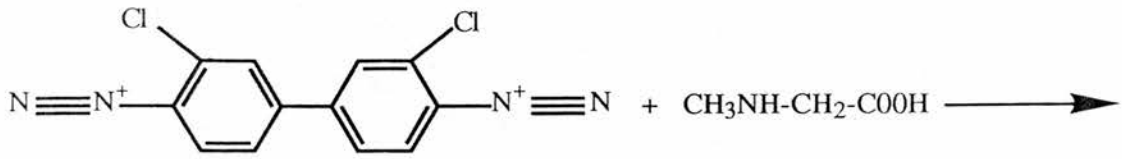
and so

$$1.61/15 \times 100\% = 10.7\% \text{ w:w}$$

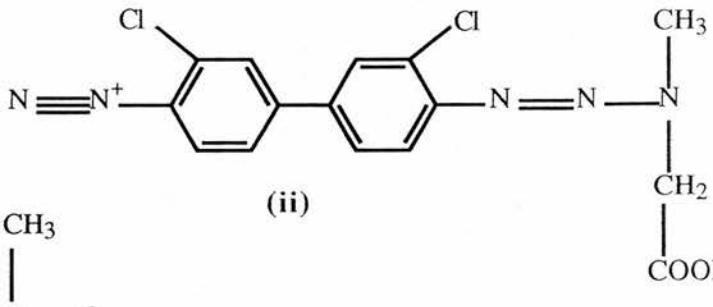
the solution is 10.7% w:w DCB tetrazo.

2.22 Synthesis of Asymmetric AAA/AAOT

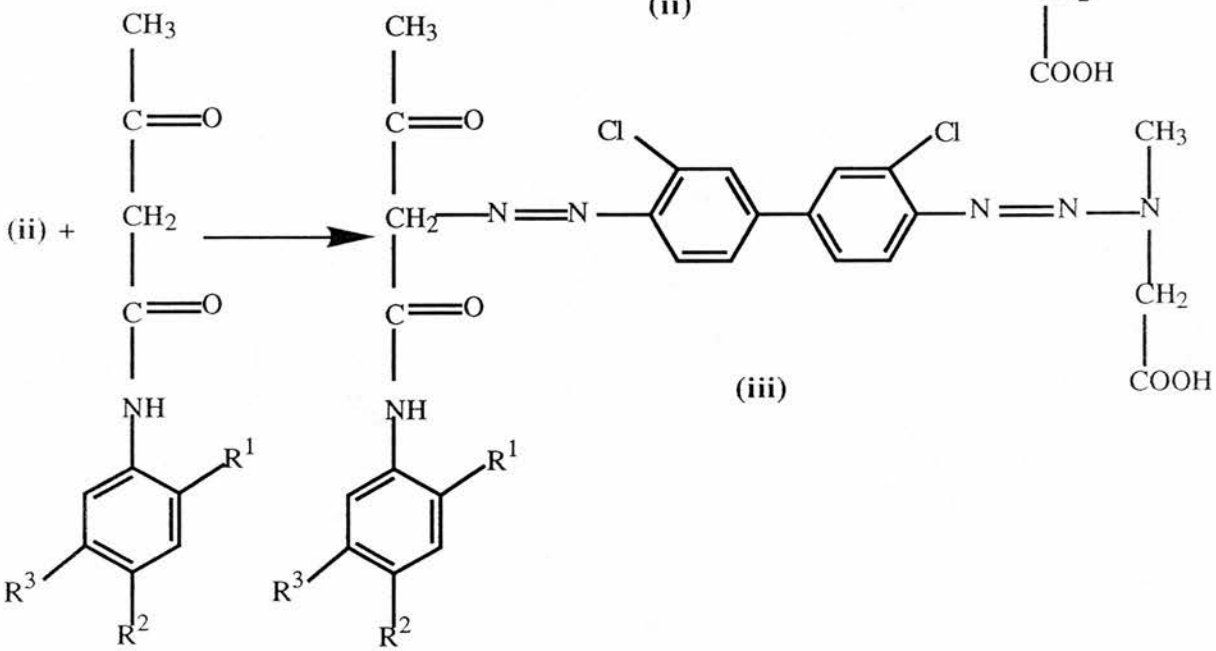
The general reaction scheme is shown in figure 3.1. The starting material (i) is the DCB tetrazo solution that is used in the synthesis of asymmetric diarylide pigments.



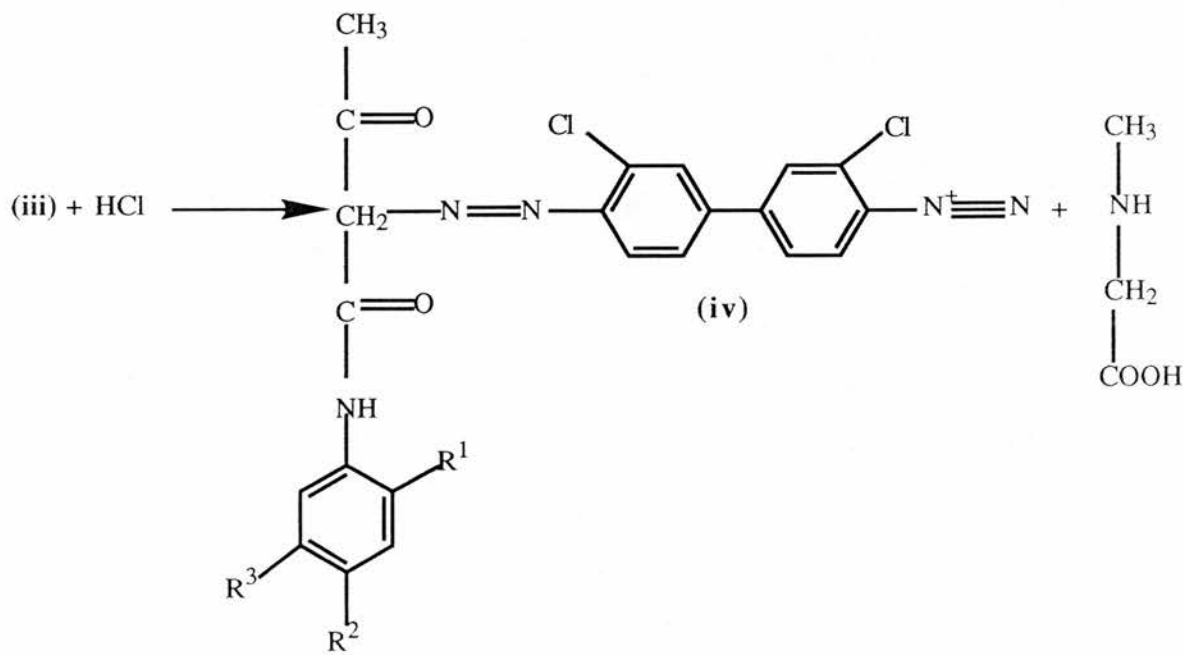
(i)



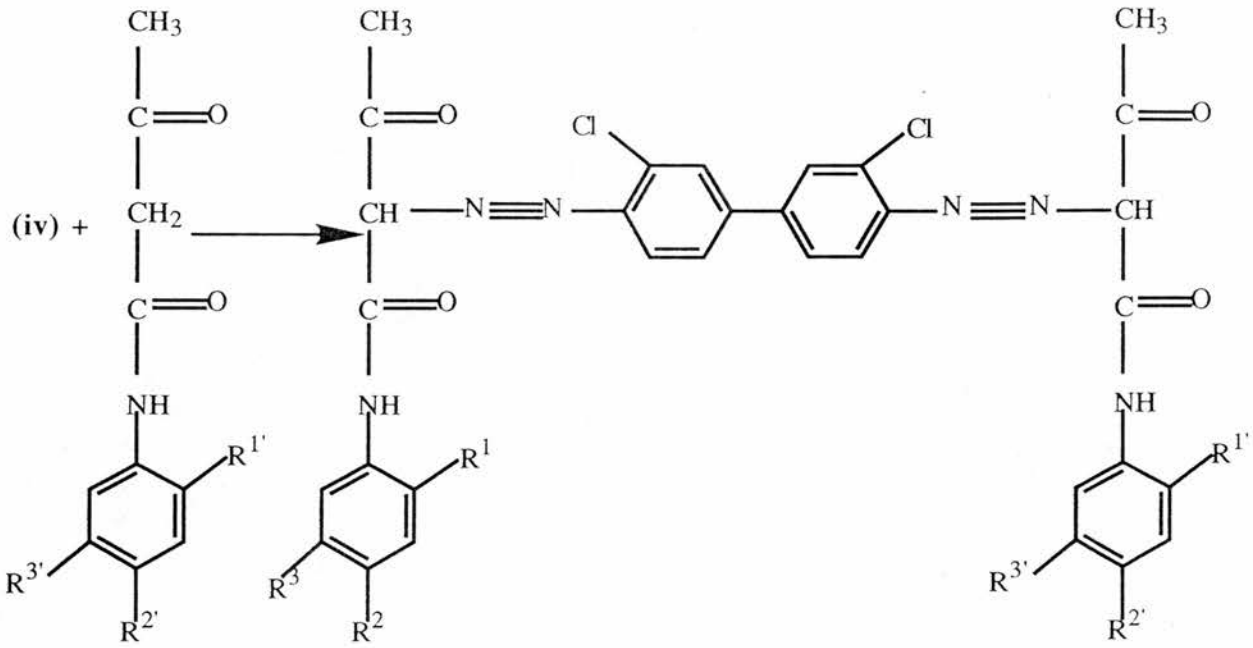
(ii)



(iii)



(iv)



(1) $R^1 = R^2 = R^3 = H$; $R^{1'} = CH_3$, $R^{2'} = CH_3$ and $R^{3'} = H$

(2) $R^1 = R^2 = R^3 = H$; $R^{1'} = CH_3$ and $R^{2'} = R^{3'} = H$

(3) $R^1 = R^2 = R^3 = H$; $R^{1'} = OCH_3$, $R^{2'} = Cl$ and $R^{3'} = OCH_3$

(4) $R^1 = CH_3$, $R^2 = CH_3$ and $R^3 = H$; $R^{1'} = OCH_3$, $R^{2'} = Cl$ and $R^{3'} = OCH_3$

fig.3.1

Some sulphamic acid is added to the DCB tetrazo (64.82 g, 0.025 moles) to destroy the excess nitrite. A solution of sarcosine (2.23 g, 0.025 moles) and sodium hydrogen carbonate (6 g, 0.07 moles) in water (75 ml) is added to the DCB tetrazo. A solution of sodium carbonate decahydrate (12.5 g, 0.045 moles) in water (75 ml) is now added over 10 minutes with stirring, with an additional 20 minutes of stirring to ensure that all the sarcosine reacts.

AAA (4.4 g, 0.025 moles), is then added in a solution of sodium carbonate decahydrate (5 g, 0.018 moles) in a mixture of 20 ml of ethanol, 5 ml of 10% NaOH and 50 ml of water. The solution is stirred for 90 minutes to complete the coupling.

ethanol, 5 ml of 10% NaOH and 50 ml of water. The solution is stirred for 90 minutes to complete the coupling.

Triazine (iii) is now cleaved by the addition over 10 minutes of concentrated HCl (25 ml) and to the resulting mixture an aqueous suspension of AAOT (4.8 g, 0.025 moles) is added with stirring. The reaction mixture was adjusted to pH 4 with sodium acetate trihydrate (ca. 30 g) and stirred for a further two hours and heated to 70-80°C for 10 minutes. The suspension is then filtered hot and washed with water until it is salt free. The pigment is then put in the oven overnight at 60 °C to dry.

2.23 Synthesis of Asymmetric AAA/AADMCA

The same conditions as (1) except, 6.8 g (0.025 moles) of AADMCA are used instead of the AAOT.

2.24 Synthesis of Asymmetric AAMX/AAOT

The same conditions as (1) except that 4.7 g (0.025 moles) of AAOT is coupled first then 5.13 g (0.025 moles) of AAMX is coupled second.

2.25 Synthesis of Asymmetric AAMX/AADMCA

The same conditions as (1) except that 5.13 g (0.025 moles) of AAMX is coupled first then 6.8 g (0.025 moles) of AADMCA is coupled second.

2.26 Synthesis of Asymmetric AAOT/AADMCA

The same conditions as (1) except that 4.7 g (0.025 moles) of AAOT is coupled first then 6.8 g (0.025 moles) of AADMCA is coupled second.

2.3 Synthesis of Mixed Coupled Pigments

The reaction scheme is the same as that for the pure diarylide pigments. The only difference is that at the start of the reaction instead of using a pure coupling component a ratio of two coupling components is used (i.e. 10:90, 50:50 or 90:10).

2.31 Mixed Coupled AAA and AADMCA

(i) 90% AAA and 10% AADMCA

The same conditions as for a diarylide yellow pigment (2.1) except that 47.9 g (0.27 moles) of AAA and 8.2 g (0.03 moles) of AADMCA are coupled to the DCB tetrazo.

(ii) 50% AAA and 50% AADMCA

The same conditions as for a diarylide yellow pigment (2.1) except that 26.6 g (0.15 moles) of AAA and 41.0 g (0.15 moles) of AADMCA are coupled to the DCB tetrazo.

(iii) 10% AAA and 90% AADMCA

The same conditions as for a diarylide yellow pigment (2.1) except that 5.32 g (0.03 moles) of AAA and 73.8 g (0.27 moles) of AADMCA are coupled to the DCB tetrazo.

2.32 Mixed Coupled AAOT/AADMCA

(i) 90% AAOT and 10% AADMCA

The same conditions as for a diarylide yellow pigment (2.1) except that 51.6 g (0.27 moles) of AAOT and 8.2 g (0.03 moles) of AADMCA are coupled to the DCB tetrazo.

(ii) 50% AAOT and 50% AADMCA

The same conditions as for a diarylide yellow pigment (2.1) except that 28.7 g (0.15 moles) of AAA and 41.0 g (0.15 moles) of AADMCA are coupled to the DCB tetrazo.

(iii) 10% AAOT and 90% AADMCA

The same conditions as for a diarylide yellow pigment (2.1) except that 5.73 g (0.03 moles) of AAA and 73.8 g (0.27 moles) of AADMCA are coupled to the DCB tetrazo.

2.33 Recrystallisation of the mixed coupled pigments.

(i) Mixed Coupled AAA/AADMCA

The solvent used for recrystallisation of diarylide yellows is generally 1,2,4-trichlorobenzene (TCB). About 0.8 g of 10:90, 50:50 and 90:10 of the mixed coupled pigment were each added to c.a. 60 ml of TCB in a 100 ml r.b. flask. The flask was then heated to 214°C to reflux the TCB. The pigment solution was then filtered hot and left to cool. The solution was left for several hours to allow the pigment to come out of solution. The amount of pigment recovered was about 0.6 g for 50:50 and 90:10 and 0.4 g for 10:90.

(ii) Mixed Coupled AAOT/AADMCA

This set of pigments were less soluble and so 80 ml of TCB were used for the recrystallisation. The 50:50 and the 90:10 gave about 0.5 g and the 10:90 about 0.6 g.

2.4 INVERSE COUPLED PIGMENTS

The basic synthetic procedure is the same as that for the standard yellow pigments except it has been scaled down and the coupling component is added to the DCB tetrazo.

2.41 Inverse Coupled AAA + AAMX

Two solutions of sodium hydroxide (1.14 g, 0.028 moles) were made

up with 21 ml of water. Into one was added AAA (2.31 g, 0.013 moles) and to the other AAMX (2.67 g, 0.013 moles). The coupling components dissolved with stirring after 5-10 minutes. A solution was made up of glacial acetic acid (1.94 g, 0.032 moles) in 7 ml of water, which was then added to the coupling component solutions to re-precipitate them. The pH of the solutions was monitored closely and when they reached pH 6 the addition of acid was stopped. The mixtures were then stirred for a further 10 minutes. The DCB tetrazo (30 g, c.a. 0.013 moles) was added to a 500 ml beaker and cooled with ice to 16°C. The AAA mixture was then added over 20 minutes with rapid stirring and a constant temperature of 16°C. The procedure was then repeated with the AAMX mixture. The pigment mixture was stirred for 90 minutes before raising the pH to 6 by addition of a solution of sodium hydroxide (4.2 g, 0.1 moles) in 11 ml of water. The mixture was heated on a hot plate to 90-95°C for 30 minutes before cooling to 70°C with ice and filtering. The pigment was finally washed salt free with water and then dried overnight in an oven at 60 °C.

Recrystallisation

0.7 g of the pigment were recrystallised from about 70 ml of 1, 2, 4-Trichlorobenzene (TCB). 0.63 g of pigment were recovered.

2.42 Inverse Coupled AAA + AAOT

The same conditions as (1a) except that 2.31 g (0.013 moles) of AAA is coupled along with 2.47 g (0.013 moles) of AAOT.

Recrystallisation

1.27 g of the pigment were recrystallised from about 75 ml of TCB. 1.13 g of pigment were recovered.

2.43 Inverse Coupled AAA + AADMCA

The same conditions as (1a) except that 2.31 g (0.013 moles) of AAA is coupled along with 3.54 g (0.013 moles) of AADMCA.

Recrystallisation

0.84 g of the pigment were recrystallised from about 50 ml of TCB. 0.66 g of pigment were recovered.

2.44 Inverse Coupled AAMX + AAOT

The same conditions as (1a) except that 2.67 g (0.013 moles) of AAMX is coupled along with 2.47 g (0.013 moles) of AAOT.

Recrystallisation

1.00 g of the pigment were recrystallised from about 70 ml of TCB. 0.88 g of pigment were recovered.

2.45 Inverse Coupled AAMX + AADMCA

The same conditions as (1a) except that 2.67 g (0.013 moles) of AAMX is coupled along with 3.54 g (0.013 moles) of AADMCA.

Recrystallisation

1.30 g of the pigment were recrystallised from about 130 ml of TCB. 1.16 g of pigment were recovered.

2.46 Inverse Coupled AAOT + AADMCA

The same conditions as (1a) except that 2.47 g (0.013 moles) of AAOT is coupled along with 3.54 g (0.013 moles) of AADMCA.

Recrystallisation

1.20 g of the pigment were recrystallised from about 70 ml of TCB. 1.04 g of pigment were recovered.

2.5 N.M.R. EXPERIMENTAL

The CP MAS solid-state ^{13}C N.M.R. spectra are recorded on an Brucker MSL 500 spectrometer operating at 125.758 MHz. The sample rotors (4 mm o.d.) are made of zirconia and are packed with 200-300 mg of sample. The sample is spun at the magic angle at anywhere between 6 and 13 Hz, but is most commonly spun at 7 and 8 Hz. Different spinning speeds are used to identify spinning side bands and to show resonances that are obscured by them. Therefore, for different samples 7 and 8 KHz may not achieve this and so other spinning speeds are used. The cross polarisation technique uses a 90^{o} ^{1}H pulse width of 3.5 μs with a contact time of 1 ms. The chemical shifts are referenced to external adamantane with the

chemical shift of the CH_2 resonance set at +38.56 ppm with respect to T.M.S. The recycle times used for the coupling components vary between 5 and 80 s for AADMCA and AAOCA respectively. The monoazos have recycle times of between 10 and 30 s and for the rest of the compounds the recycle delay is 10 s. These times are quite large and so the time to analyse a sample is around 30 minutes for between 200 and 300 acquisitions. This number of acquisitions is needed for the full pigment molecules, but for the coupling components less than one hundred acquisitions gives good signal to noise. The monoazos require 100-200 acquisitions.

3 DIARYLIDE PIGMENTS

A diarylide yellow pigment has a basic structure that contains a minimum of 32 carbons and so can be expected to give a complex solid-state ^{13}C N.M.R. spectrum. There has not been any solid-state ^{13}C N.M.R. work on diarylide pigments reported in the literature. For that reason, as well as out of interest, the coupling components as well as the monoazo or "half disazos" were analysed first. This meant that when we were faced with the quite complex spectra of the pigments there was enough information from the precursors to identify most of the resonances and to assign them.

The technique used to analyse the pigments and their precursors is called CP/MAS ^{13}C N.M.R.. MAS unfortunately produces spinning side bands (ssb), these are dependent on the spinning frequency and so by spinning at two frequencies and comparing the two resulting spectra the ssb peaks can be eliminated. This has been gone into in more detail in Chapter 1. A third dipolar dephased spectrum is also run. This is more commonly called a Non Quaternary Suppression (NQS) spectrum. This leaves only quaternary carbons plus methyl carbons at reduced intensity on the spectrum. The methyl resonances are usually at a lower frequency than any quaternary carbons and so this is a very useful editing technique.

3.1 Coupling components

The ^{13}C chemical shifts of the seven coupling components analysed are given in table 3.1 with the structure and carbon numbering scheme shown in figure 3.1.

scheme shown in figure 3.1.

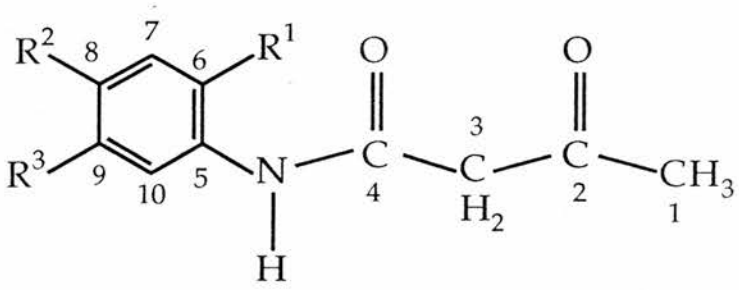


fig.3.1

	R-1	R-2	R-3
AAA	H	H	H
AAMX	CH_3	CH_3	H
AAOT	CH_3	H	H
AAOA	OCH_3	H	H
AADMCA	OCH_3	Cl	OCH_3
AAPT	H	H	CH_3
AAOA	Cl	H	H

Table 3.1: solid-state ^{13}C N.M.R. chemical shifts of the coupling components

C.No.	AAA*	AAMX	AAOT	AAOA	AADMCA*	AAPT	AAOCA
1	30.9 + 31.6	30.6	31.0	30.2	31.5	31.2	31.2
2	203.9 + 206.9	207.0	208.9	210.5	206.7	205.3	209.4
3	53.1	45.8	46.1	47.7	46.6	52.2	46.7
4	167.2	165.2	164.7	165.0	164.3	167.8	165.1
5	138.6	135.8	138.2	147.2	148.6	138.2	137.0
6		126.4	126.4	129.3	129.0		121.4 + 124.4
7							
8		132.8			110.6 + 113.8	131.2	
9					142.7		
10							
R-1		17.8	18.1	56.0	56.8		
R-2		21.7					
R-3					56.8	21.7	

* spectra 1 and 2 (AAA and AADMCA respectively) are given as examples of the coupling components.

The chemical shifts of all the aliphatic carbons in the coupling components can be unequivocally assigned. The aromatic carbons, however, are very difficult to assign unless they are quaternary carbons.

The methyl resonances (C-1) are all in the range of 30.0-31.6 ppm. Acetoacetanilide (AAA) has the only methyl resonance that is split (30.9 and 31.6) of all the coupling components. The carbonyl resonance (C-2) is also split in AAA this time by 3 ppm. The rest of the carbon resonances show no sign of splitting and so suggests that it is the two structures shown in figure 3.2 that are responsible for the splittings. However, the hydrogen bond shown might be expected to give a somewhat larger chemical shift difference for the two C-2 carbons shown.[8] Alternatively it could be the crystal packing producing two different environments for the end of the molecule or it could be due to weak intermolecular hydrogen bonding.

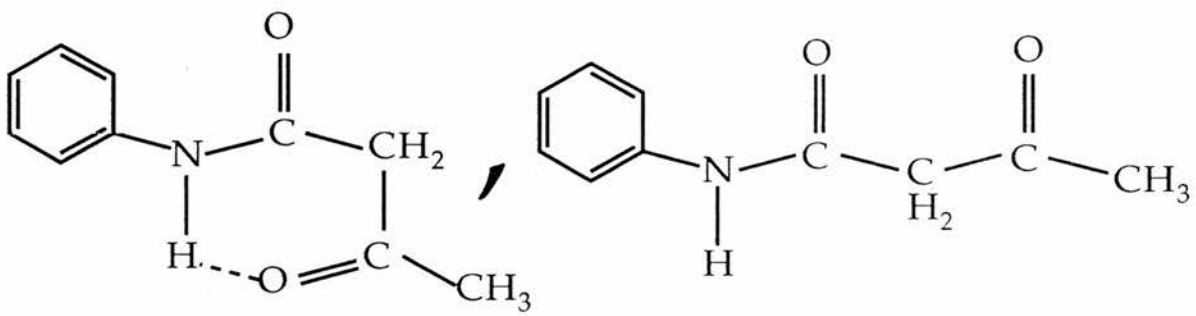


fig.3.2

A sample of AAA recrystallised from NaOH with acetic acid has also been analysed since it is in this form it is used when a pigment is synthesised. The resulting spectrum showed that the C-1 and C-2 resonances are still split. The fact that there are different forms of the AAA could affect the structure of P.Y.12.

The methylene (C-3) resonances give a wide range of chemical shifts (45.8-53.1). These differences could be caused by slight changes in the structure. One explanation is that there is a change in the crystal packing involving overlap of a ring in one molecule with the tail of another molecule. The similarity in AAA and AAPT indicates that they have similar structures probably because they are the only two coupling components that do not have an *ortho* substituent.

The resonances for C-5 are affected by the substituent R-1, the largest effect being the methoxyl groups of AAOA and AADMCA which push the C-5 resonance to higher frequencies. In AAMX (*o*- and *p*-methyl) the C-5 resonance moves to lower frequency but in AAOT (*o*-methyl) there is no real effect on the C-5 resonance.

The particularly interesting feature in terms of N.M.R. is that when a coupling component has a chlorine attached to it (AAOCA and AADMCA) the resonance of the carbon bonded to chlorine is split by about 377 Hz (Prof. R.K. Harris personal communication). This is called residual dipolar coupling and arises from an interaction between the ^{35}Cl and the ^{13}C to which it is bound. The resonances are, therefore, doublets in which each component has half the

intensity of the other resonances. This allows easy identification of these resonances in the coupling components. The residual dipolar splitting is best seen in the NQS spectra where any overlap of resonances from the CH groups has been removed because the aromatic carbons carrying chlorine carry no directly bound hydrogen.

3.2 Monoazo compounds

The ^{13}C chemical shifts of these compounds are given in table 3.2 and the carbon numbering scheme in figure 3.3.

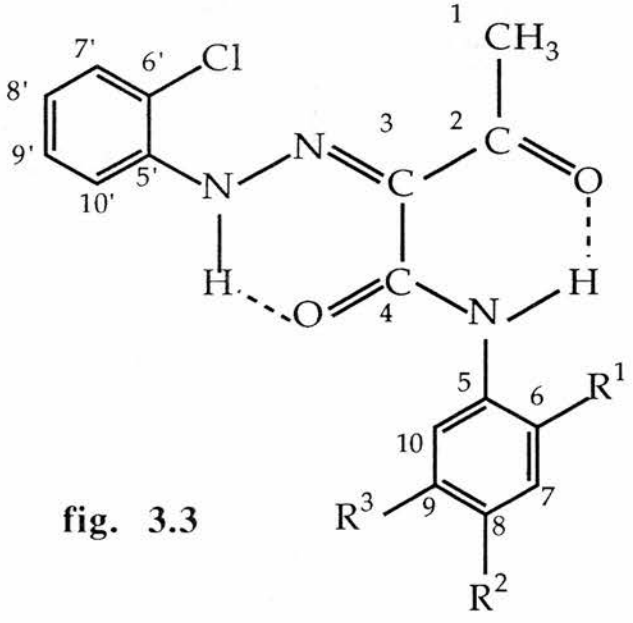


fig. 3.3

Table 3.2: solid-state ^{13}C N.M.R. chemical shifts of the monoazos.

C.No.	MON0 12*	MONO13	MONO14	MONO17	MONO83*
1	25.9	26.2	26.8	27.5	27.4
2	199.4	199.0	199.3	200.4	199.7
3	127.1	126.9	126.4	128.0	126.7
4	162.8	161.4	161.6	162.3	161.3
5	137.3	135.3	138.1 + 139.5	150.0	149.4
5'	137.3	140.0	138.1	138.4	138.3
6		126.9		128.0	126.7
6'	120.4 + 123.7	117.6 + 120.9	118.7 + 122.3	119.5 + 123.1	119.9 + 123.2
7				110.2	113.2
8		131.0			113.9 + 117.4
9					141.6
10					105.0
R-1		21.7	18.1	55.4	56.0/56.7
R-2		21.7	21.0		
R-3					56.0/56.7

* spectra 3 and 4 (mono12 and 83 respectively) are given as examples of the monoazo compounds mono12 and 83

The chemical shifts are similar to those in the coupling components. The biggest differences are the lower and more consistent values for the C-1 and C-2 chemical shifts. This suggests a more rigid structure than the coupling components and that C-2 is in a very similar environment where it is no longer affected by the substituents on the anilide ring. No splitting of any of the C-1 or C-2 resonances is observed. A new resonance that is identified is that for C-3 (126.7-128.0) which is a quaternary carbon in the monoazos as opposed to a methylene carbon in the coupling components.

The residual dipolar coupling to chlorine of C-8 in mono 83 is observed to be 440 Hz compared to 402 Hz in AADMCA. There is now

mono 13, 17 and 83. The splitting is consistent only varying from 415 Hz in mono 13 and 83 to 453 Hz in mono14 and 17. The splitting in C-Cl resonances in mono 12 is difficult to see because the spectrum is a little noisy and the peaks are quite broad in comparison to the rest of the monoazo compounds. The resonance given at 120.4 ppm for C-Cl is broad and appears to be split. There is a shoulder on the C-3 resonance (127.1 ppm) at approximately 123 ppm which is probably the other C-Cl resonance, but it may only be some noise.

The aromatic methyls in mono 13 are equivalent in chemical shift whereas in AAMX they are separated by 3.9 ppm. The chemical shift of the methyls in mono 13 is the same as the *p*-methyl in AAMX (i.e. 21.7 ppm). The opposite effect is seen in mono 83 where the methoxyl carbons are split by 0.7 ppm whereas they were equivalent in AADMCA. In mono 14 the aromatic methyl group is split by 2.9 ppm with each resonance of the same intensity. This could be caused by the crystal packing arrangement of the compound but it is hard to imagine why it is only the aromatic methyl that is split. It almost appears that the samples of mono 13 and 14 have been mixed up because there is only one resonance on the mono 13 spectra for the two methyls and there are two resonances on the mono 14 spectra for the one aromatic methyl. The intensities of the resonances however indicate otherwise and the characteristic resonance for the C-5 (C-N) of mono 13 at 135.3 ppm leaves no doubt to the validity of the samples. Therefore, assuming the sample of mono 14 is pure it is very difficult to explain the splitting of the aromatic methyl resonance.

In Mono 14 the C-5, 5' resonances are split by 1.5 ppm which is not seen in any of the other monoazos but, probably indicates a slight difference in the two C-N resonances or even a small residual dipolar coupling of one of the carbons to the nitrogen although this is less likely because there is no sign of it in the other monoazos and it should not be visible at our field strength.

3.3 COLOUR INDEX (C.I.) DIARYLIDE PIGMENTS

The carbon numbering scheme for the diarylide yellow pigments is given in fig.3.4. The two halves of the molecule are treated as identical when assigning carbons, therefore, each ^{13}C chemical shift accounts for at least two carbons. For that reason in fig.3.4 there is only one half of the molecule numbered.

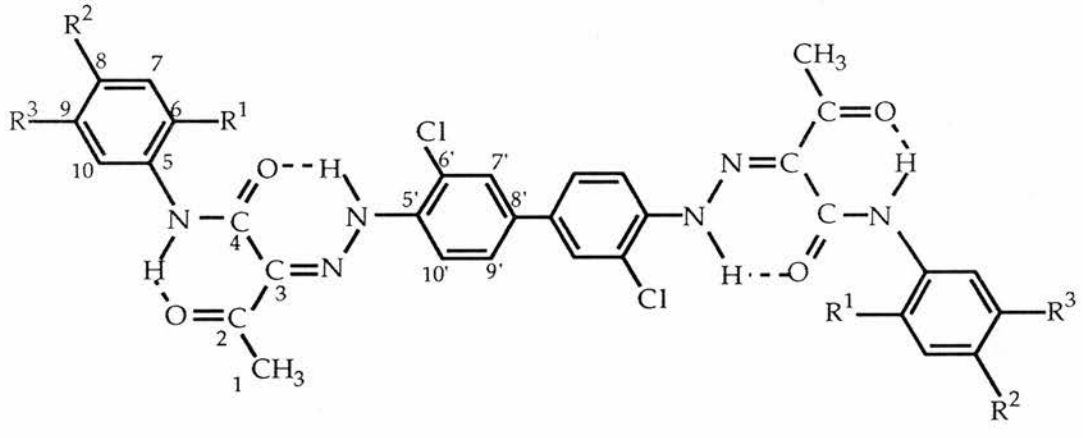


fig. 3.4

The pigments were all supplied by Ciba-Geigy all having been recrystallised from TCB apart from pigment yellow (P.Y.) 83 which was made at the Ciba-Geigy factory in Paisley and then recrystallised at St.Andrews.

The solid-state ^{13}C N.M.R. chemical shifts for all the recrystallised diarylide yellow pigments supplied by Ciba-Geigy are given in Tables 3.3 and 3.4. Where there is no assignment made this is because the carbon could not be assigned to any particular peak. Generally the only carbons that are not assigned are the aromatic carbons with a hydrogen substituent, because these peaks tend to overlap and so individual peaks are obscured.

Table 3.3: Solid-state ^{13}C N.M.R. chemical shifts of the diarylide yellow pigments.

C.No.	P.Y. 12*	P.Y. 13	P.Y. 14	P.Y. 17	P.Y. 83 (C)	P.Y. 83*
1	26.7	26.8	27.6	25.5 + 27.3	26.7	27.0
2	199.0 + 199.9	199.4	199.4	197.8 + 199.5 (s)	200.4	200.6
3	127.0	126.7	126.5	126.2	127.1	127.4
4	162.2	161.4	161.8	162.1	160.9	161.1
5	138.2	135.8	137.8	148.5	150.0	149.8 + 150.3
5'	138.2	138.7	137.8	138.0	137.2	137.4
6		126.7	126.5	126.2	127.1	127.4
6'	120.0 + 123.4	118.9 + 123.0	120.5 + 123.0	119.3 + 123.1		119.2 + 124.0
7				109.1	106.5	106.8
7'						
8		131.7				113.9 + 117.0
8'	134.3 + 135.0 (s)	131.7	131.0	133.5 + 134.6 (s)	131.5	131.6
9					142.3	142.4
10						
R-1		20.2	19.4	54.7	56.7	56.9
R-2		22.8				
R-3					56.7	56.9

(C) : crude pigment.

* spectra 5 and 6 (P.Y.12 and 83 respectively) are given as examples of the C.I. pigments.

Table 3.4: solid-state ^{13}C N.M.R. chemical shifts of the diarylide yellow pigments (cont'd).

C.No.	P.Y. 55	P.Y. 63	*p*- Br	P.O 16
1	27.6	27.9	27.3	27.1
2	199.4	200.1	201.1	197.9
3	127.9	126.5	127.5	127.2
4	161.0	162.2	162.5	162.4
5	134.9	136.4	137.2	138.2
5'	137.5	137.5	137.2	148.4
6		122.6 + 125.3		
6'	120.5 + 124.0	120.8+ 123.2		129.8
7				
7'				
8	131.0		120.8	
8'	134.9	132.4	133.6 + 134.2	132.4
9				
10				
R-1				*R-4 =
R-2	21.9			56.8
R-3				

*R-4 (OCH_3) is attached to C-6' instead of Cl.

The diarylide pigments in general give very similar ^{13}C chemical shifts to the monoazo compounds. The main differences in the spectra are the C-8' peaks and the splitting of C-1 and C-2 in P.Y.17 and of C-2 in P.Y.12.

3.31 C.I. Pigment Yellow 12
(spectrum 5)

The biggest change in the ^{13}C chemical shifts of the pigment compared to the monoazo is the 0.8 ppm shift to higher frequency of the acetyl methyl (C-1). This is a very small change in terms of N.M.R. and indicates very similar environments in both the monoazo

and diarylide pigments for the carbons. The only indication of a structural change from the monoazo to the pigment is that the acetyl carbonyl (C-2) is split by 0.9 ppm. This is much smaller than the splitting of 3.0 ppm seen in AAA and is most likely to be some sort of asymmetric packing arrangement rather than any isomerism in the pigment structure. Although the acetyl methyl peak is not split it is 2-3 ppm broad compared to the 1-2 ppm of most peaks.

The C-8' peak at 134.3 ppm has the peak at 135.0 ppm as a shoulder and these peaks are of less than half the intensity of most quaternary peaks. The peak at 130.4 ppm is yet smaller and is tentatively assigned to be a C-8' peak because all the other quaternary peaks are accounted for, but the peak could, however, be an impurity because it is of such low intensity

The C-Cl residual dipolar splitting (428 Hz) is much easier to see in the pigment as opposed to the monoazo where it is badly resolved.

3.32 C.I. Pigment Yellow 13

The ^{13}C chemical shifts of P.Y.13 are again very similar to that of the mono compound. The residual dipolar splitting of C-Cl has increased from 402 Hz to 515 Hz. The aromatic methyls are distinguishable, but are at different ^{13}C chemical shifts to AAMX and mono 13. The C-8 peak at 131.7 ppm also appears to be the C-8' carbon.

3.33 C.I. Pigment Yellow 14

The only apparent differences to the monoazo spectra are the slight changes in the ^{13}C chemical shift of the acetyl methyl (C-1) and the aromatic methyl and they are only 0.8 and 1.3 ppm moves to higher frequency.

3.34 C.I. Pigment Yellow 17

The spectra for this pigment reveal a splitting of the acetyl methyl and carbonyl peaks by 1.8 and 1.7 ppm respectively. The C-3, 5 and 6 carbons all show changes of between 1.5-1.8 ppm. These are small changes but are bigger than in any of the other three pigments looked at so far. The C-8' peak is split by 1.1 ppm with the peak at 134.6 ppm a shoulder on the peak at 133.5 ppm.

3.35 C.I. Pigment Yellow 83
(spectrum 6)

The two sets of data for the crude and the recrystallised pigment are a good demonstration that the pigment structure is unaltered by the recrystallisation despite the colour change. The recrystallised spectrum is somewhat less noisy and the peaks are a little sharper.

The differences between mono 83 and P.Y.83 are 0.9 ppm at the most (C-2, 5'). The most interesting point is the small splitting of 0.5 ppm of the C-N (C-5) peak which could well be due to the quadrupolar nature of nitrogen.

The peaks for C-Cl are not obvious because the noise level in the NQS spectrum is high. The two pairs of C-Cl resonances are deduced from the spectra of AADMCA and mono 83 as well as the small peaks on the NQS spectrum of the pigment.

3.36 C.I. Pigment Yellow 55

In P.Y.55 the peak assigned to C-5' at 137.5 ppm is very low in intensity. The other C-N peak (C-5) is at 134.9 ppm compared to the 138.2 ppm seen in AAPT. The rest of the C-5 peaks are very consistent from coupling component to the final pigment. The biggest change in the chemical shift from coupling component to the pigment is 1.4 ppm between AADMCA and P.Y.83. The C-5 peak in AAOA and mono 17 changes by 2.8 ppm, but these are the exceptions. The environment of the C-5 peak has altered and it is only P.Y.55 and the AAMX derivatives that have a C-5 peak below 136 ppm. It is a small feature, but perhaps the two pigments are also similar in structure.

3.37 C.I. Pigment Yellow 63

The peaks for P.Y.63 are broader than in general for the diarylide pigments. There is a lot of overlap of resonances because the molecule contains four *ortho* chloro anilide rings.

The four peaks for the C-6 and 6' (C-Cl) are of greater intensity than in any of the other pigments. The peaks are separated into two pairs to give a splitting (302 and 340 Hz) that is similar in magnitude to that seen for the the rest of the diarylide pigments.

3.38 *p*-Br Pigment

The sample is similar in quality to P.Y.63 and as such gives slightly broad peaks and the spectrum is somewhat noisy. The only new aspect of *p*-Br is the broad C-Br peak at 120.8 ppm. The C-Cl peaks are lost in the noise and possibly contribute to a peak at 120.8 ppm.

3.39 C.I. Pigment Orange 16

The chemical shifts in table 3.4 are very similar to those of the diarylide yellow pigments. The "orange" structure therefore, does not cause a big enough change to be identified by N.M.R..

CONCLUSION

The spectra of the diarylide yellow pigments have a number of small differences, but in general they are very similar and the changes in chemical shifts are very small. The most interesting features observed are the small splitting of carbons. In P.Y.17 the C-1, 2 and 8' carbons are all split and in P.Y.12 the C-2 and C-8' carbons are split. The splitting of C-1 and 2 in P.Y.17 could be due to a flipping of the C-2 to C-3 bond (fig.3.5).[4]

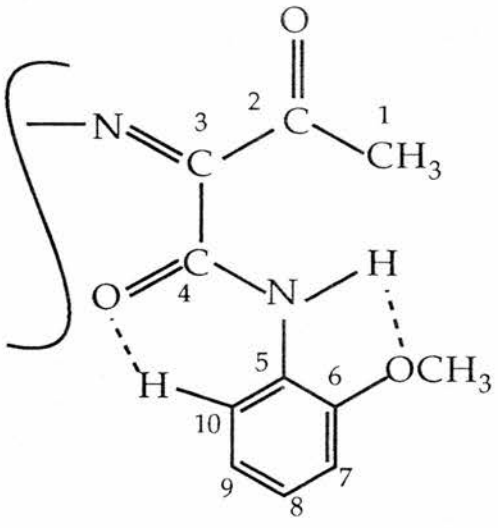


Fig.3.5

The H-bonding shown in fig.3.5 between the *o*-methoxyl and the hydrogen attached to the nitrogen could free the normal weak H-bond between the acetyl carbonyl and the same hydrogen and allow the C-2 to C-3 bond to flip. The H-bonding between the amide carbonyl and the *o*-phenyl hydrogen is well documented.[9] The question is why in P.Y.83, where there is also an *o*-methoxyl, is the same splitting not observed ? The answer could be that in P.Y.83 the H-bonding of the acetyl carbonyl is slightly stronger than the *o*-methoxyl and so the equilibrium is almost completely over to that side. The splitting of the C-2 peak in P.Y.12 is not caused by a flip of the C-2 to C-3 bond as in P.Y.17, but by the twisting about the central carbons (C-8') and the C-N bonds (C-5). The crystal structure of P.Y.12 (fig.3.6) has been obtained by XRD along with those of P.Y.12, 14 and 63 and the monoazos 12 and 13. The angles between the rings in these compounds (table. 3.5) shows how much P.Y.12 differs from the other pigments.[4]

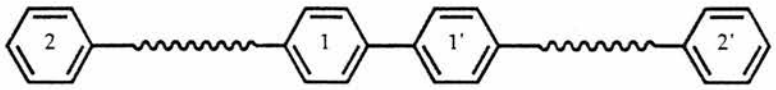


Table 3.5: angles between the planes of the phenyl rings

Pigment	1 and 2	1' and 2	1 and 1'	2 and 2'
mono 12	6.14	-	-	-
mono 13	0	-	-	-
P.Y.12	25.84	2.01	26.71	47.76
P.Y.13	9.03	9.03	0	0
P.Y.14	7.45	7.45	0	0
P.Y.63	6.6	6.6	0	0

The two halves of the molecule become non-equivalent and this could well affect the H-bonding of the two acetyl groups. The ^{13}C chemical shift is very sensitive to such changes and so this could easily account for the small splitting of the acetyl carbonyl peak in P.Y.12.

The splitting of the C-8' peak in P.Y.12 could also be caused by the twist in the molecule. The twist is centred on the C-8' carbons. Therefore, the two carbons are different and give different ^{13}C N.M.R. signals. The problem with this explanation is that the peak at 135.0 ppm is a shoulder on the peak at 134.3 ppm and the peak at 130.4 ppm is only about one third the intensity of the peak at 134.3 ppm. The intensities of the peaks do not appear to suggest that it is a simple matter of the twist in the molecule causing the difference in the two C-8' peaks. It would appear that the structure breaks down at certain points and gives a shift to lower frequency (130.4 ppm) when there is no twist to the molecule about the C-8' carbons. The other peak at 135.0 ppm could be due to slight alterations to the degree of twist. If we assume that the flat molecule gives a

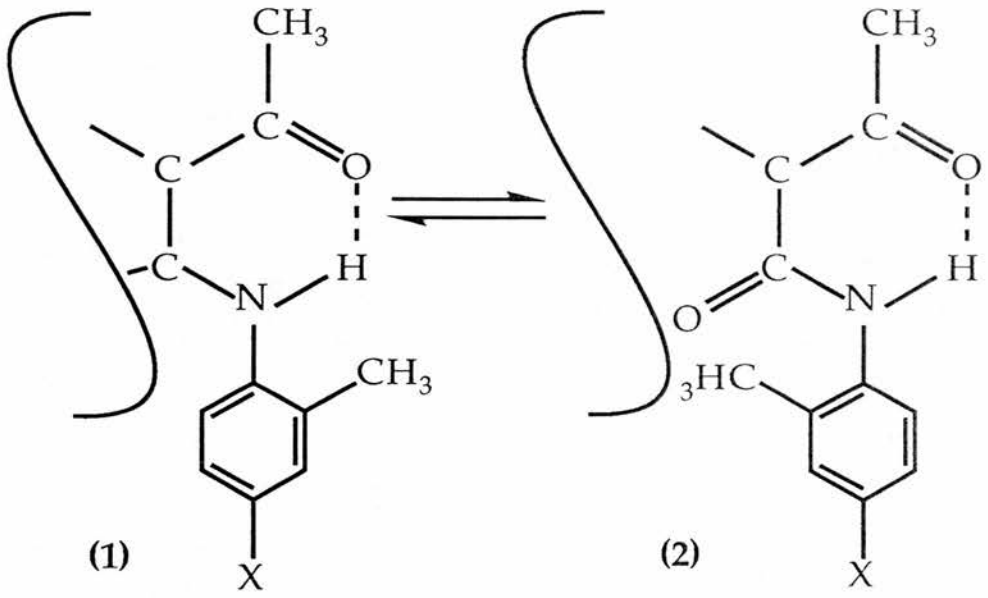
C-8' shift of 130.4 ppm then the shift at 135.0 ppm would indicate a slightly greater degree of twist. This is very much a hypothesis and with such a small splitting of 0.7 ppm it is very difficult to provide a definitive answer because the smallest change in environment of the carbons could easily cause this splitting.

The splitting of the C-8' peaks in P.Y.17 by 1.1 ppm with the shoulder again at lower frequency must also be treated in the same way as P.Y.12 and be attributed to a slight increase in the angle of twist. The XRD data on P.Y.17 is not available yet, but is currently under investigation.

The variation in chemical shifts of the aromatic methyl and methoxyl groups observed in the diarylide yellow pigments is curious. Taking the *m*-xylidide derivatives first (i.e. AAMX, mono 13 and P.Y.13), the methyl resonances are split in AAMX and P.Y.13, but overlap in mono 13. The splitting in AAMX and P.Y.13 is 2.9 and 2.6 ppm respectively. In mono 13 the methyl resonance at 21.7 ppm (same ^{13}C chemical shift as *p*-methyl in AAMX) has a shoulder (ca 20 ppm). In mono 13 the *m*-xylidide ring is probably rotating or flipping and causing the resonance of the *o*-methyl to move close to that of the *p*-methyl.

In *o*-toluidide derivatives (i.e. AAPT, mono 14 and P.Y.14) the *o*–methyl resonance is at 18.1 ppm in AAPT, 18.1 and 21.0 ppm in mono 14 and at 19.4 ppm in P.Y.14. The splitting in mono 14 is of the same magnitude as the shift seen in mono 13 for the aromatic methyls. Therefore, in mono 14 (*o*-methyl) the ring is in two different orientations (1 and 2) with the equilibrium at 50:50. In

mono 13 (*o* - and *p* -methyl) it is in the new orientation (2) i.e the equilibrium is over to the right (fig. 3.7).



X = H is mono 14

X = CH_3 is mono13

fig. 3.7

In the dimethoxylchloroanilide derivatives (AADMCA, mono 83, P.Y.83) the methoxyls give one sharp peak for AADMCA and P.Y.83, but in mono 83 a small splitting of 0.7 ppm is observed. The sharp peaks for the two methoxyls in AADMCA and P.Y.83 indicate that the carbon resonance is unaffected by the ring position. The possibility of hydrogen bonding between the *o* -methoxyl and the hydrogen on the nitrogen has already been looked at in P.Y.17 (fig. 17) and it could be a factor in the splitting of the methoxyls in Mono 83. The methoxyl in P.Y.17 is shifted to lower frequency (55.4 ppm in mono 17 to 54.7 ppm in P.Y.17) and the two peaks in mono 83 are at 56.0

and 56.7 ppm. Therefore, a weak hydrogen bond from the *o*-methoxyl oxygen to the hydrogen attached to the nitrogen (fig.3.5) seems the most likely explanation.

In P.Y.12 the linewidths of the aromatic carbons are greater than in the rest of the pigments. This is because of the interleaving of the molecules in the structure which brings the unsubstituted phenyl rings of one molecule at an angle which facilitates a dipolar attraction to the phenyl hydrogens of another molecule (fig.3.8).[4]

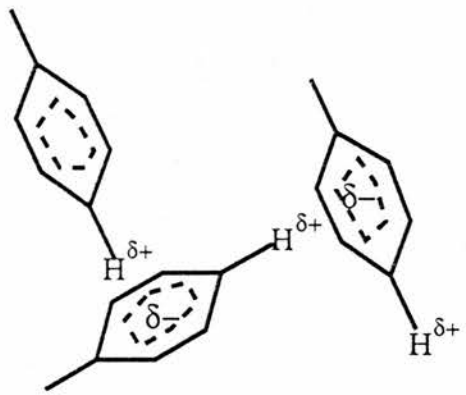


fig.3.8

Therefore, the carbon resonances are broadened by the interaction of the phenyl rings. The rest of the pigments have very little to distinguish themselves in term of structure. The changes in resonances of the aromatic ring substituents come in the monoazo compounds which are really just a stepping stone to help in the assignment of the pigments. The monoazos here are not actually pigments as shown in table 1.1 of the Hansa yellows.

4 ASYMMETRIC PIGMENTS

An asymmetric diarylide pigment is one where two different coupling components are coupled to the same central DCB tetrazo unit. This is achieved by first adding sarcosine (CH_3NHCH_2COOH) to the DCB tetrazo to protect one of the azo groups. The first coupling component is then added to the other azo group. The sarcosine is then stripped off and the second coupling component is added.

The impetus for making asymmetric pigments is in order to synthesise a cheaper pigment of say P.Y.83 quality using half as much AADMCA by substituting it with a cheaper coupling component like AAA. If an asymmetric pigment can be made to have properties close to a desirable pigment (e.g. P.Y.83) then this becomes commercially interesting. The most important C.I. pigment yellows are generally rated in improving properties as follows: P.Y.12<13<14<17<83. The study by solid-state ^{13}C N.M.R. of the asymmetric pigments should be able to show if the structure of the pigment is the same as either of the two Colour Index yellow pigments that can synthesised from the two coupling components used. Therefore, if the two coupling components used are AAA and AADMCA the asymmetric pigment is compared to P.Y.12 and 83. The asymmetric pigments may reveal new interactions and structures which could result in a pigment with better properties but, the knowledge of what makes a good pigment in terms of the structure is limited, so any new information is useful. In Chapters 4 and 5 the compounds that are discussed will contain varying degrees of the asymmetric pigment along with two C.I. pigments. Therefore, if specific resonances can be identified which belong to the

asymmetric pigments that would be very useful in the analysis of these compounds.

The six crude asymmetric pigment samples are a dark brown colour and not yellow like the crude C.I. diarylide pigments therefore immediately indicating the presence of impurities. The spectra have poor signal to noise and many partially overlapping resonances with large linewidths which are the effects of the high levels of impurities. The signal to noise ratio can be improved by running samples for long periods (e.g. overnight) but, the resolution is not improved. Therefore, the information that can be obtained from these samples is very limited because, several of the resonances are lost in the noise or are just not resolved. To compound this problem the samples have proved very difficult to recrystallise, of the six pigments that were synthesised from AAA, AAMX, AAOT and AADMCA only (5) AAMX/AADMCA and (6) AAOT/AADMCA have proved capable of recrystallisation.

Table 4.1: solid-state ^{13}C N.M.R. chemical shifts for 4.1-4.4

C No.	AAA/AAMX (C)	AAA/AAOT (C)	AAA/AADMCA (C)	AAMX/AAOT (C)
1	26.5	26.3 + 29.9	26.4 + 29.9	26.1+29.6
2	199.1	198.4	199.2	199.2
3	127.4	127.4 ?	127.1	
4	161.9	162.6	161.9	162.2
5	134.7 +138.0	136.9	137.5 + 148.8	135.8
5'	138	136.9	137.5	135.8
8	131.5			130.4
8'	131.5			130.4
9			142.5	
R-1	21.4	19.8	55.9	18.7
R-2	21.4			18.7
R-3			55.9	

4.1 Asymmetric Pigments AAA/AAMX

(i) Crude pigment
(spectrum 7)

The spectra indicate that the two methyls in AAMX give more than one resonance with the main resonance at 21.4 ppm. The spectra are not consistent but, on the spectrum run overnight there are resonances at 19.3 and 14.3 ppm which are a shoulder and one third the intensity of the resonance at 21.4 ppm respectively. The sample proved too difficult to recrystallise and so the true structure of the pigment cannot be ascertained and the chemical shifts cannot be assigned fully or very accurately. The chemical shift differences between resonances in the C.I. pigments are often quite small and so samples of this quality are of no use unless there are new resonances at quite different chemical shifts.

4.2 Asymmetric Pigment AAA/AAOT

(i) Crude pigment

These spectra are even poorer than 4.1 and give only the basic resonances. There appears to be two peaks for the acetyl methyl resonance (C-1), the resonance at 26.3 ppm is about double the intensity of the resonance at 29.9 ppm. The aromatic methyl resonance from AAOT can also be seen at 19.8 ppm. The only other resonances that can be identified are the two carbonyls (C-2 and 4) and C-5 and 5'.

The pigment again has not been recrystallised and so the crude sample does not give enough information to draw any conclusions.

4.3 Asymmetric Pigment AAA/AADMCA

(i) Crude pigment

The intensity of the signals is a little improved for this sample and so the characteristic quaternary carbon resonances from AADMCA and the amide carbonyl (C-4) are apparent although, they are still very broad resonances. The resonance at about 30.5 ppm is one third the intensity of the methyl resonance at 26.4 ppm. This is also seen in 4.2 and so must be real but the second methyl resonance at around 30 ppm is probably a C-1 resonance from some unreacted coupling component. The pigment also did not recrystallise.

4.4 Asymmetric Pigment AAMX/AAOT

(i) Crude Pigment

The sample is brown, like the other asymmetric pigments and the spectra are very noisy and the resonances are very broad. There are some points of interest and comparisons to P.Y.13 and 14 show some differences in chemical shifts and even new resonances.

The methyl resonances ($\delta\ ^{13}C$ 18-30 ppm) are broad and the aromatic methyls give one main broad resonance at 18.7 ppm. There is a shoulder on this resonance at 22.0 ppm. The aromatic methyl resonance in P.Y.14 is at 19.4 ppm but has been seen in mixed coupled AAOT/AADMCA to be anywhere between 17.5 ppm and 19.5

ppm. The shoulder at 22.0 ppm could be due to the *p*-methyl since it is likely that the main resonance at 18.7 ppm is from the two *o*-methyls. The *ortho* and *para* aromatic methyls in P.Y.13 have chemical shifts of 20.2 ppm and 22.8 ppm respectively. Therefore, the aromatic methyls indicate a shift towards the structure of P.Y.14.

The acetyl methyl is at slighter higher frequency than in a pure pigment and has a small shoulder at 29.6 ppm. These features have also been seen in some of the other asymmetric pigments and are attributed to unreacted coupling component.

The C-5 and 5' resonances only appear to give a resonance at 135.8 ppm (i.e. $\delta\ ^{13}C$ for C-5 of P.Y.13). There is only a small shoulder to indicate the resonance for C-5 from AAOT and C-5' which is usually at 137-139 ppm. Therefore, this contradicts the conclusion made earlier and indicates that the pigment has more P.Y.13 character. The large linewidth of the resonances, however, make the chemical shifts less well defined and so a change in chemical shift of a couple of ppm is not very significant.

The pigment proved impossible to recrystallise from TCB.

Table 4.2: solid-state ^{13}C N.M.R. chemical shifts of 4.5 and 4.6.

C No.	AAMX/AADMCA (C)	AAMX/AADMCA (R)	AAOT/AADMCA (C)	AAOT/AADMCA (R)
1	26.4+29.1 +30.4	26.6	25.9 + 29.8	26.9
2	200.0+202.0	199.3+200.2	201.1	200.6
3	127.6	127.4	127.9	127.4
4	162.9	161.4	162.9	161.1
5		135.6+150.0	138.2	137.2+150.0
5'		137.2	138.2	137.2
8		131.5		
8'		131.5		131.5
9				142.5
R-1	17.1+19.5 /56.5	20.0/56.8	16.7/56.1	56.6 (18.4)
R-2	22.1	22.6		
R-3	56.5	56.8	56.1	56.6

4.5 Asymmetric pigment AAMX/AADMCA

(i) Crude Pigment

The pigment is a dark brown colour, the spectra are noisy and the resolution is not very good but there are some points of interest.

The acetyl methyl (C-1) at ca 27 ppm and the aromatic methyls at c.a. 20 ppm appear to be split into at least three and four resonances respectively. The acetyl methyl has a main resonance at 26.3 ppm and then two smaller resonances at 29.1 and 30.6 ppm. The resonance at 26.3 ppm is presumably due to the asymmetric pigment and the other two resonances due to the coupling components. The C-1 ^{13}C chemical shifts of AAMX and AADMCA are 30.6 ppm and 31.5 ppm respectively therefore, it is possible that these two resonances are from the two coupling components.

In the aromatic methyl region the four resonances are at 16.8, 18.6, 20.3 and 21.5 ppm. In P.Y.13 the *o*-methyl is at 20.2 ppm and the *p*-methyl is at 22.8 ppm. It looks as though the methyls are in different environments either due to crystal lattice effects or just random interactions between the different halves of the asymmetric pigment.

The rest of the spectrum is very unclear and there is no sign of the two carbonyl resonances in the spectra or the other quaternary carbons from AADMCA. There are two NQS spectra and from these the two carbonyls can be tentatively assigned. The C-N and $\underline{C}$-OCH_3 (C-5 and 9) can be identified (table 4.2). There is a large resonance at ca 132 to 139 ppm which is in the range of C-8', C-5 (AAMX) and C-8 (AAMX). The width of the resonance suggests that it is not a single resonance, but contains several overlapping lines.

(ii) Recrystallised Pigment

The sample is a much cleaner looking dark orange crystalline solid. The spectra are also much improved from the crude pigment with less noise and better resolution. The only resonance that is not clear is the acetyl carbonyl because, in the NQS spectrum the low intensity of this resonance makes it difficult to pick out. The intensity of the acetyl carbonyl in the spectrum at 12.5 kHz is even lower and the resonance can not be seen in this spectrum at all.

The amide carbonyl (C-4) and C-9 both from AADMCA are close to their expected chemical shifts, but are very low in intensity. The

NQS shows most of the rest of the quaternary carbons. There are three resonances for C-N as expected although the resonance at 137.9 ppm appears to be slightly split. This is the resonance from the C-5' carbon and, therefore, this is the first time this has been seen to be beginning to split. The spectra are, therefore, similar to those of the crude sample but are cleaner. There are also a few features that separate this sample from just a physical mixture of P.Y.13 and P.Y.83 meaning that it is genuinely an asymmetric pigment.

4.6 Asymmetric Pigment AAOT/AADMCA
(spectra 8 and 9)

(i) Crude pigment

The characteristic AADMCA resonances can again be identified and there is also a broad resonance at about 17 ppm for the aromatic methyl from AAOT. The acetyl methyl (C-1) is split by 3.9 ppm and the resonance at 29.8 ppm is about half the intensity of that at 25.9 ppm.

(ii) Recrystallised Pigment

The spectra are are similar to those for the mixed coupled 10:90 AAOT/AADMCA pigment. There is a bit more noise but, the pigment is still quite brown. The aromatic methyl from AAOT is present and is slightly larger than it was in the mixed coupled pigment.

CONCLUSION

The crude samples do not provide much information about the structure of an asymmetric pigment. The large linewidths and high noise levels mean the chemical shifts are not very accurate. The impurities seem to include the coupling components (methyl resonance at ca 30 ppm) indicating that the reaction is incomplete. The resonances that can be assigned do not give any thing new to separate these pigments from the C.I. yellow pigments. The recrystallisation was, unfortunately, only successful twice. In both cases the pigments were synthesised with the coupling component AADMCA. The spectra of the recrystallised AAMX/AADMCA sample show that the resonances from the derivatives of the two coupling components are of equal intensity, thus indicating that there is a high probability that this is a genuine asymmetric pigment. The only sign of the asymmetric pigment is the splitting of the acetyl carbonyl resonance by 0.9 ppm. The recrystallised AAOT/AADMCA sample is curious, because the aromatic methyl resonance from AAOT is only one tenth the intensity of the of the acetyl methyl resonance whereas it should be half its intensity. This means that P.Y.83 is formed at some stage, either initially, because of incomplete reaction of the sarcosine or latterly when the sarcosine is removed. The second case arises due to incomplete coupling of the first coupling component to the diazo with sarcosine (see figure 1 in the experimental). An investigation into which part of the reaction was not going to completion in this pigment might also help in the synthesis of purer pigments for all the asymmetric pigments.

5 MIXED COUPLED PIGMENTS

The definition of the term mixed coupled pigment is that of a pigment made by the addition of DCB tetrazo to two different coupling components simultaneously. The composition of the final pigments will depend on the relative rates of initial competing coupling reactions and the subsequent second coupling. It is likely that a mixture of C.I. pigments with a certain amount of asymmetric pigment will result from this method of making pigments. The aim of making mixed coupled components is to get a solid solution which takes the structure of one of the possible pigment components. Therefore, if the coupling components used are AAMX and AAA and the resulting structure is that of P.Y.13 then the properties should be the same as P.Y.13. AAA is cheaper than AAMX and so the production cost of a P.Y.13 type pigment can be lowered by replacing AAMX with AAA. The three sets of mixed coupled pigments that have been synthesised are: (1) AAA +AAMX (P.Y.12/13), (2) AAA + AADMCA (P.Y.12/83) and (3) AADMCA + AAOT (P.Y.83/14). For each set three ratios of coupling component were used; 90:10, 50:50 and 10:90. 50:50 physical mixtures of the crude pigments of (1) i.e. P.Y.12 and 13 and (2) i.e. P.Y.12 and 83 were made up with some available samples. This is to check if any features that show up on the N.M.R. spectra are not related to the overall structure of the mixed coupled pigments, but just to the interference from the other component.

The solid-state ^{13}C N.M.R. of both the crude and recrystallised (TCB) mixed coupled pigment were obtained. In the following discussion the differences between the crude and recrystallised mixed coupled

pigments and the C.I. yellow pigments are highlighted. The chemical shifts of the corresponding asymmetric pigments are also examined to see to what extent, if any, they are present in the 50:50 mixed coupled pigments.

5.1 Mixed coupled AAA and AAMX

Table 5.1: solid-state ^{13}C N.M.R. chemical shifts of the AAA/AAMX set of mixed coupled pigments.

C.No.	A	RA	B	RB	C	RC
1	26.7	26.9	26.9	26.4 + 27.4	26.8	26.8
2	199.2	199.3	199.2	199.3	199.4	199.4
3	127.3	127.1	127.4	127.7	127.6	127.7
4	162.1	162.4	161.6	161.7	161.4	161.3
5	138.2	138.3	135.4 + 138.2	135.6 + 138.5	135.8	135.7
5'	138.2	138.3		138.5	138.3	138.6
6			127.4	127.7	127.6	127.7
6'	119.3 + 123.2	119.4 + 123.3	119.7 + 122.6	119.6 + 122.4		119.5 + 122.7
7						
8			131.4	131.6	131.7	131.6
8'	134.0 + 135.6	134.3 + 135.7	131.4	131.6	131.7	131.6
9						
10						
R-1			20.1	20.2	20.1	20.3
R-2	-	-	-	-	-	-
R-3			22.1 + 23.8	22.6 + 24.4	22.8	22.7

A = 90% AAA + 10% AAMX

B = 50% AAA + 50% AAMX R = Recrystallised

C = 10% AAA + 90% AAMX

5.11 90% AAA and 10% AAMX

(i) Crude pigment (A) (spectrum 10)

The solid-state ^{13}C chemical shifts are very similar to P.Y.12 except for the acetyl carbonyl (C-2) which is no longer split by 0.9 ppm although the resolution in general is not as good for this sample as for P.Y.12. The C-2 resonance linewidth is 2-3 ppm for (A) and it is 1-2 ppm in P.Y.12.

In Table 5.1 there is no mention of the resonances for AAMX i.e. the two methyls at 20-23 ppm. It is possible that these resonances will be lost in the noise when you consider that they would be one tenth the size of the resonances from AAA. They could, however, be split or broad since they could be part of either P.Y. 13 or an asymmetric pigment. The signal to noise ratio is commonly about 10:1, except when a long run has been done (e.g. overnight). In the case of this sample an overnight run was done which showed a broadish resonance at about 20 ppm about one tenth the intensity of the acetyl methyl. The other two spectra were not run for long enough to verify this resonance, but it seems a reasonable assignment to make. Unfortunately a long run was not done on all the mixed pigments with a 10% component and so low intensity resonances quite often can not be seen.

(ii) Recrystallised pigment (RA)

The resonances have sharpened up, apart from the C-2 resonance which is 2-3 ppm across. The resonances all stay within

acceptable limits of the crude chemical shifts. The deepening of the colour from yellow to orange observed is attributable to the increase in crystal size on recrystallisation.

5.12 50% AAA and 50% AAMX

(i) Crude pigment (B) (spectrum 11)

The *p*-methyl resonance is split in the spectrum spun at 7 kHz and is broad and reduced in height in the other two spectra at 8 kHz. The 1.7 ppm splitting of the resonance indicates a slightly different environment for the tail of the molecule. This is most likely to be the presence of the asymmetric pigment which causes the *p*-methyl resonance to move to higher frequency in the slightly different structure. The resonance for the two methyls in asymmetric AAA/AAMX is at 21.4 ppm, but the resonances are so broad that a chemical shift of 23.8 ppm is quite feasible for the *p*-methyl in the asymmetric pigment.

The C-8' resonances for P.Y.12 are absent, therefore the twisting of the C-8' to C-8' bond and the herringbone structure of P.Y.12 are not present in the mixed coupled pigment. The structure may be that of P.Y.13 from the N.M.R.

(ii) Recrystallised pigment (RB) (spectrum 12)

The recrystallised pigment offers slightly better resolution and also reduced noise. The splitting of the *p*-methyl is confirmed

with the two resonances for *p*-methyl moving to higher frequency by 0.5 and 0.6 ppm. The resonance at 24.4 ppm is, therefore, from the asymmetric pigment and from the intensity of the resonance the asymmetric pigment makes up about half of the mixed coupled pigment.

5.13 10% AAA and 90% AAMX

(i) Crude pigment (C) (spectrum 13)

The spectra show all the characteristics of P.Y.13 but with the main group of aromatic carbons slightly increased in intensity. The *o*-methyl is broader than seen for P.Y.13 and the *p*-methyl is reduced in intensity. The *p*-methyl in the 50:50 physical mixture of P.Y.12 and 13 is also of lower intensity and so it seems the presence of an impurity which in this case is P.Y.12 causes the signal of the *p*-methyl to be obscured. The structure of (C) is disordered and this is borne out by the broadness and lack of resolution of the resonances of the aromatic ring substituents.

(ii) Recrystallised pigment (RC)

The recrystallised pigment appears from the spectra to be P.Y.13 and so any P.Y.12, asymmetric pigment or impurities have all gone.

5.2 Mixed Coupled AAA and AADMCA

Table 5.2: solid-state ^{13}C N.M.R. chemical shifts for the AAA/AADMCA set of mixed coupled pigments.

C.No.	(A)	(RA)	(B)	(RB)	(C)	(RC)
1	26.6	27.0	26.7	27.0 + 25.8 (s)	26.8	26.9
2	199.6	199.2 + 200.4 (s)	200.7	200.7	200.6	200.7
3	126.9	127.2	127.1	127.2	127.2	
4	162.1	162.5	161.4	161.2	161.1	161.0
5	138.1	138.5	137.8 + 150.1	138.3 (s) + 150.1	150.0	149.9
5'	138.1	138.5	137.8	137.5 + 138.3 (s)	137.3	137.1
6			127.1	127.2	127.2	
6'	121.4 + 124.3	122.7 + 124.1	120.1 + 123.5	120.2 + 123.1		120.0 + 122.9
7						
8						
8'	134.0 + 136.0 (s)	134.5 + 136.1 (s)	131.7 + 134.1	131.5	131.7	131.6
9			142.3	142.3	142.4	142.4
10						
R-1			56.5	56.7	56.7	56.6
R-2	-	-	-	-	-	-
R-3			56.5	56.7	56.7	56.6

A = 90% AAA + 10% AADMCA

B = 50% AAA + 50% AADMCA R = Recrystallised

C = 10% AAA + 90% AADMCA (s) = shoulder

5.21 90% AAA and 10% AADMCA

(i) Crude pigment (A)

The resolution of the sample is not as good as that seen for P.Y.12 and yet the C-8' resonance is split by 2.0 ppm compared with only

0.7 ppm in P.Y.12. The resonances are also equal in intensity as far as can be determined, but this may just be due to the extra noise boosting the resonance at 136.0 ppm. The acetyl carbonyl (C-2) is not split, but is broad enough to contain the two resonances seen in P.Y.12. The small resonance at 130.4 ppm also attributed to C-8' in P.Y.12 could be present in the mixed coupled pigment, but the noise and poorer resolution mean that a resonance of such low intensity in this range would be obscured.

There is no indication of the resonances from AADMCA.

(ii) Recrystallised pigment (RA)

The acetyl carbonyl (C-2) is split because of the better resolution of this sample than in (A). The C-8' resonance is split by 1.6 ppm and with resolution enhancement the resonance at 136.0 ppm is seen to be much reduced in intensity when it is no longer a shoulder on the resonance at 134.4 ppm. The change in the resonances for C-8' could mean that the twist between the central aromatic rings is slightly reduced with the introduction of a different pigment into the sample.

5.22 50% AAA and 50% AADMCA

(i) Crude pigment (B)

The sample is a little impure and so the resonances are broader than for the previous crude mixed coupled pigments. However, all the main quaternary resonances (C-2, 3, 4, 5, 6 and 9) from AADMCA

along with the methoxyl resonance are present. From AAA the two C-8' resonances at about 135 ppm are evident. The chemical shift of the acetyl carbonyl (C-2) corresponds to that of P.Y.83. There is also a new resonance of low intensity at 112.6 ppm which from its chemical shift must be from an aromatic ring carbon.

(ii) Recrystallised pigment (RB) (spectrum 14)

The methyl resonance (C-1) is split for the first time with a new resonance of less than half its intensity occurring as a shoulder 1.2 ppm to lower frequency at 25.8 ppm. The spectra are very similar to those for P.Y.83, there are, however, a few resonances which are not seen in any P.Y.83 spectra and they are a resonance 129.0 ppm and two small resonances at 112.6 ppm and 134.0 ppm. The resonance at 129 ppm is an aromatic carbon from AAA, but could also be from the central rings. The C-5' resonance at 137.5 ppm has a shoulder on it at 138.3 ppm which corresponds to a C-5, 5' resonance from P.Y.12. Therefore, the sample is similar to P.Y.83 but retains some P.Y.12 character. It is hard to gauge whether P.Y.12 recrystallises in equal quantities because it has so few characteristic resonances. The reduction in intensity of the C-8' resonance from P.Y.12 can mean a crystal structure effect or that P.Y.12 and P.Y.83 do not recrystallise in equal proportions. The resonance at 131.5 ppm is not of the correct intensity to be from the C-8' carbons of the whole sample. In the physical mixture of the P.Y.12 and P.Y.83 the C-8' resonances are of the same intensity. The C-8' resonance from AADMCA is of low intensity and so the presence of P.Y.12 dampens the signal from C-8' of AADMCA. The resonances from the asymmetric pigment (4.3) are not distinctive

not distinctive enough to be able to say how much is present in this sample.

5.23 10% AAA and 90% AADMCA

(i) Crude pigment (C)

The only change from the spectra for P.Y.83 is that there is a slight increase in intensity of the aromatics at around 127 ppm (C-3, 6) and also for the acetyl carbonyl C-2.

(ii) Recrystallised pigment (RC)

On recrystallisation the intensities of the acetyl carbonyl (C-2) and C-3 and 9 have decreased. This is possibly the P.Y.83 component recrystallising in preference to P.Y.12. The spectra are now very similar to those of P.Y.83.

5.3 Mixed Coupled AAOT and AADMCA

Table 5.3: solid-state ^{13}C N.M.R. chemical shifts of the AAOT/AADMCA set of mixed coupled pigments.

C.No.	A	RA	B	RB	C	RC
1	27.3	27.4	26.8	26.9 + 25.7 (s)	26.8	26.9
2	199.2	199.9	199.7	200.4	200.4	200.7
3	127.3	127.2	127.5	127.3	127.4	127.2
4	161.6	162.2	161.5	161.5	161.1	161.1
5	137.6	138.1	137.5 + 150.0	137.5 + 150.0	149.9	149.7 + 150.2
5'	137.6	138.1	137.5	137.5	137.3	137.3
6	127.3	127.2	127.5	127.3	127.4	127.2
6'	120.6 + 123.3	120.6 + 122.4	122.2	121.1 + 123.6		120.0 + 122.8
7						
8						
8'	131.0	131.3	131.2	131.3	131.5	131.5
9			142.6	142.4	142.4	142.4
10						
R-1	19.2	19.3	18.1+19.1 /56.4	17.6 +19.0 /56.6	56.7 (18.2)	56.8 (18.4)
R-2						
R-3			56.4	56.6	56.7	56.8

A = 90% AAOT + 10% AADMCA R = Recrystallised

B = 50% AAOT + 50% AADMCA s = shoulder

C = 10% AAOT + 90% AADMCA

5.31 90% AAOT and 10% AADMCA

(i) Crude pigment (A)

This pigment shows very little change from P.Y.14 with no sign of any characteristic resonances from AADMCA derivatives. The spectra show a slight increase in the intensity of the aromatic

carbons compared to P.Y.14 and they are not as well resolved. The acetyl carbonyl (C-2) is obscured by noise and ssb to some extent in all three spectra, but is at about 199.2 ppm. The C-8' resonance is somewhat low in intensity.

(ii) Recrystallised pigment (RA)

The spectra are now identical to those for P.Y.14. The C-8' resonance is now more intense and the C-2 and methyl resonances are much sharper. The recrystallisation has removed the slight impurities which were causing some broadening of resonances and a loss of intensity for C-8'.

5.32 50% AAOT and 50% AADMCA

Crude pigment (B)

These spectra have a few new features compared to the pure pigments.

The aromatic methyl resonance is split by 1 ppm in the spectrum spun at 7 kHz. In the two 8 kHz spectra (one is an NQS) it is a broad and misshapen resonance. The intensity of the C-2 resonance is large and it is broad (2-3 ppm) and the resonances from AADMCA are well resolved for a crude pigment. Small splitting of *o*-methyl from AAOT (1 ppm) probably indicates the presence of the asymmetric pigment because, in the crude and recrystallised asymmetric pigment AAOT/AADMCA the *o*-methyl resonances are at 16.7 and 18.4 ppm respectively.

(i) Recrystallised pigment (RB) (spectrum 15)

The spectra show a shoulder at 25.7 ppm. It has about half the intensity of the acetyl methyl (C-1) resonance and is 1.2 ppm to lower frequency of C-1. The same feature was also seen in the recrystallised mixed coupled 50% AAA and 50% AADMCA spectra. The aromatic methyl is seen to be split by 1.4 ppm in the 12 kHz spectrum. There is little or no change in the rest of the spectrum apart from the slightly better resolution of the aromatic carbons.

5.33 10% AAOT + 90% AADMCA

(i) Crude pigment (C)

The spectra show a close resemblance to that of P.Y.83. There is a very small resonance at 18.4 ppm which must be the *o*-methyl from AAOT. Therefore, this is the first crude pigment to show the presence of a 10% component.

(ii) Recrystallised pigment (RC)

The spectra are almost identical to that of P.Y.83 except that C-2 has doubled in intensity. The noise level is very low and the resolution is very good but the small resonance for the aromatic methyl has halved in intensity from (C). The AAOT component has not recrystallised to the same extent as the AADMCA component. This is the first proof we have that the pigments recrystallise

preferentially. There is a small splitting of C-5 (AADMCA derivative). The C-5' resonance also show a similar splitting at a high spinning speed (12 kHz).

CONCLUSION

The recrystallisation in terms of the mixed coupled pigments does not necessarily give the same proportions of each component, this was seen in 83/14 90:10. The crude pigment had a small resonance for the aromatic methyl from AAOT, but this resonance was no longer evident in the recrystallised pigment. This indicates that P.Y.14 or the asymmetric pigment AADMCA/AAOT is more soluble than P.Y.83.

The main points of interest from the solid-state spectra for the mixed coupled pigments is the shoulder on C-1 and the small splitting of the C-5 and 5' resonances. The splitting of C-1 is seen in all three of the 50:50 recrystallised pigments and therefore, suggests that this arises from the asymmetric pigment or its influence on the mixed coupled pigment structure. The small splitting (~0.5 ppm) of the C-5 and 5' resonances is seen in 12/83 10:90,12/83 50:50 and 83/14 90:10. The only resonance that is not split out of the six C-5 and 5' resonances is the C-5 in 12/83 50:50. The splitting of the C-5 and 5' resonances could mean that there is a twist of the carbon nitrogen bonds to both phenyl rings relative to the opposite carbon in the other half of the molecule. Alternatively, some sort of asymmetric interaction with another

Alternatively, some sort of asymmetric interaction with another pigment molecule could split these resonances. Further clarification is needed.

The two 90:10 ratio samples in each of the three sets of mixed coupled pigments show little of interest. The 50:50 ratio samples, however, all have new resonances when compared to the relevant C.I. pigments. This suggests that the rates are comparable for the reaction of both the coupling components and the DCB tetrazo. The intensity of the new acetyl methyl resonances in 50:50 AAA/AADMCA and AAOT/AADMCA are ca half that of the acetyl methyl resonances at the chemical shift of the C.I. pigments. In 50:50 AAA/AAMX the *p*-methyl is split with each resonance the same intensity. These factors suggest that the mixed coupled 50:50 pigments are made up of the two possible C.I. pigments plus the asymmetric pigment, with all three in equal quantities. This is assuming that the new resonances are from the asymmetric pigments.

6 INVERSE COUPLED PIGMENTS

The definition of an Inverse Coupled (I.C.) pigment is that of a pigment made by adding the coupling component to the DCB tetrazo. The I.C. pigments reported here were made using two coupling components which were added sequentially to the DCB tetrazo. The reaction is therefore, controlled by the relative rates of the addition of the first coupling component. If the rate of addition of the first coupling component (A) to the DCB tetrazo is slow, and then fast for addition to the half coupled DCB then the resulting pigment will not contain any or only very little asymmetric pigment. On the other hand if addition of A is fast to the uncoupled DCB tetrazo, then when we add the second coupling component (B) the resulting pigment will be asymmetric. If the rates of addition of A to the DCB tetrazo and the half coupled DCB are comparable then we get a mixture of pure A and B coupled pigments and the asymmetric pigment. The experimental indicates that after the addition of the first coupling component a solid is formed because the reaction mixture becomes very viscous. The colour of the pigment is obscured though by the strong colour of the DCB tetrazo.

The solid-state ^{13}C N.M.R. spectra were run to attempt to establish to what extent the first coupling component reacts with the DCB tetrazo and the half coupled DCB.

The I.C. pigments that have been synthesized are: (1) AAA/AAMX; (2) AAA/AAOT; (3) AAA/AADMCA; (4) AAMX/AAOT; (5) AAMX/AADMCA; (6) AAOT/AADMCA.

The six pigments were all recrystallised from TCB and these samples are also reported. The pigments are compared to the mixed coupled equivalents where possible and to the constituent pigments otherwise.

Table 6.1: solid-state ^{13}C N.M.R. chemical shifts of the inverse coupled pigments 6.1-6.3.

C No.	AAA/AAMX (C)	AAA/AAMX (R)	AAA/AAOT (C)	AAA/AAOT (R)	AAA/AADMCA (C)	AAA/AADMCA (R)
1	26.8	27.0	27.2	27.4	26.7	27.0+25.7
2	199.3	199.2	199.5	199.7	200.3	200.8
3	127.3	127.5	127.1	127.2	127.1	127.3
4	161.6	161.8	162	162.1	161.6	161.2
5	135.4 +138.3	135.6 +138.2	138.1	138.2	150.1 +137.9	150.2 +137.4
5'	138.3	138.2	138.1	138.2	137.9	137.4
6	127.3	126.1	127.1	127.2	127.1	127.3
6'	119.6 +122.6	119.5 +122.9	119.9 +123.1	120.2 +123.3	123.4	120.1 +123.1
7						
8	131.4	131.7				113.9 +117.2
8'	131.4	131.7	130.9	131.1	131.8 +134.6	131.6
9					142.5	142.5
10						
R-1	20.0	20.2	19.3	19.6	56.5	56.6
R-2	23.3	23.1+25.0				
R-3					56.5	56.6

(C): Crude pigment. (R): Recrystallised pigment.

6.1 Inverse Coupled AAA/AAMX

(i) Crude pigment

The spectra are, apart from a few minor differences, the same as the spectra for mixed coupled AAA/AAMX 50:50.

The aromatic methyls are at 20.0 and 23.3 ppm compared with 20.2 and 22.8 ppm in P.Y.13. The resonance at 23.3 ppm (*p*-methyl) is a little over half the intensity of the resonance at 20.0 ppm (*o*-methyl) whereas as in P.Y.13 they are of similar intensity. The chemical shifts of the whole spectrum in general correspond closely to those of the mixed coupled AAA/AAMX 50:50 pigment.

(i) Recrystallised pigment (spectrum 16)

The sample is still a little impure and so the noise level and the resolution are not much better than in the crude sample. There are three aromatic methyl resonances (20.1, 23.2, and 24.7 ppm) and their intensities are approximately in the ratio 3:2:1 respectively. Therefore, the *o*-methyls have the same chemical shift as seen in P.Y.13 and the *p*-methyl is split. The splitting must be due to two different structures which involve the tail of the molecule. The structural change is obviously very small because no other peaks are affected and the aromatic methyl is only split by 1.5 ppm. The C-8' resonances from AAA derivatives (130.4 and 134-135 ppm) are not apparent but could be under the stronger resonance of the C-5 and C-8' (AAMX derivatives) at 135.4 and 131.7 ppm. The C-5' resonance (138.2 ppm) is broad (4-5 ppm) when spun at 7 kHz and

has a shoulder at 139.6 ppm when spun at 8 kHz. This could be related to the splitting of the *p*-methyl resonance although a 4.2 ppm shift from 135.4 ppm is large compared to the splitting of the *p*-methyl. The intensity of the C-5 resonance is low and so with the resonance for C-8' (AAA derivative) also at around 135 ppm this new resonance seems likely to be from C-5 (AAMX derivative). The other possibility is that the tail of the molecule which often lies close to the central ring of another molecule, has a different interaction to P.Y.12 and the asymmetric pigment than to P.Y.13. The splitting would then be of the *p*-methyl and the C-5' resonances and since the splittings are comparable in size this is also a reasonable suggestion.

6.2 Inverse Coupled AAA/AAOT

(i) Crude pigment

There is no mixed coupled equivalent for this pigment therefore, it can only be compared to P.Y.12 and P.Y.14.

The resolution is good and the chemical shifts for the methyls and the carbonyls are very similar to those for P.Y.14. The sample is different to P.Y.12 in that there there are no resonances at around 134-135 ppm and the acetyl carbonyl shows no signs of the splitting seen in P.Y.12. The biggest difference in the rest of the spectrum is that the resonance at 129.2 ppm has moved to become a small shoulder at 128 ppm. The resonances correspond closely to those for P.Y.14. Therefore, from these observations it seems that the structure is much more like that of P.Y.14.

(ii) Recrystallised pigment

The sample shows similar levels of noise and only slightly better resolution compared to the crude pigment. The spectra of the recrystallised pigment show no change in terms of chemical shift of the resonances nor are there any new resonances.

6.3 Inverse Coupled AAA/AADMCA

(i) Crude pigment

The sample is not very pure and so the noise obscures and distorts the spectrum and impairs the resolution. The distinctive features from both P.Y.12 and 83 are retained. The resonance for C-8' (AADMCA) is the same intensity as the resonances for C-9 and C-5. The C-8' resonances associated with AAA are present as low intensity shoulders at 133.8 and 134.9 ppm in the normal spectra but on the NQS spectrum the signal to noise is worse as is generally true and so the resonances cannot be confirmed. The rest of the chemical shifts show little change from the values in P.Y.12, 83 and the mixed coupled AAA/AADMCA 50:50 pigment. The acetyl carbonyl is very broad (4-6 ppm) suggesting that there is more than one resonance at the given chemical shift.

The structure appears to contain the both the structure from P.Y.12 and 83 and the presence of any asymmetric pigment, if there is any, has little effect.

(ii) Recrystallised pigment
(spectrum 17)

The spectra are much better in terms of noise and resolution than the spectra for the crude pigment. The spectra are very similar to those of P.Y.83 with the main difference being the aromatic carbon resonance at 129.3 ppm which indicates that some coupled AAA is still present in the sample. The resonances from AADMCA at 142.5, 150.2 and 131.6 ppm are all increased in intensity relative to the methyls and methoxyl groups. This is when the relative intensities of these resonances are compared to the crude sample. This could be an artefact of the crystal structure and indicates that the structure is better defined. However, the opposite effect is seen in for C-5 and 5' (137.4 ppm) with the resonances somewhat reduced in intensity from what they were in the crude pigment. The resonance between 133 and 135 ppm for C-8' (AAA) has become very small and could account for the increase in the intensity of the resonance at 131.6 ppm (C-8'). These factors suggests that there is a change to a structure more like P.Y.83 which moves resonances that are seen in P.Y.12 to the corresponding position in P.Y.83. Similar changes in intensity are seen in recrystallised mixed coupled AAA/AADMCA 50:50.

The spectra show the same main features as that of the recrystallised mixed coupled pigment even with the small shoulder on the acetyl methyl resonance at 25.7 ppm which is at 25.8 ppm in the mixed coupled pigment. Therefore, the recrystallised inverse and mixed coupled pigments both seem to have the same composition in which the P.Y.83 structure predominates.

Table 6.2: solid-state ^{13}C N.M.R. chemical shifts of the inverse coupled pigments 6.4-6.6.

C No.	AAMX/AAOT (C)	AAMX/AAOT (R)	AAMX/ AADMCA (C)	AAMX/ AADMCA (R)	AAOT/ AADMCA (C)	AAOT/ AADMCA (R)
1	27.0	27.3	26.6	26.9	26.6	27.1
2	199.3	199.3	199.8	199.3 +200.6	200.1	199.2 +200.6
3	127.2	127.3	127.2	127.6	127.5	127.1
4	161.6	161.6	161.1	161.3	161.4	161.4
5	135.4 +138.0	135.5 +138.2	150.1 +134.4	135.9 +150.4	137.3 +150.0	137.6 +150.1
5'	138.0	138.2	137.4	137.2 +138.5	137.3	137.6
6	125.8	126.1	127.2	127.6	127.5	127.1
6'	122.8	119.5 +122.8	121.3	120.4 +123.2	122.8	119.5 +122.6
7						
8		131.8	131.4	131.7		
8'	131.3	131.8	131.4	131.7	131.1	131.6
9			142.4	142.6	142.5	142.4
10						
R-1	19.5	20.0 22.6	18.7+20.1 /56.0	20.1+57.0 22.9	18.1/56.3	19.2+56.7
R-2	22.4		22.3+18.7	57.0		56.7
R-3			56.0		56.3	

(C): Crude pigment.

6.4 Inverse Coupled AAOT/AAMX

(i) Crude pigment

The spectra are a little noisy and the resolution of some resonances is poor. Resolution enhancement of the CP spectrum at 7 kHz and of the NQS spectrum has identified a few extra resonances.

The aromatic methyls from AAMX and AAOT only have one resonance at 19.5 ppm with a small broad shoulder at 22.4 ppm. The rest of

the spectrum has resonances very similar to both P.Y.13 and 14 with no new resonances to indicate a specific structure. Therefore, from the aromatic methyl resonances alone the sample structure is more like that of P.Y.14.

(ii) Recrystallised pigment (spectrum 18)

The chemical shifts and the intensities are very similar to the values for the crude pigment. The only differences are due to the better resolution and the reduced noise of the spectra. The two C-Cl resonances are now evident instead of just the one in the crude pigment. The resonance of the *p*-methyl (22.6 ppm) is well resolved and is half the intensity of the *o*-methyl resonances (20.0 ppm). The *o*-methyl resonances of P.Y.13 and 14 are at 19.4 and 20.2 ppm respectively, therefore the overlap at 20.0 ppm is not surprising.

The structure appears, therefore, to be intermediate between a P.Y.12 and 13 structure.

6.5 Inverse Coupled AAMX /AADMCA

(i) Crude pigment

The spectra are of similar quality to the rest of the inverse coupled pigments.

The *o*-methyl gives a broad resonance at 19.9 ppm at 7 kHz which splits at 8 kHz into two resonances at 19.7 and 20.1 ppm.

In general the resonances are at the same chemical shift as the corresponding resonances in P.Y.13 and 83. The main exception is the resonance at 134.7 ppm which is presumably the C-5 resonance from AAMX which is at 135.8 ppm in P.Y.13.

The aromatic ring carbon at 116.2 ppm in P.Y.13 is not apparent but could have shifted to become the slight shoulder on the resonance at 114.0 ppm. The C-Cl resonance (121.3 ppm) is not split but is very broad which is a feature of P.Y.83 and not P.Y.13. The acetyl carbonyl is also very broad suggesting there are two distinct carbonyl resonances.

The position of the resonances indicates the structure to be closest to that of P.Y.83.

(ii) Recrystallised pigment (spectrum 19)

The resolution is much improved from the crude sample and the aromatic methyls only give two resonances now. The aromatic carbon resonance at 116.1 ppm is also resolved unlike the crude pigment. The C-5' resonance is again at the same chemical shift as P.Y.13 and the C-5' resonance is split slightly, indicating two discrete structures. Therefore, the sample appears to be a mixture of the structures of P.Y.13 and P.Y.83.

6.6 Inverse Coupled AAOT/AADMCA

Crude pigment

The spectra seem to be noisier than earlier inverse coupled pigments, especially the NQS spectrum.

The ^{13}C chemical shifts for C-1 and 3 are both closer to values for P.Y.83 than P.Y.14. The aromatic methyl resonance is at 18.1 ppm compared to 19.4 ppm in P.Y.14. In the mixed coupled AAOT/AADMCA 50:50 pigment the aromatic methyl is split (18.1 and 19.1 ppm). The effect of coupled AADMCA is therefore to shift the aromatic methyl resonance to lower frequency. The reason that it is shifted could be structural or it could just be the presence of the methoxy groups in the structure that affect the aromatic methyl.

The spectra are very much like that of the mixed coupled equivalent apart from in the quality. There is also some indication of the structure being dominated by that of P.Y.83.

(ii) Recrystallised pigment (spectrum 20)

The resolution is improved from the crude pigment and the methyl resonance is at 19.2 ppm, which is the close to value in P.Y.14. With the help of resolution enhancement a resonance at 18.0 ppm is observed which is about half the intensity of the resonance at 19.2 ppm. The acetyl methyl resonance has a small shoulder at 25.8 ppm which is about a third of its intensity. The acetyl carbonyl resonance also has a shoulder this time 1.4 ppm to lower frequency

and about half its intensity. The structure is, therefore, a curious one and is either made up of asymmetric units or it is just the different interactions of the P.Y.14, 83 and the asymmetric pigment which is causing these small changes in chemical shift.

CONCLUSION

The last two crude asymmetric pigments have much the same spectra as the four pigments previously reported. The crude asymmetric pigment AAMX/AADMCA has multiple splitting of the aromatic methyls. This could be brought about by the impurity of the sample, but why therefore, does it only influence this compound. Another, and more likely, possibility is that the structure is very irregular and so causes these splittings. The recrystallised pigment has only two resonances for the aromatic methyls and so the structure must have been changed as well as the obvious removal of the impurities.

The recrystallisation of the asymmetric pigments has not provided any further success. Xylene was used in an attempt to abstract some impurities from the pigments dissolved in TCB but this failed as the xylene only seemed to abstract a little of the dirty brown pigment.

Changes in the synthetic conditions were also looked at very briefly with some pigments being made using different pH's when coupling but the resulting pigment was still very brown.

The inverse coupled pigments on the other hand are much cleaner looking pigments and give reasonable spectra even when crude. The recrystallisation is also straight forward and gives very nice bright crystalline solids.

The spectra of the inverse coupled AAA/AAMX, AAA/AADMCA and AAOT/AADMCA are all very similar to those for the mixed coupled 50:50 equivalents. The three inverse coupled pigments without a mixed coupled equivalent i.e. AAA/AAOT, AAMX/AAOT, AAMX/AADMCA all have features not seen in any other similar pigments.

In AAA/AAOT the C-8' resonances for P.Y.12 are not evident. In AAMX/AAOT there is a shoulder on the resonance at 127.2 ppm (C-4, C-6) which is only of sufficient intensity to be one carbon and seems most likely to be a C-6 resonance from either AAMX or AAOT. In AAMX/AADMCA the resonance for C-5 (AAMX) has been shifted to lower frequency by 1.4 ppm compared with P.Y.13. The aromatic methyls are dominated in intensity by a new resonance at 18.7 ppm with smaller resonances at similar shifts to those seen in P.Y.13. The structures of the last two seem to be new, whereas the structure of AAA/AAOT is like that of P.Y.14.

The addition of the first coupling component brought about a thickening of the solution but it remained dark red due to the DCB tetrazo still present. On further investigation the addition of AAA brought about pigment formation in considerable quantities. Therefore, it seems that all the effects noted that could have been due to the asymmetric pigment appear now to be caused by changes

to the structure of the solid and interactions between the two pigment components. There will be a small amount of asymmetric pigment present but it does appear to be very small. Therefore, with the corresponding mixed coupled pigments being so similar to the inverse coupled pigments they also appear to contain very little asymmetric pigment. The main difficulty with this conclusion is that we do not have a pure sample that is definitely an asymmetric pigment. This means that there are no resonances that we can look for in the mixed and inverse coupled pigments to confirm the presence of some asymmetric pigment. An analysis of the addition of all the coupling components to excess DCB tetrazo to check to what extent pigment is formed would be useful.

In conclusion, the obvious differences found between the mixed and inverse coupled pigments and the pure pigments could probably be simulated by recrystallisation of a physical mixture.

APPENDIX 1

X-RAY DIFFRACTION RESULTS

APPENDIX 1

X-ray Powder Diffraction Results

The effects on the ^{13}C N.M.R. chemical shifts of the different substituents of the tail phenyl rings does not seem to go beyond the carbons adjacent to the one directly bonded to the substituent. This is demonstrated by the consistency of the ^{13}C chemical shifts between C.I. pigment yellows and the similarity of the values for these pigments and both the mixed coupled and inverse coupled pigments. The structures could, therefore, be said to be much the same for all the samples, but powder X-ray diffraction (XRD) of the sample structure are all different. The XRD patterns of some of the samples are given in the appendix. The XRD patterns cannot give individual interactions, but they do show which of the C.I. pigment yellows the mixed and inverse coupled pigments resemble most. The XRD patterns show that the mixed coupled 90:10 samples are as you would expect very similar to the C.I. pigment yellow made with the 90% coupling component. The XRD patterns of the three sets of mixed coupled 50:50 samples have been plotted together with the two relevant C.I. pigment yellows. The mixed coupled 50:50 AAA/AAMX (pattern 1) sample shows only slight differences when compared to P.Y.13 and is considerably different to P.Y.12. The XRD of the inverse coupled AAA/AAMX sample (pattern 4) also shows a similarity to P.Y.13 and is almost identical to the mixed coupled sample. The ^{13}C chemical shifts of these samples are very close and they both have a resonance between 24 and 25 ppm which is not seen in any other samples.

The mixed coupled 50:50 AAA/AADMCA sample (pattern 2) is at first glance is like that of P.Y.83, but the peaks do not quite overlap in some places and there are peaks from AAA present as well. The inverse coupled AAA/AADMCA sample has a very similar trace to the mixed coupled sample. The structure is, therefore, new but seems to have a lot more characteristics of P.Y.83. This fits in with the ^{13}C N.M.R. data which shows that the samples are very similar, but they have the new resonance at c.a. 26 ppm which is only seen in these two samples and the mixed coupled 50:50 AAOT/AADMCA sample. The mixed coupled 50:50 AAA/AADMCA also has an extra resonance for C-5 and C-5' indicating further differences to P.Y.83.

The mixed coupled 50:50 AAOT/AADMCA sample (pattern 3) is certainly not like that of P.Y.14 but, also has quite a few differences to the P.Y.83 trace. The inverse coupled sample is also shows the same features. The ^{13}C chemical shifts of the two AAOT/AADMCA show them to be different in a few respects. In the mixed coupled sample the acetyl methyl has a new resonance at 25.7 ppm and the aromatic methyl resonance is also split, the two resonances coming at 17.6 and 19.0 ppm. The C-Cl resonances are at 121.1 and 123.6 ppm for the mixed coupled sample and for the inverse coupled sample they are at 119.5 and 122.6 ppm. The inverse coupled sample only has one resonance each for the two methyls, but has two resonances for the acetyl carbonyl group. The crude inverse coupled AAA/AAMX sample (pattern 4) is very similar to that for the mixed coupled equivalent. On recrystallisation the structure becomes much more ordered and the trace for the recrystallised inverse coupled AAA/AAMX (pattern 5) is much

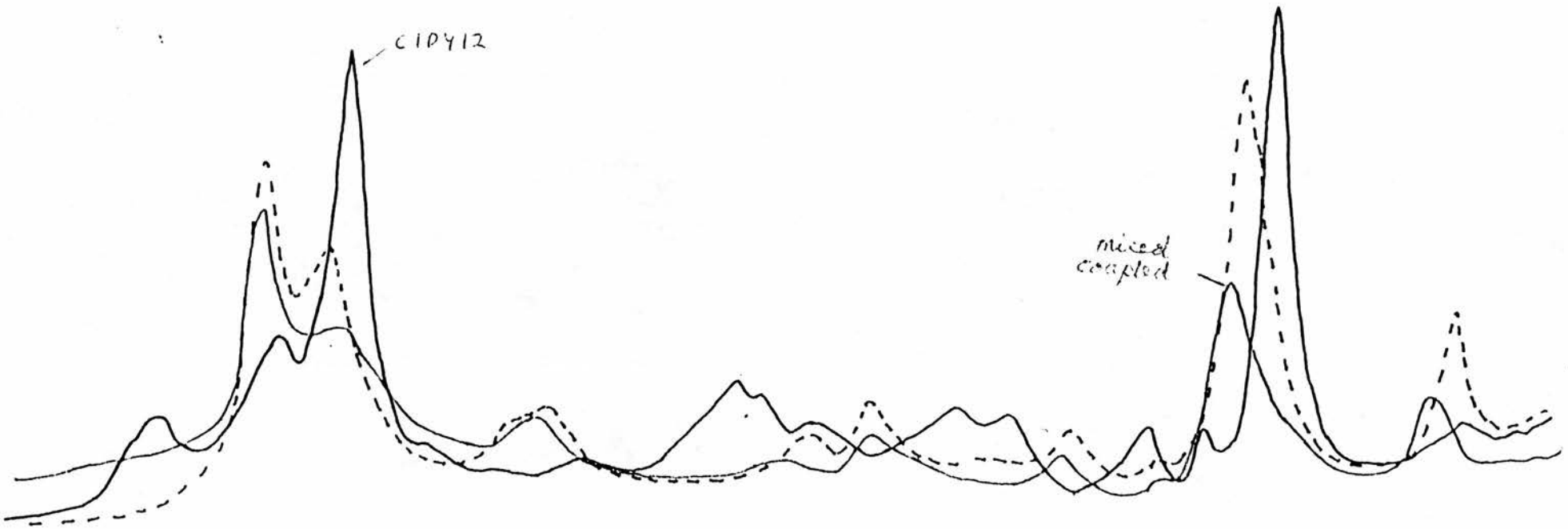
stronger and therefore clearer. The rest of the inverse coupled XRD traces are all somewhere in between the two relevant C.I. pigment yellow XRD traces.

pattern 1

—— CIPY12

--- CIPY13

—— MIXED COUPLING: 50% AAA, 50% AAMX

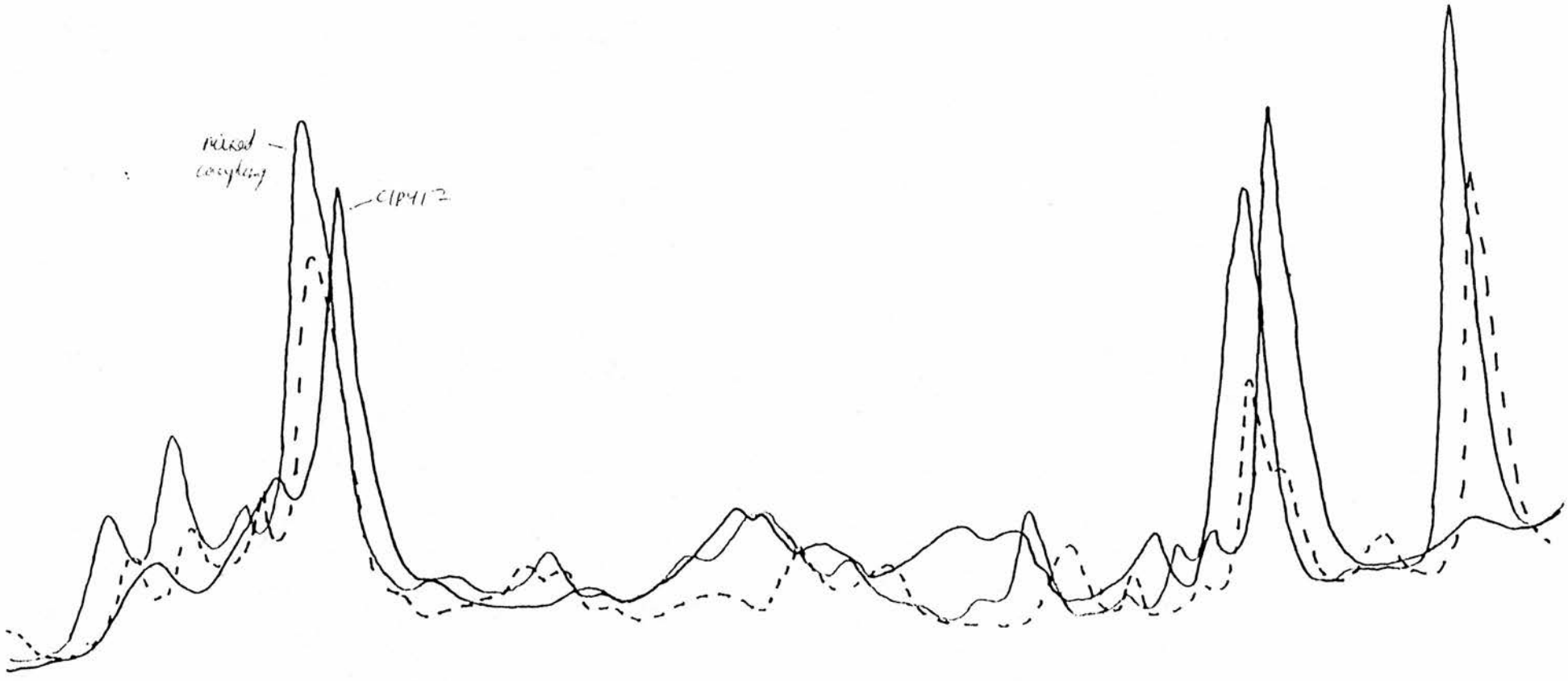


pattern 2

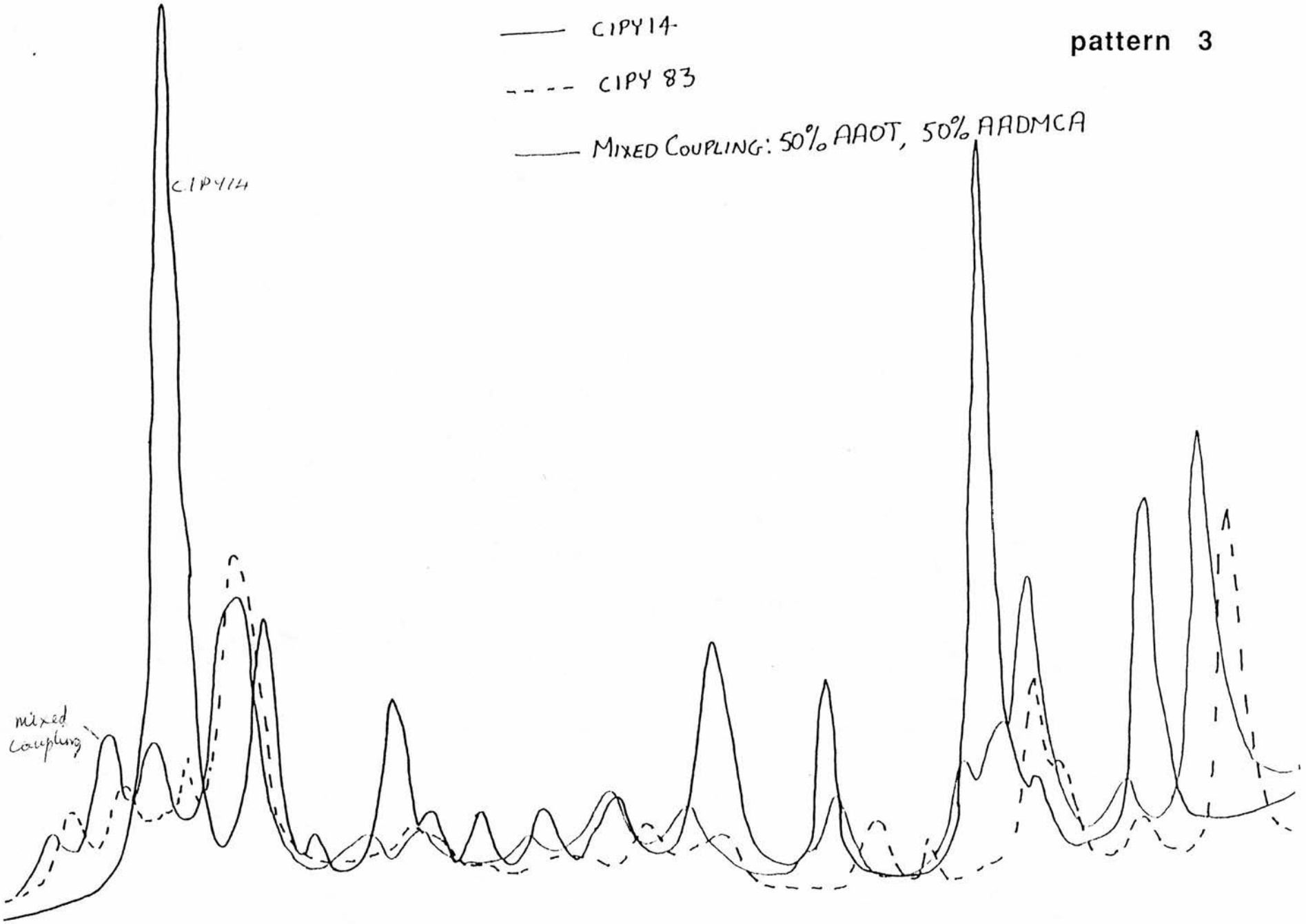
—— CIPY12

- - - - CIPY83

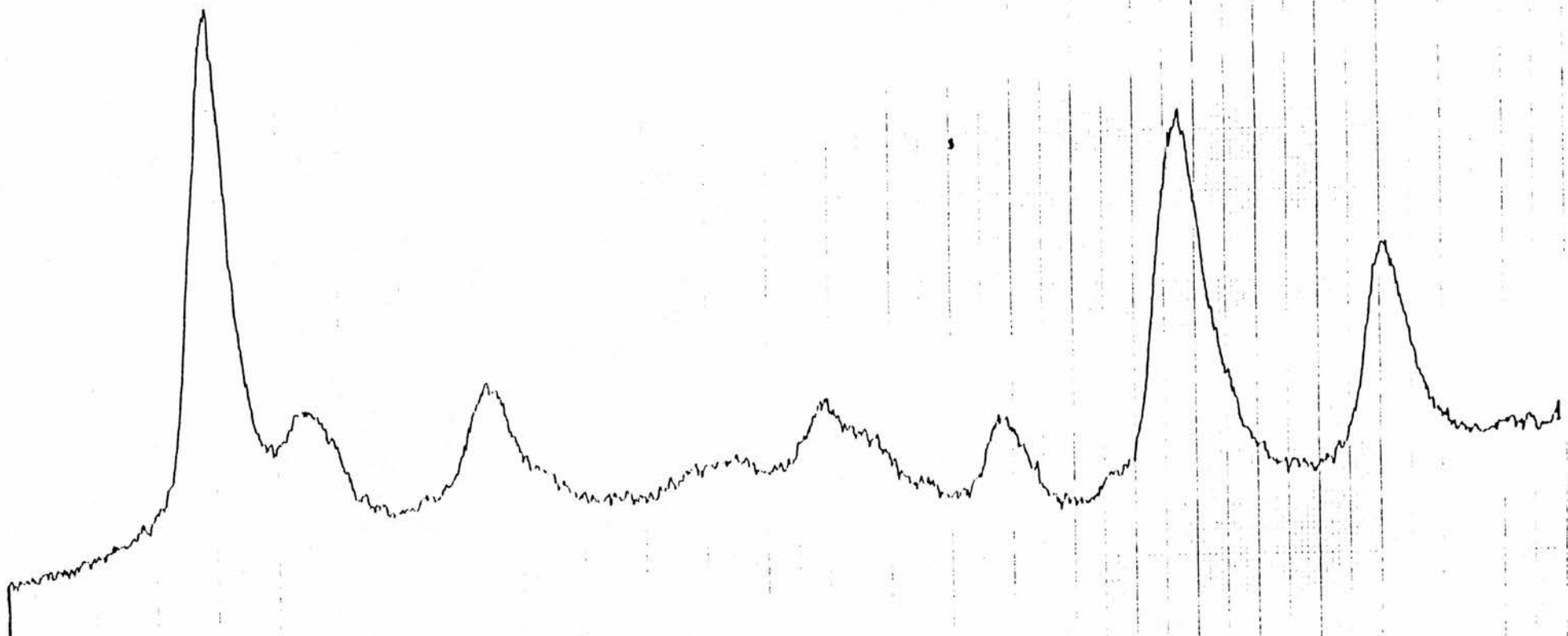
—— MIXED COUPLING: 50% AAA, 50% AADMCA

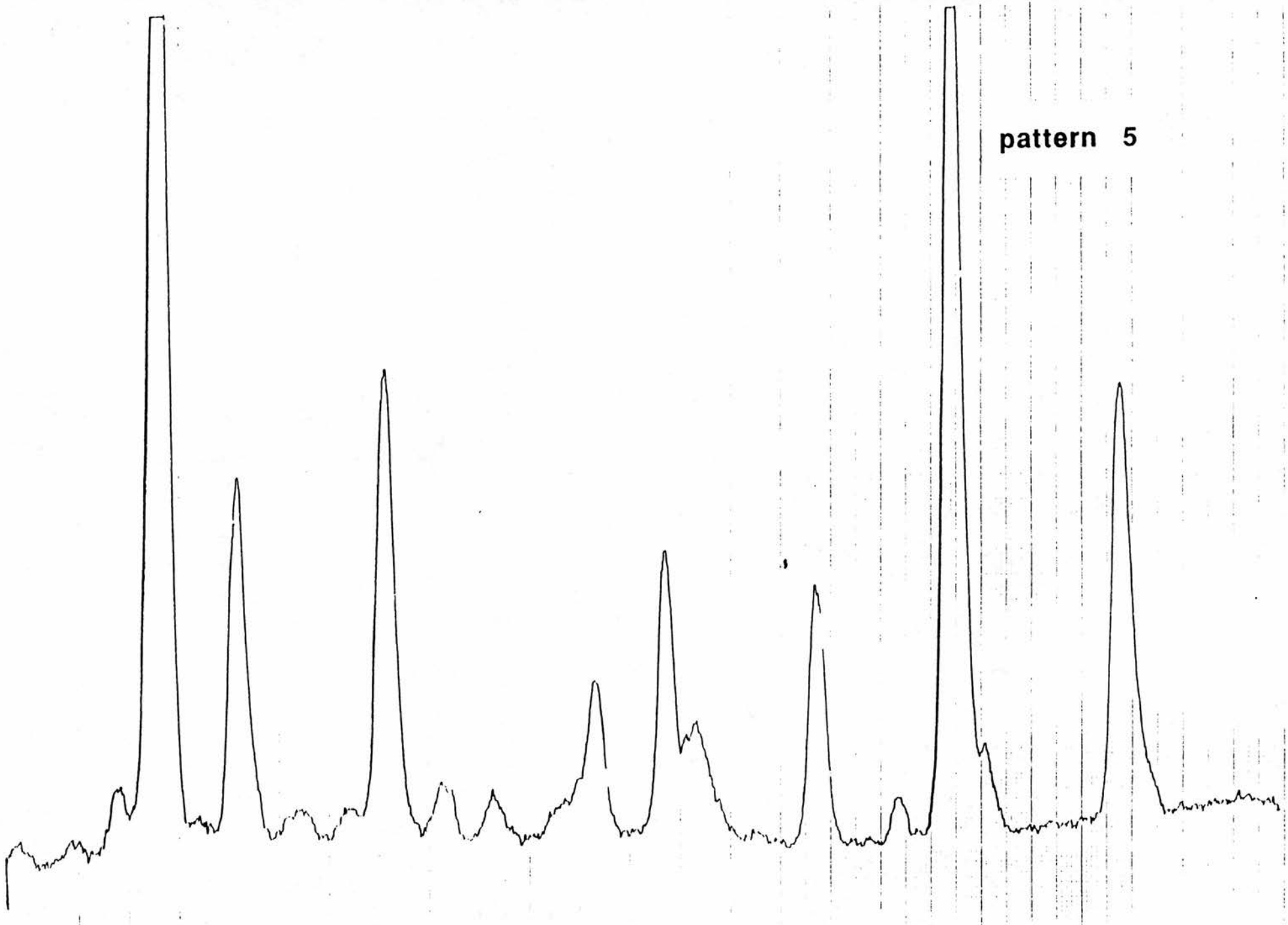


pattern 3


CIPY14-
CIPY 83
MIXED COUPLING: 50% AAOT, 50% AADMCA
CIPY14
mixed coupling

pattern 4



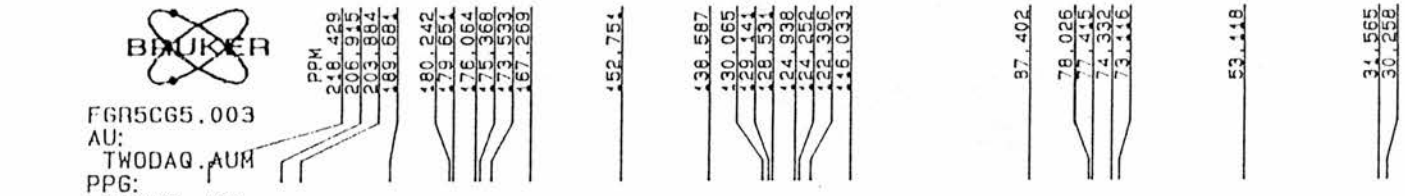

pattern 5

APPENDIX 2

SOLID-STATE ^{13}C N.M.R. SPECTRA

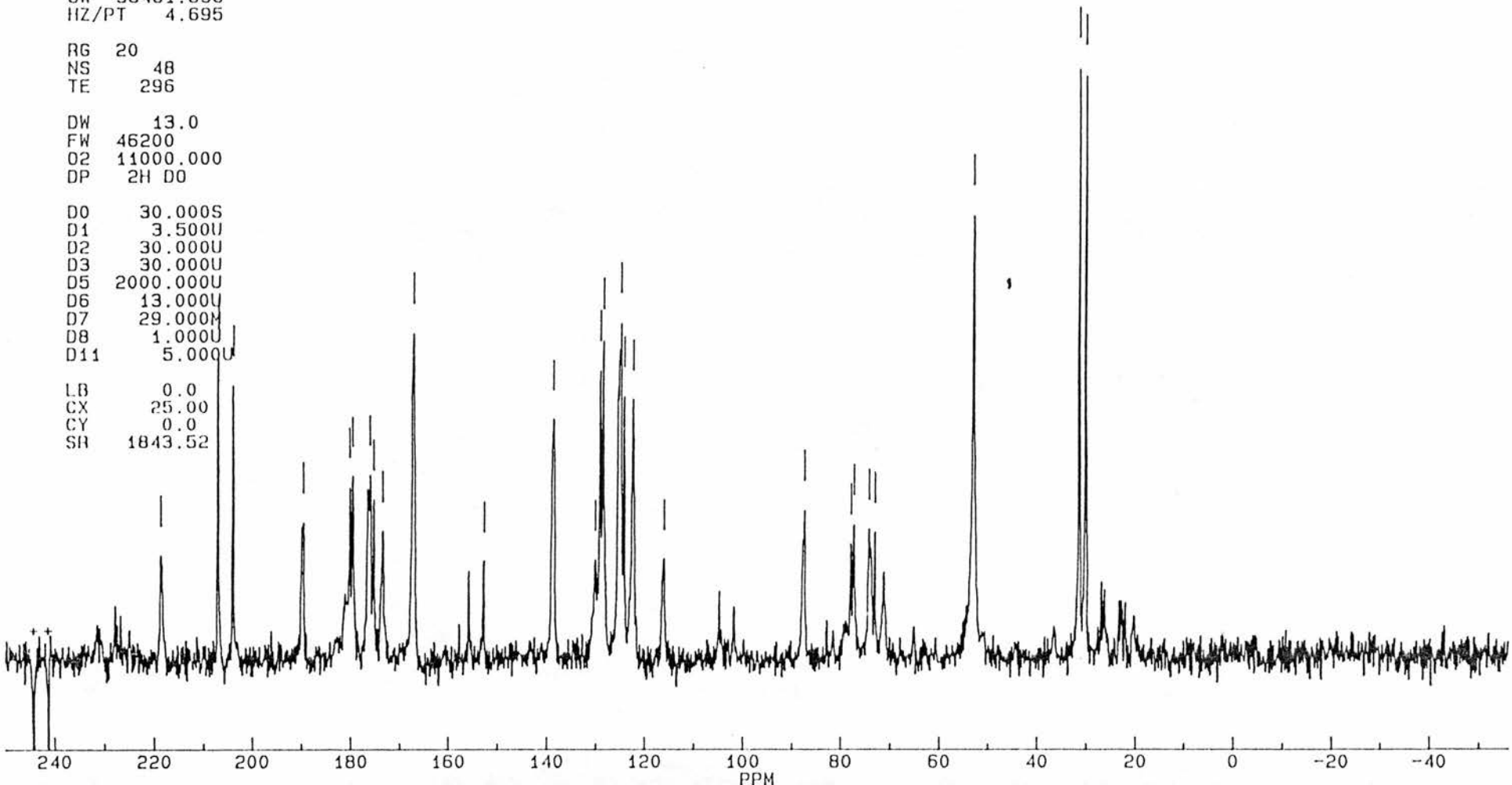
AAA SPUN AT 6.4 KHZ AND AT 293K

spectrum 1



FGR5CG5.003
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 7-10-91

SF	125.758
O1	14000.000
SI	16384
TD	2048
SW	38461.538
HZ/PT	4.695
RG	20
NS	48
TE	296
DW	13.0
FW	46200
O2	11000.000
DP	2H D0
D0	30.000S
D1	3.500U
D2	30.000U
D3	30.000U
D5	2000.000U
D6	13.000U
D7	29.000M
D8	1.000U
D11	5.000U
LB	0.0
CX	25.00
CY	0.0
SR	1843.52



AADMCA SPUN AT 6 KHZ AND AT RT. (293K)

spectrum 2

BRUKER

PPM
212.421
206.597
196.447
190.910
177.137
164.303
158.537
152.680
148.488
142.718
128.946
116.107
113.663
110.260
104.488
100.070
94.532
80.571
61.926
56.795
46.467
31.507
8.644

FGR5CG1.002
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 7-10-91

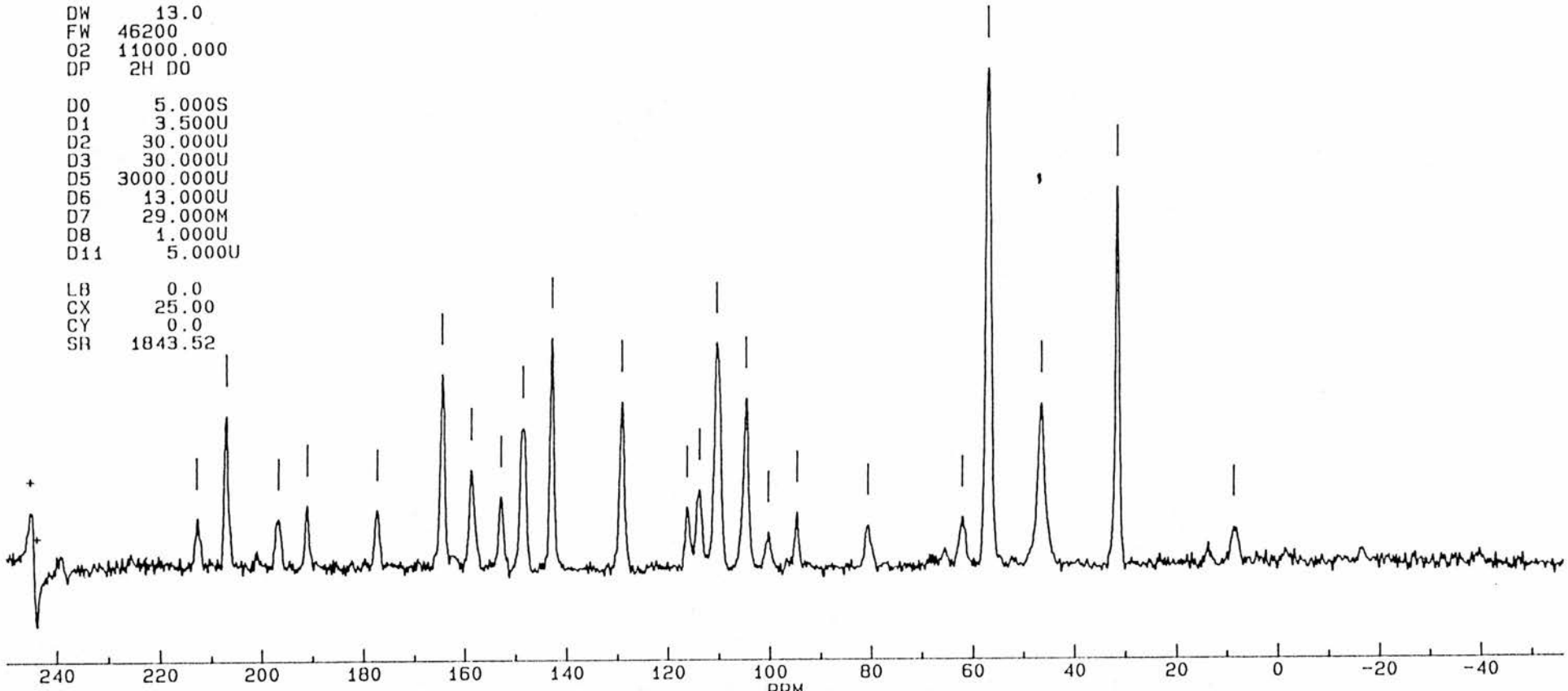
SF 125.758
O1 14000.000
SI 16384
TD 1200
SW 38461.538
HZ/PT 4.695

RG 20
NS 64
TE 296

DW 13.0
FW 46200
O2 11000.000
DP 2H D0

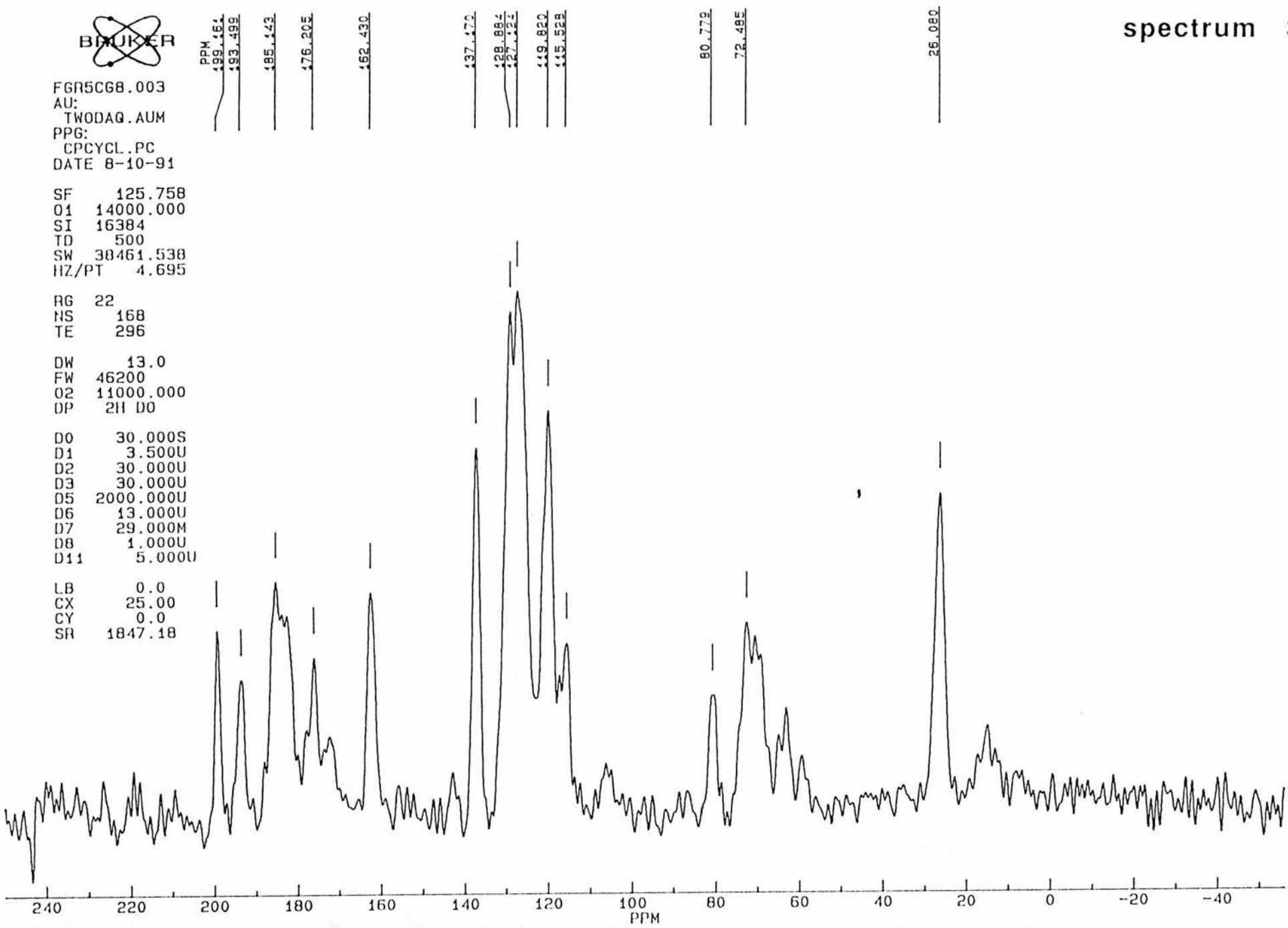
D0 5.000S
D1 3.500U
D2 30.000U
D3 30.000U
D5 3000.000U
D6 13.000U
D7 29.000M
D8 1.000U
D11 5.000U

LB 0.0
CX 25.00
CY 0.0
SR 1843.52



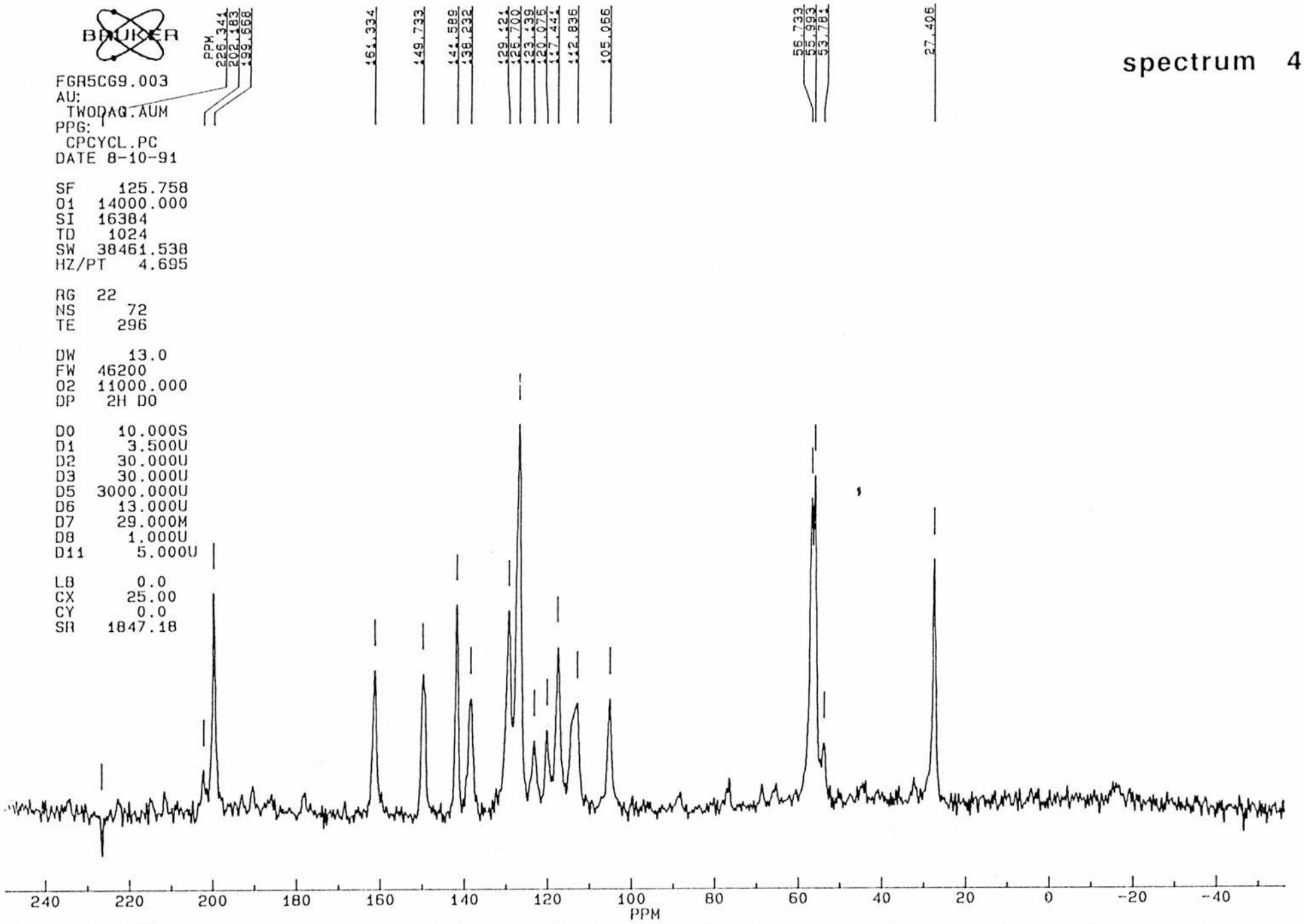
MONO 12 AT 7 KHZ AND AT 293K

spectrum 3

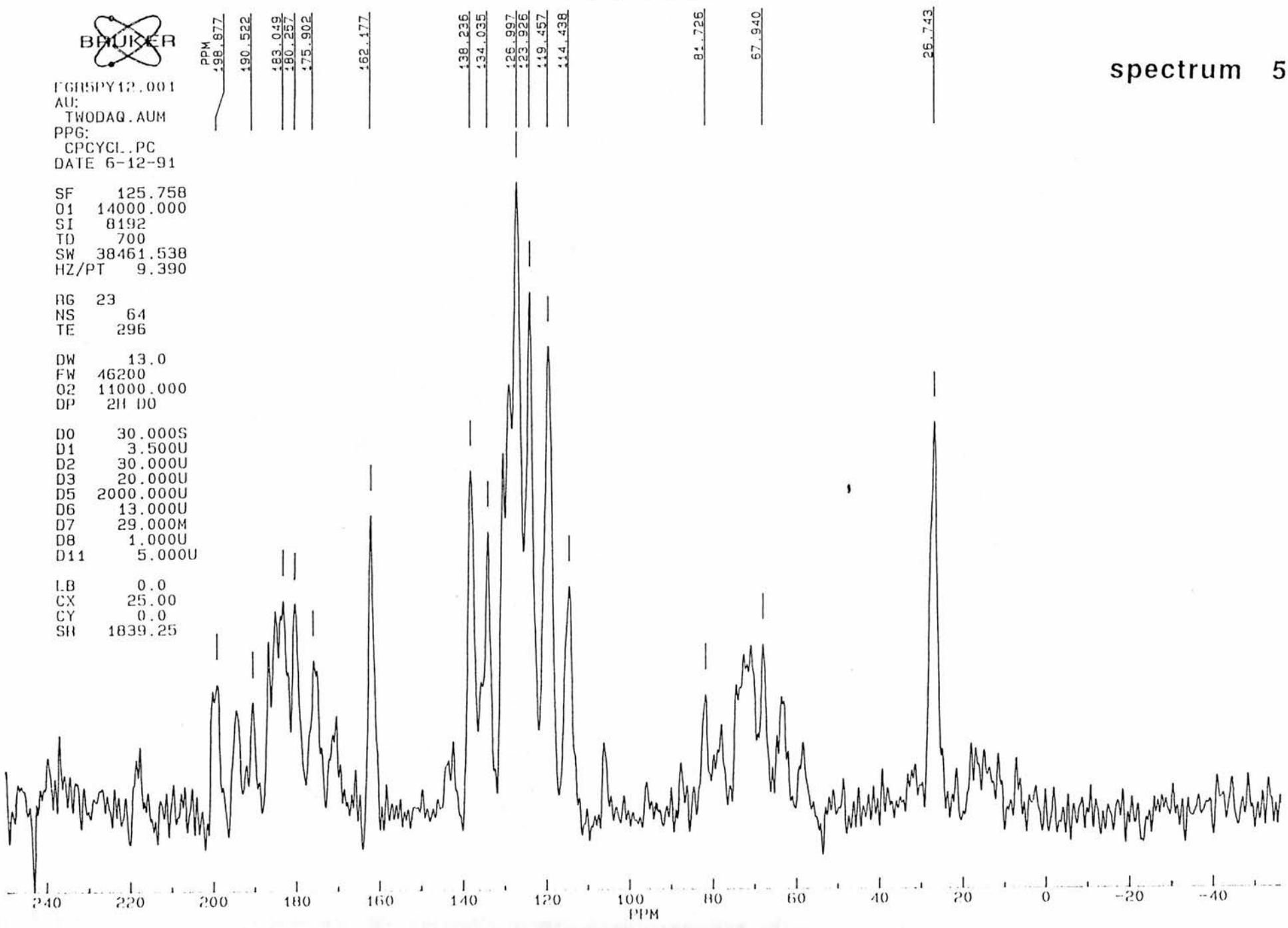


MONO 83 AT 9.0 KHZ AT 293K

spectrum 4



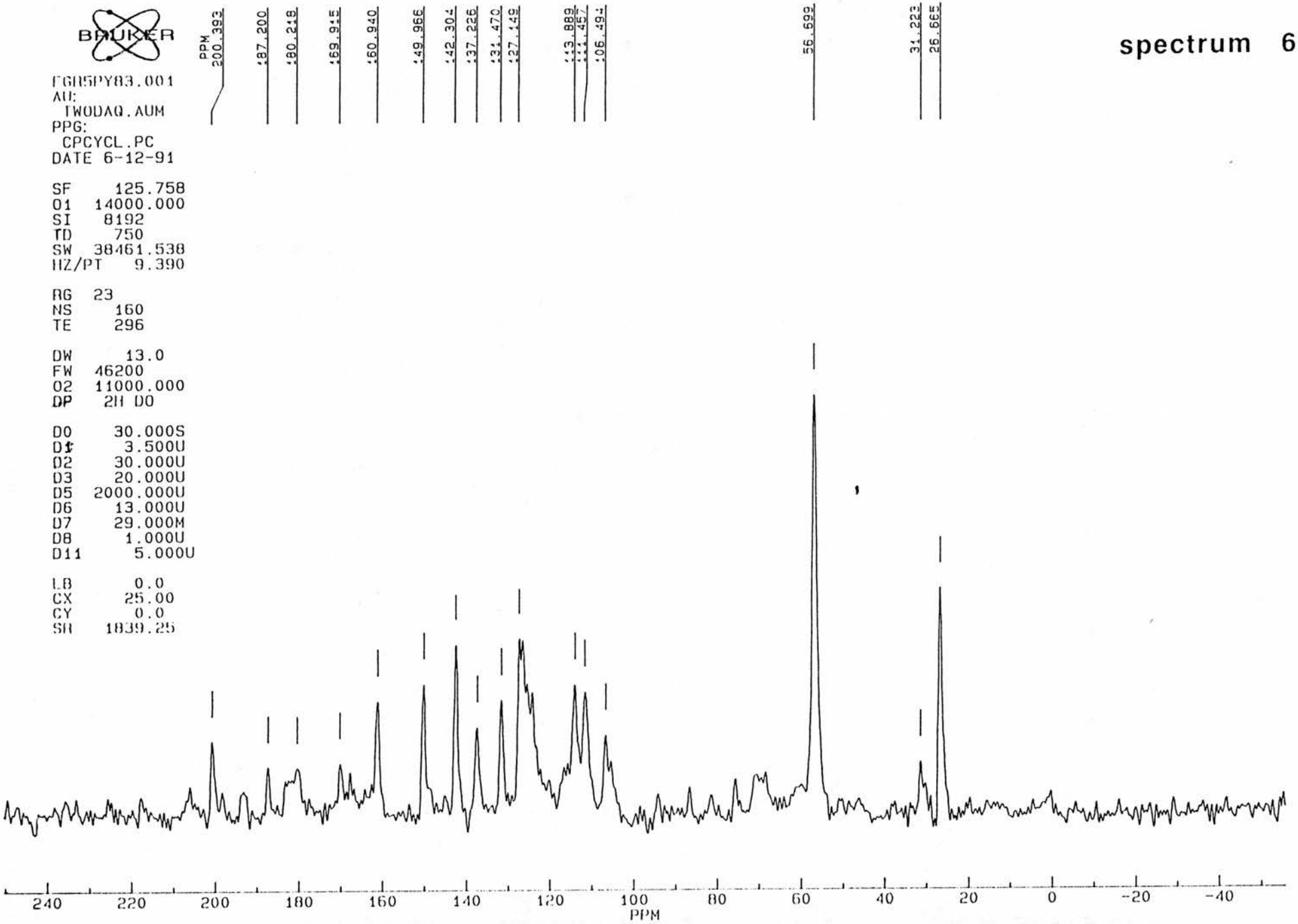
PY12 AT 7.1 KHZ



spectrum 5

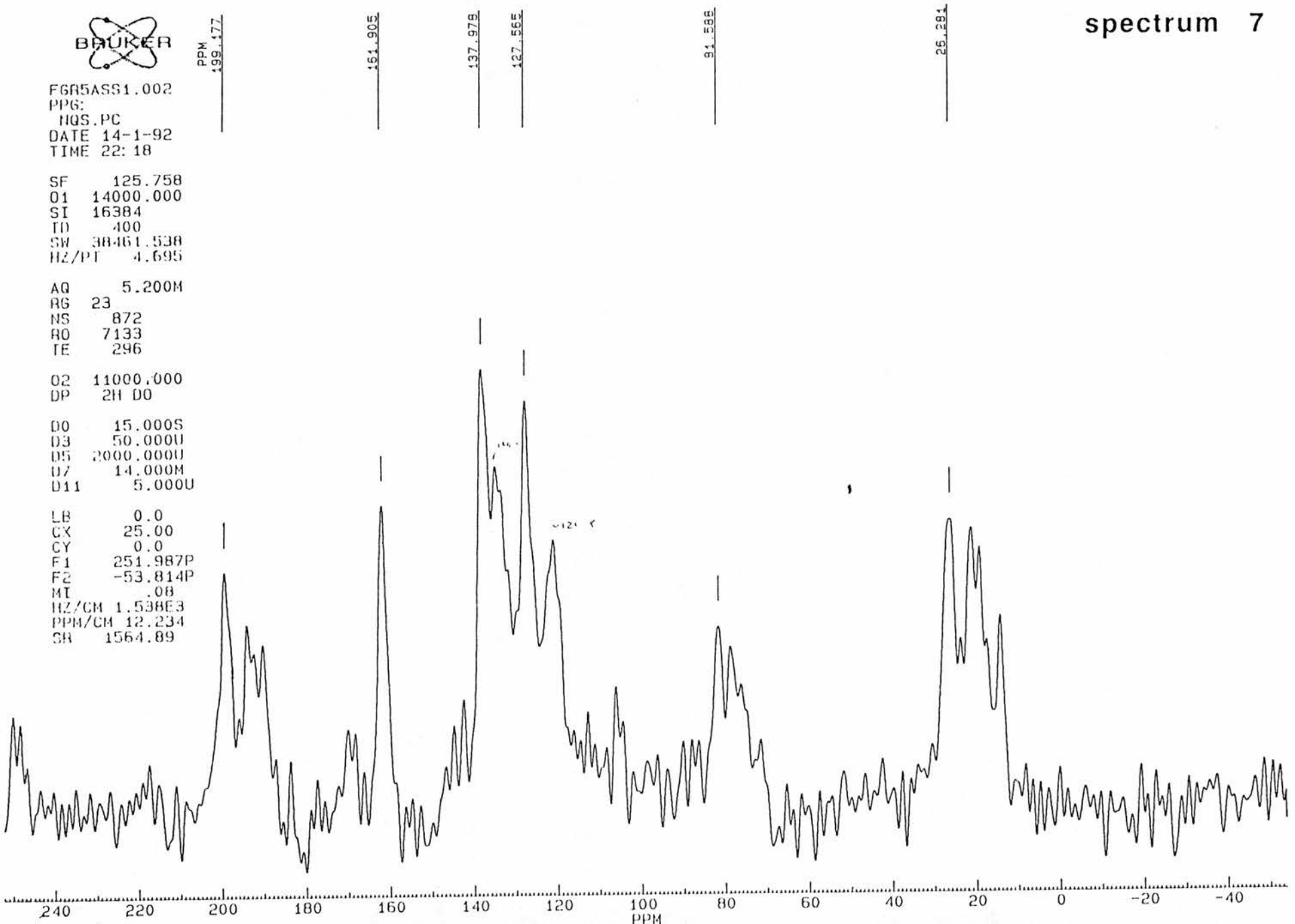
PY83 AT 7.0 KHZ

spectrum 6



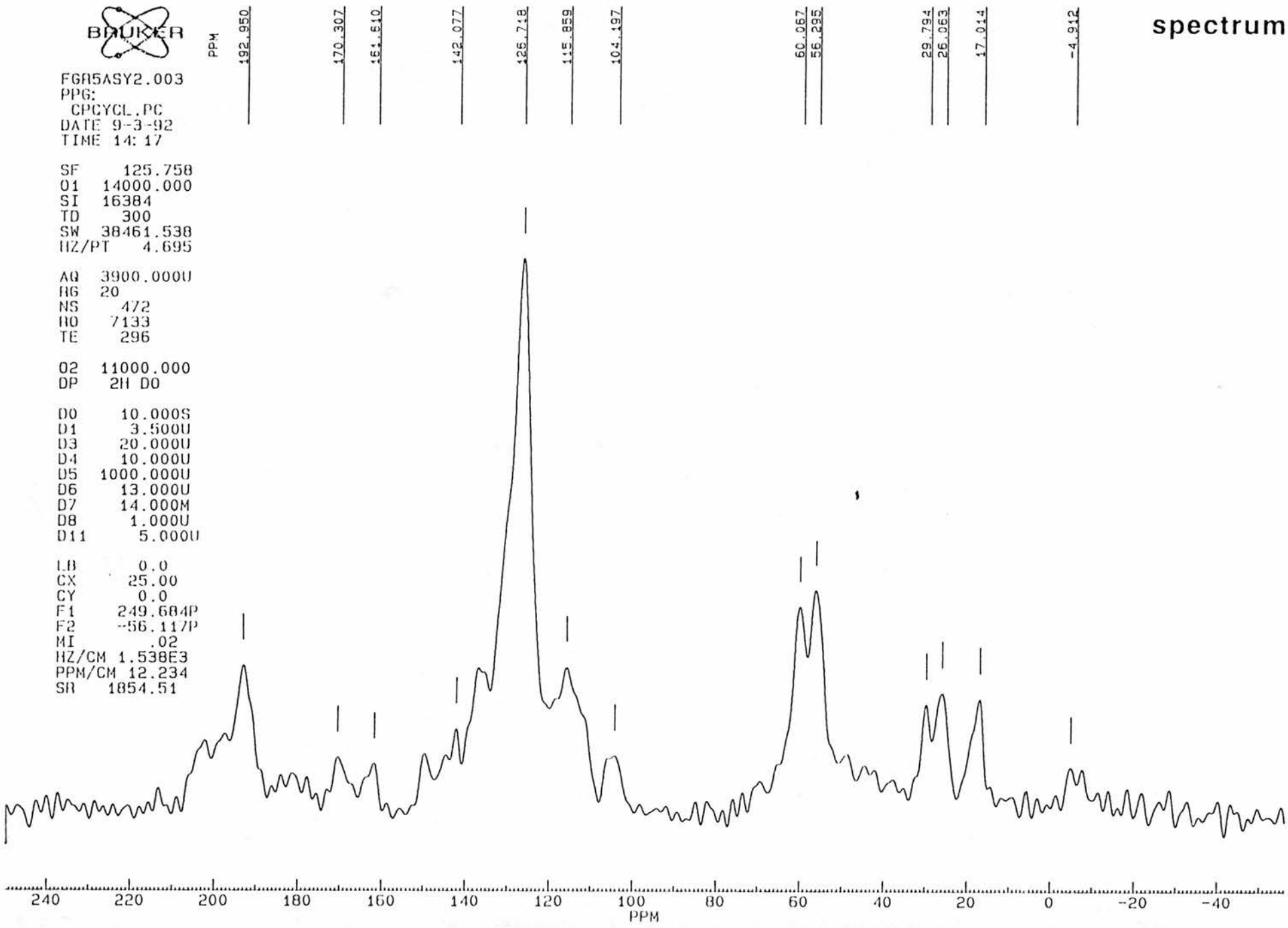
ASSYM. PY 12/13 NQS SPUN AT 7 KHZ

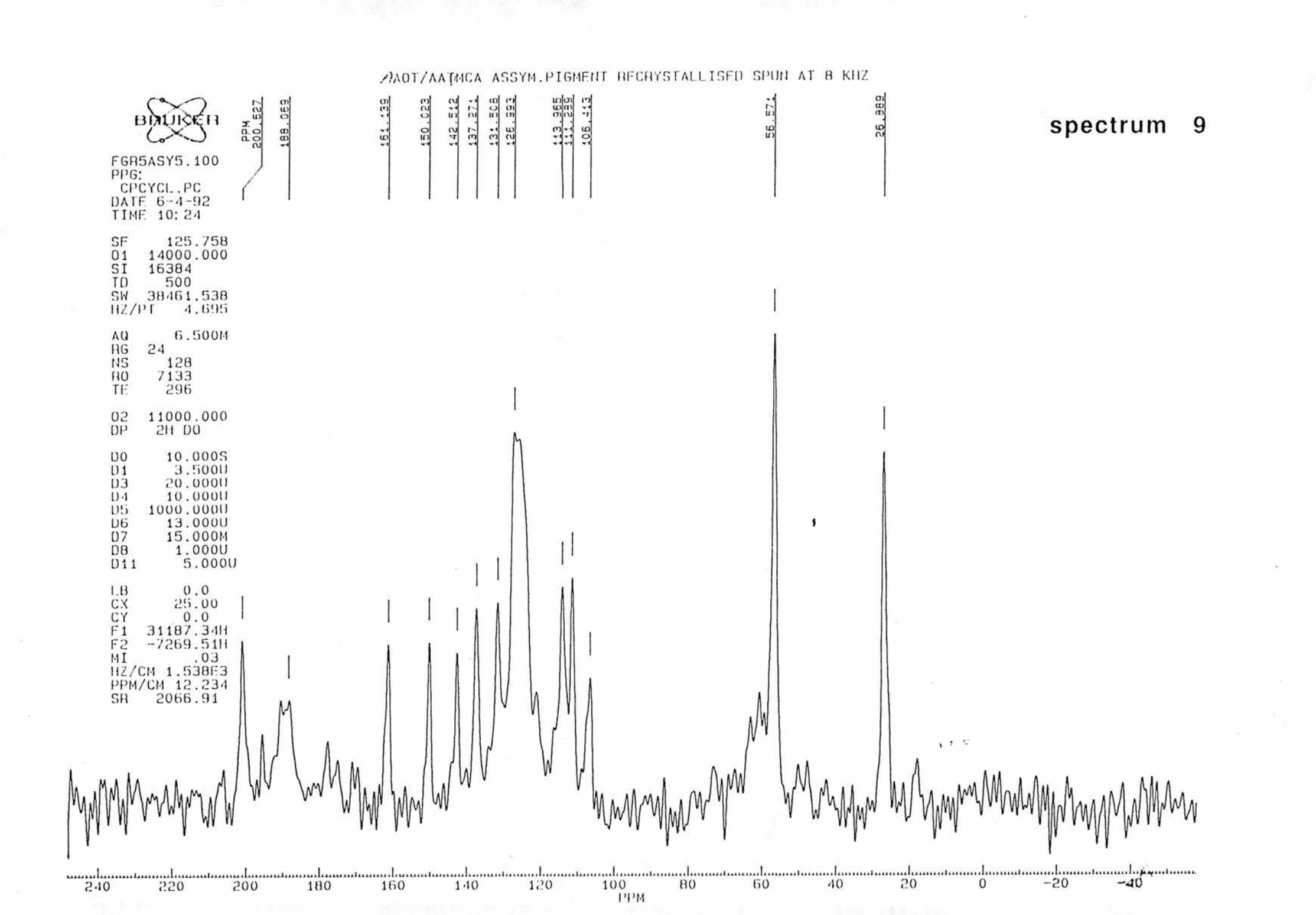
spectrum 7



ASYM. PIGMENT AAOT+AADMCA AT 8.3 KHZ

spectrum 8

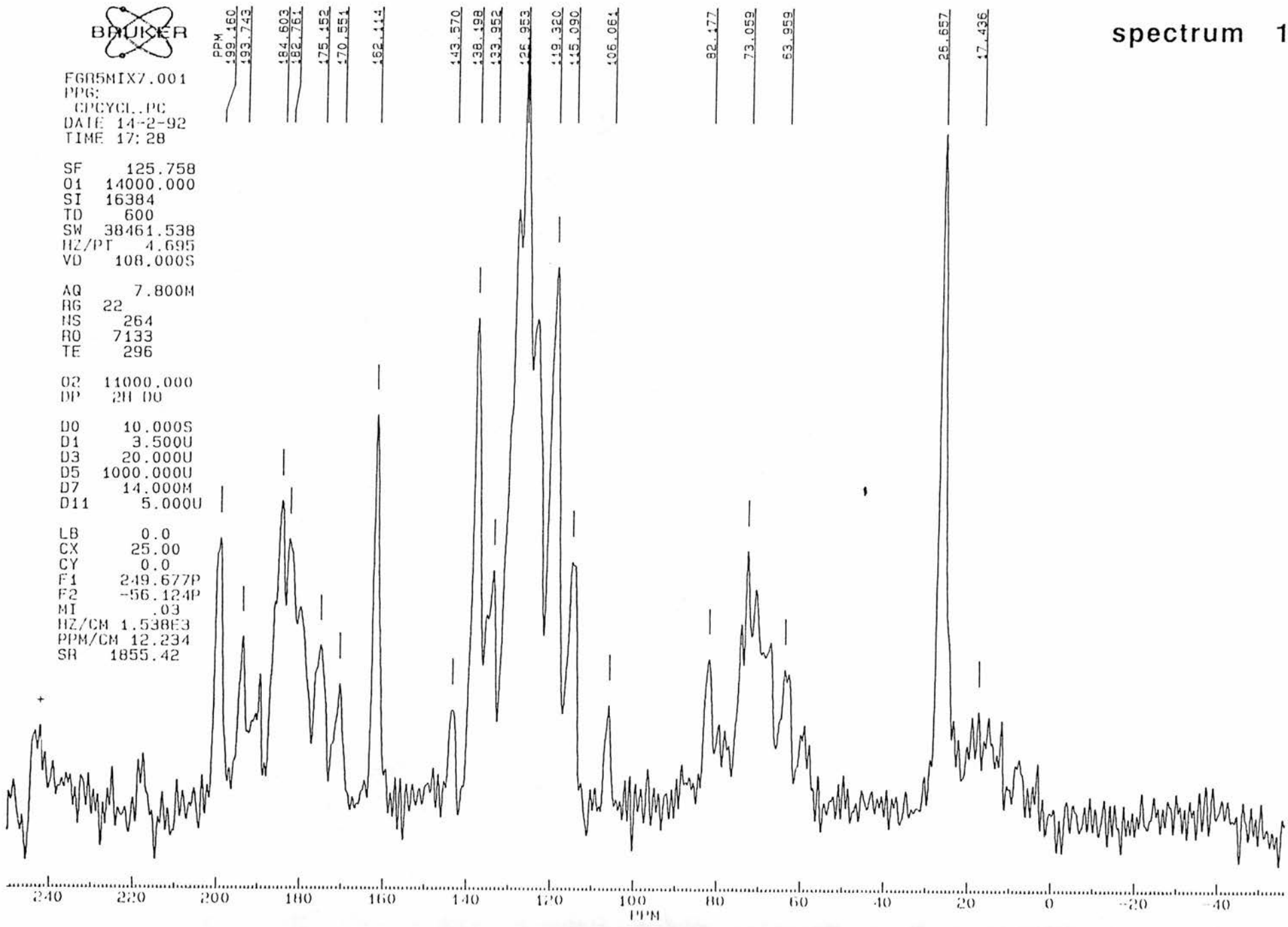



/AAOT/AA[MCA ASSYM.PIGMENT RECRYSTALLISED SPUN AT 8 KHZ
BRUKER
PPM
200.627
188.069
161.139
150.023
142.512
137.274
131.508
126.393
113.965
111.289
106.443
56.571
26.989
FGR5ASY5.100
PPG:
CPCYCL.PC
DATE 6-4-92
TIME 10:24
SF 125.758
O1 14000.000
SI 16384
TD 500
SW 38461.538
HZ/PT 4.695
AQ 6.500M
RG 24
NS 128
RO 7133
TE 296
O2 11000.000
DP 2H D0
D0 10.000S
D1 3.500U
D3 20.000U
D4 10.000U
D5 1000.000U
D6 13.000U
D7 15.000M
D8 1.000U
D11 5.000U
LB 0.0
CX 25.00
CY 0.0
F1 31187.34H
F2 -7269.51H
MI .03
HZ/CM 1.538E3
PPM/CM 12.234
SR 2066.91
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
PPM

spectrum 9

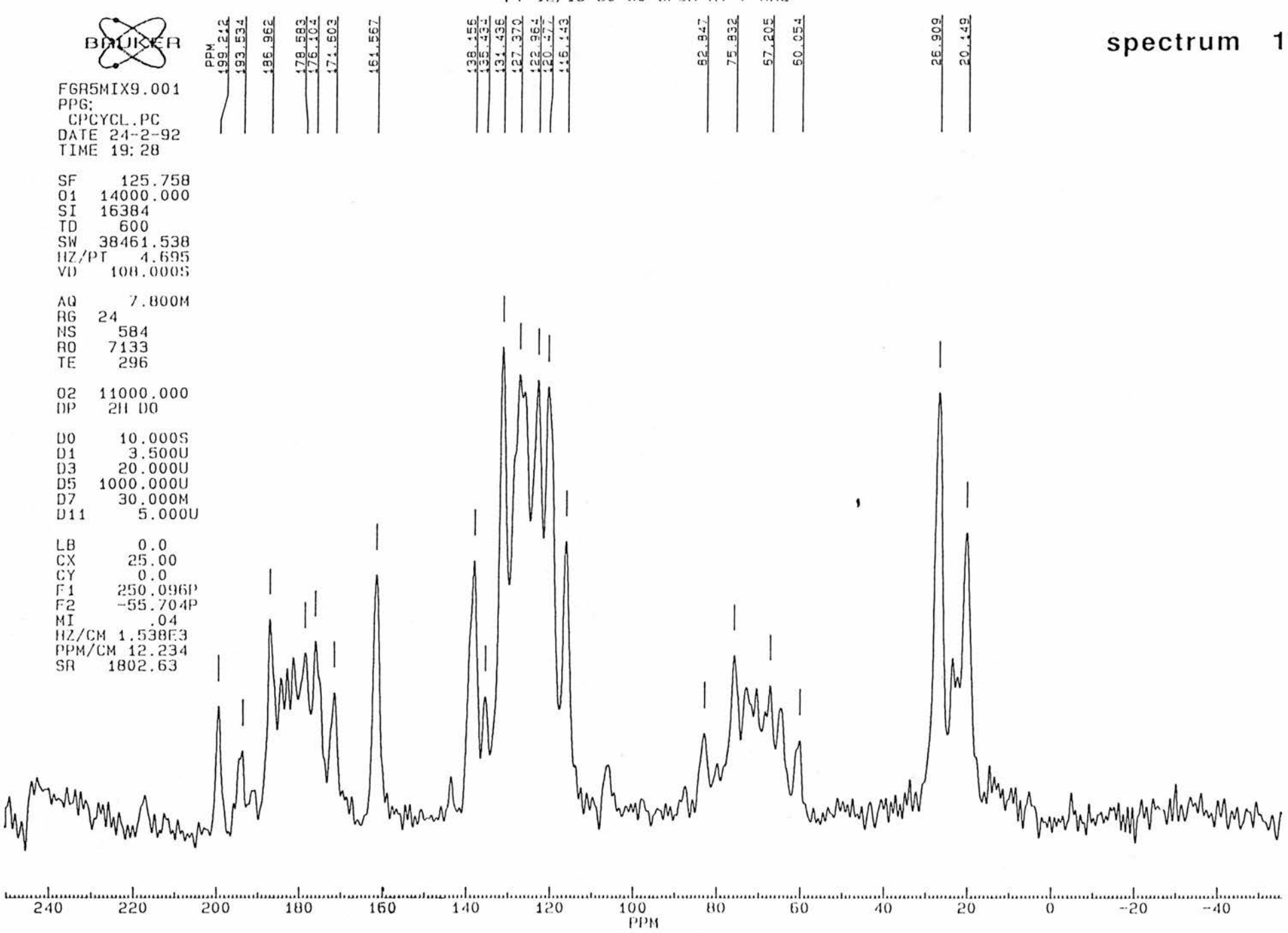
MIXED COUPLING 12/13 90/10 SPUN AT 7 KHZ

spectrum 10



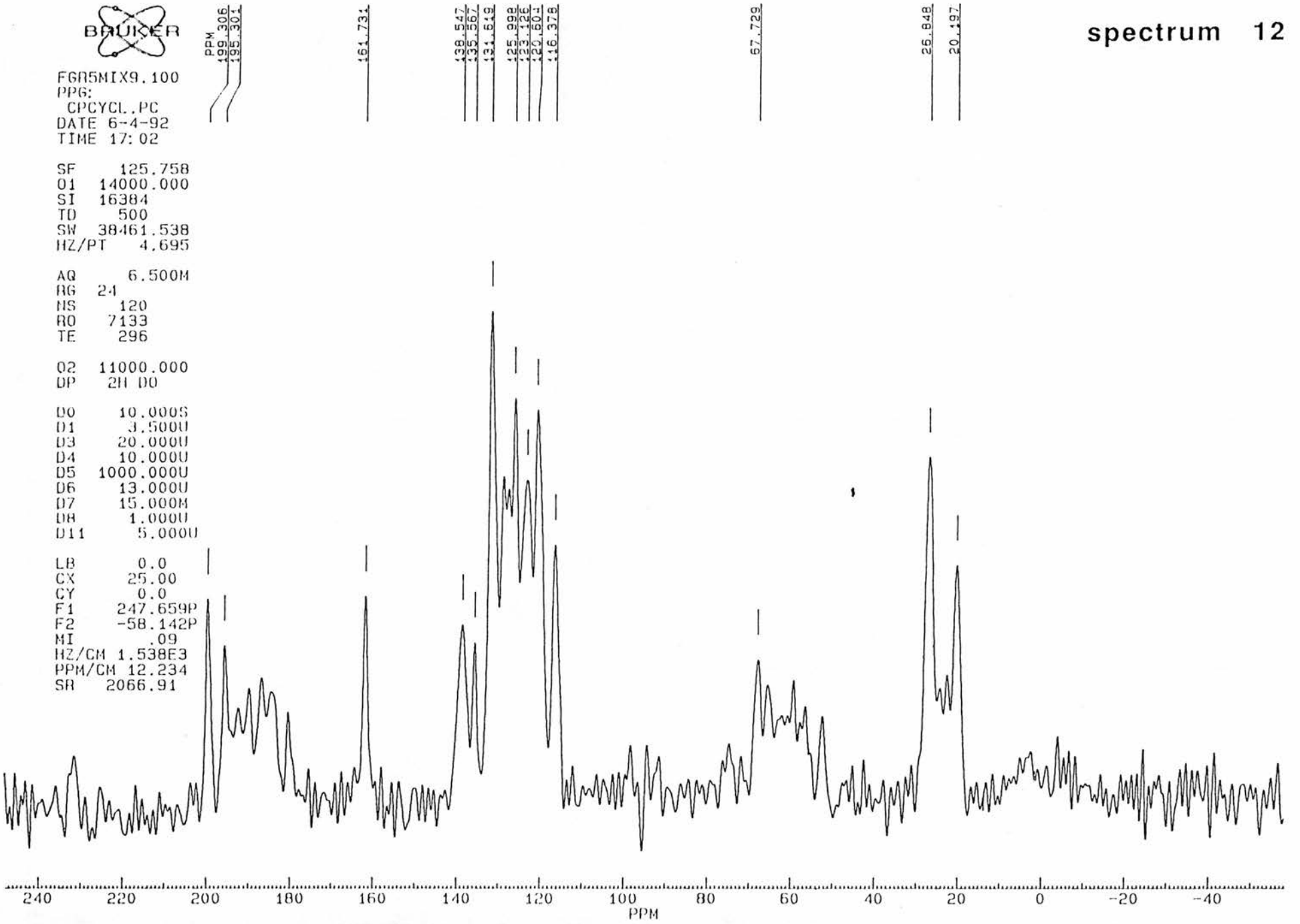
PY 12/13 50-50 SPUN AT 7 KHZ

spectrum 11



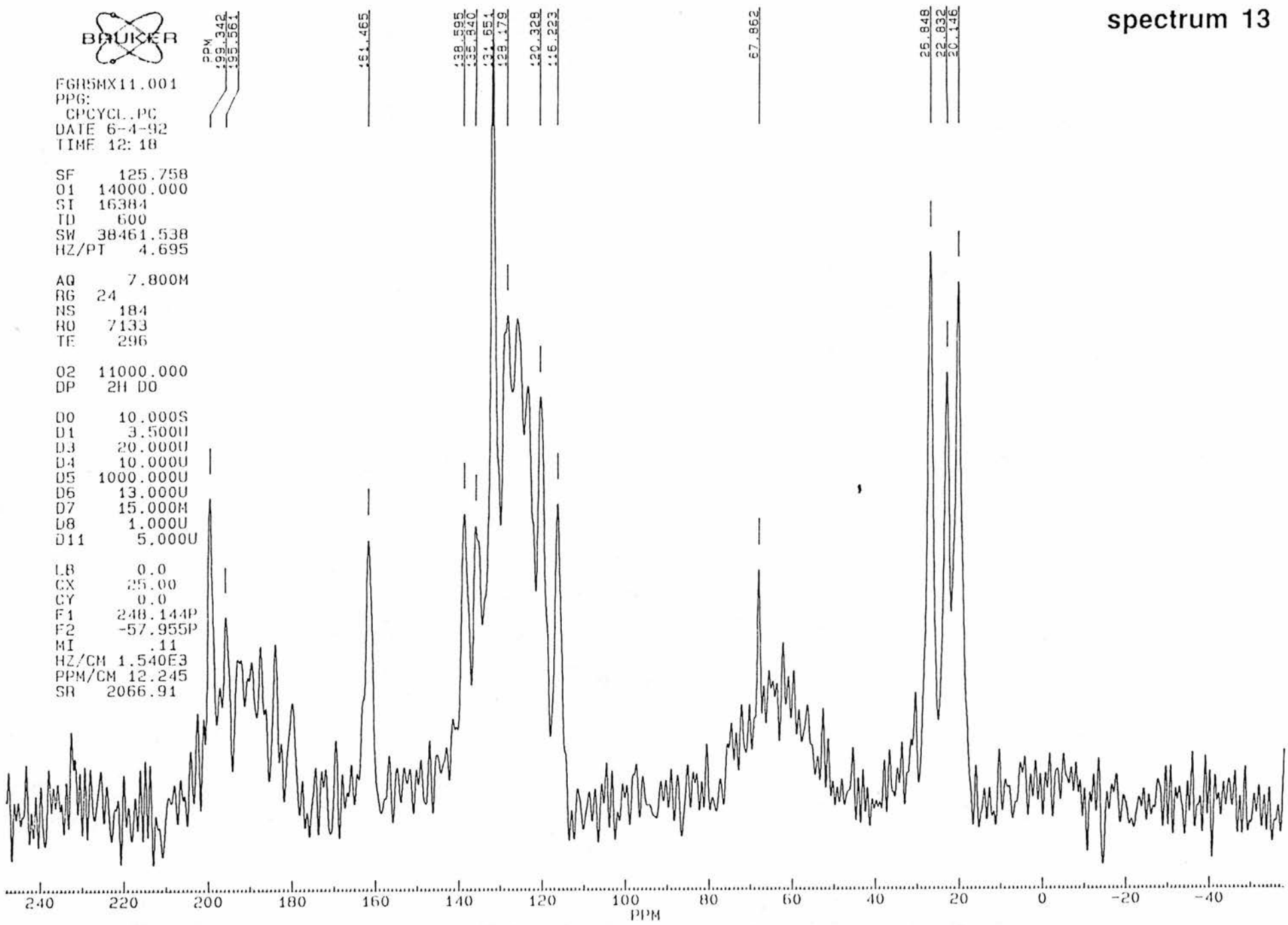
RECRYSTALLISED MIXED COUPLED P.Y. 12/13 50:50 SPUN AT 8 KHZ

spectrum 12



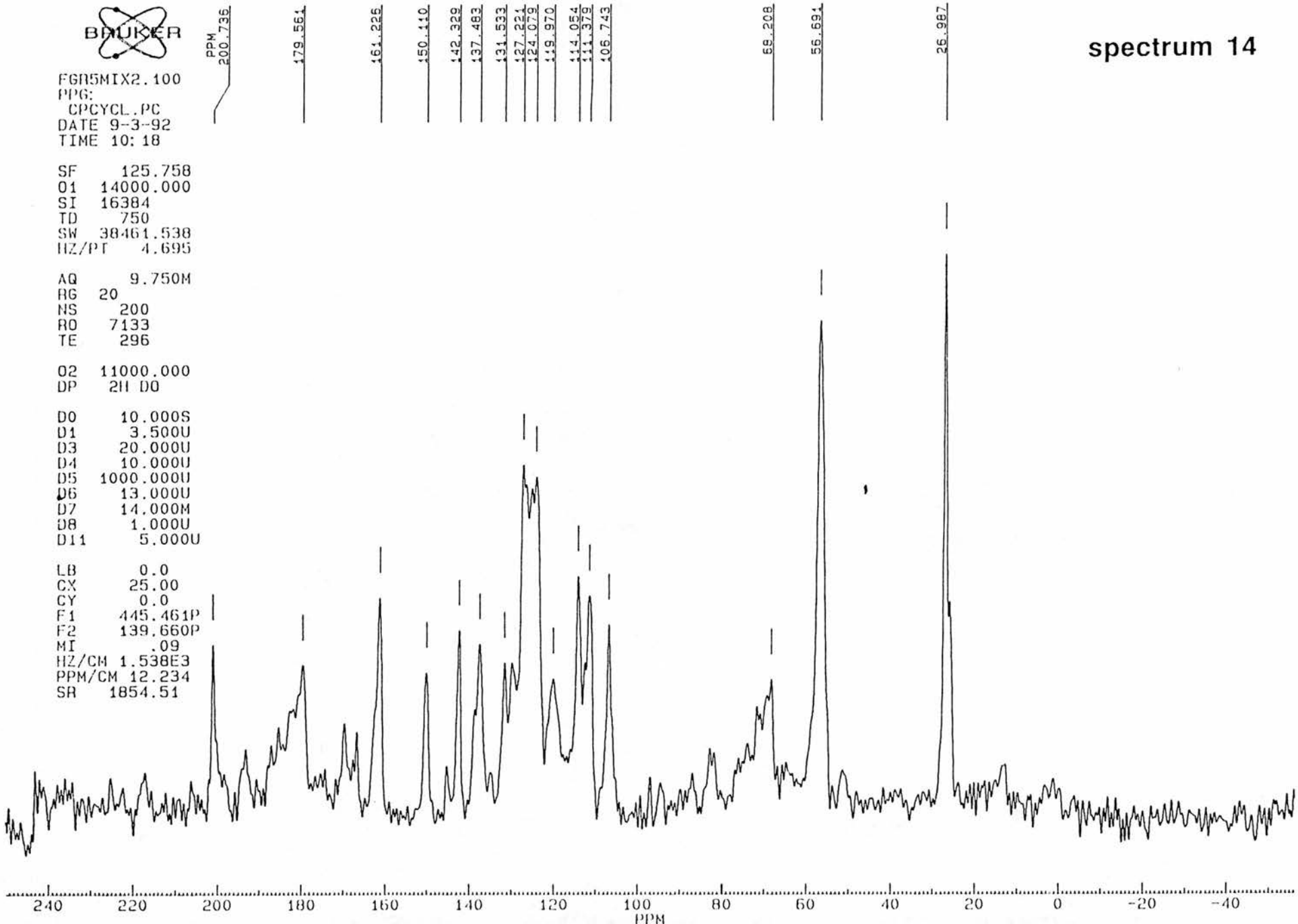
MIXED COUPLED P.Y. 12/13 10:90 SPUN AT 8 KHZ

spectrum 13

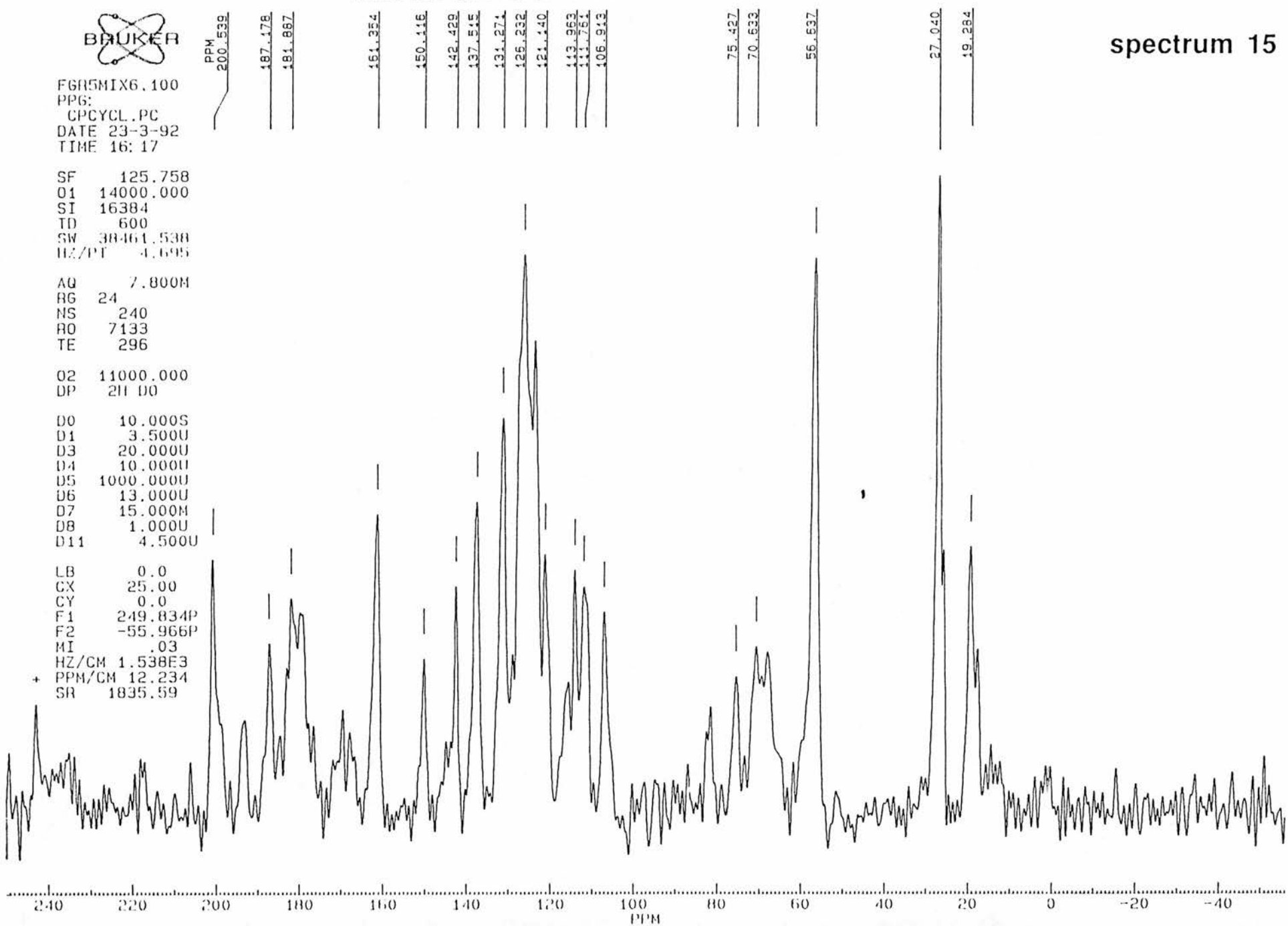


RECRYSTALLISED MIXED COUPLING 12/83 50-50% AT 7 KHZ

spectrum 14

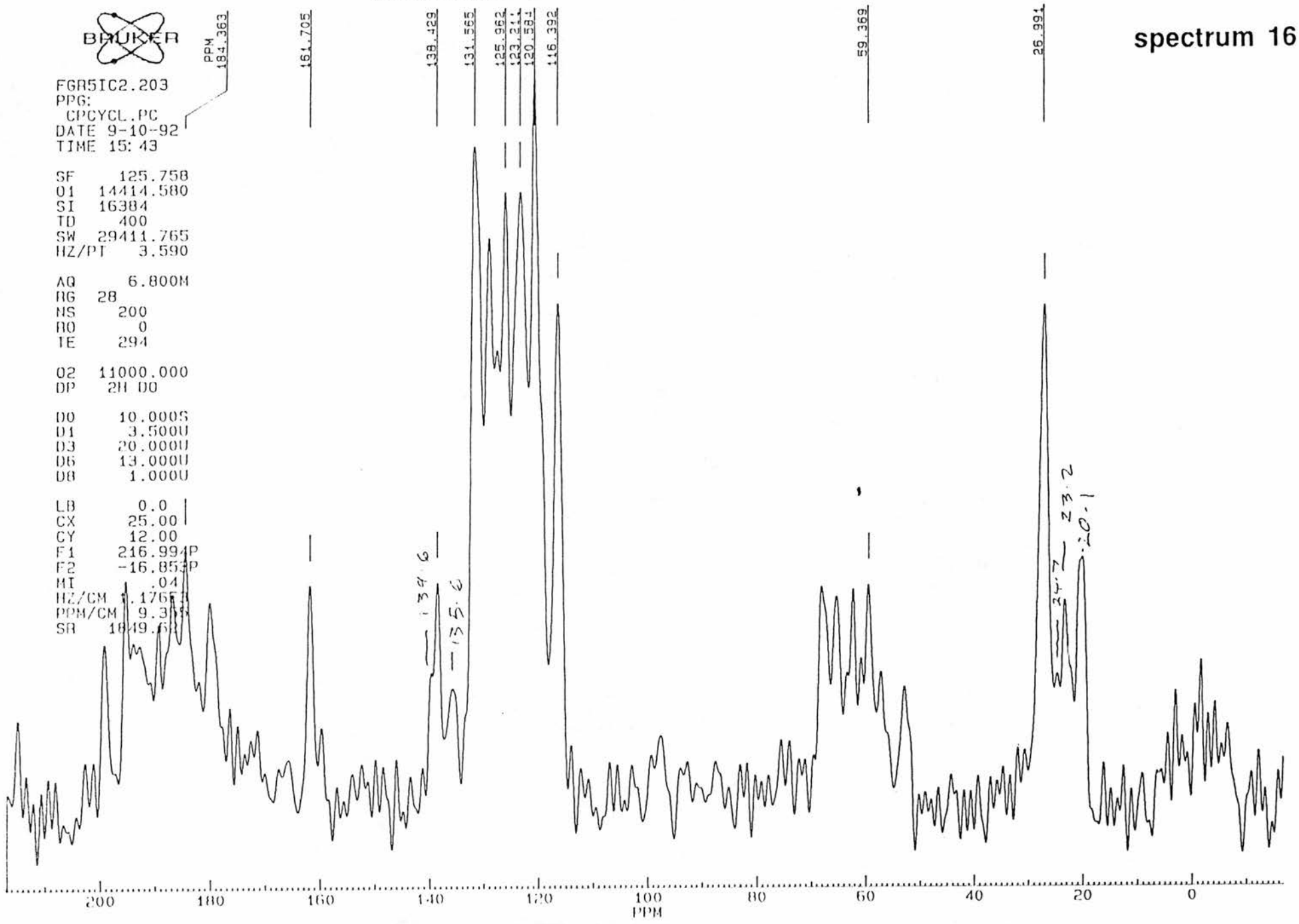


MIXED COUPLING 83/14 50-50 RECRYSTALLISED SPUN AT 7.02 KHZ



spectrum 15

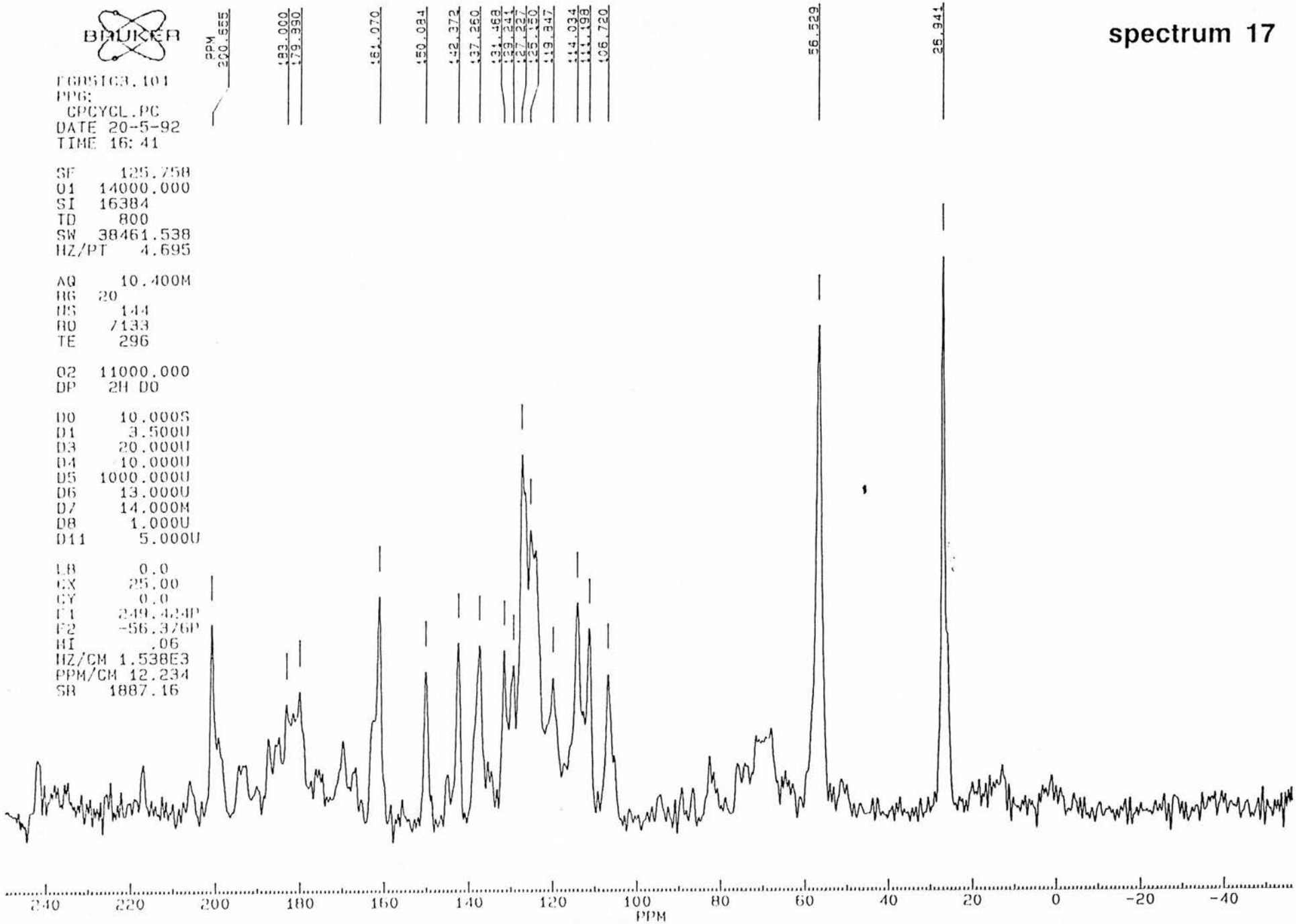
RECRYSTALLISED INVERSE COUPLED AAA/AAMX SPUN AT 8 KHZ



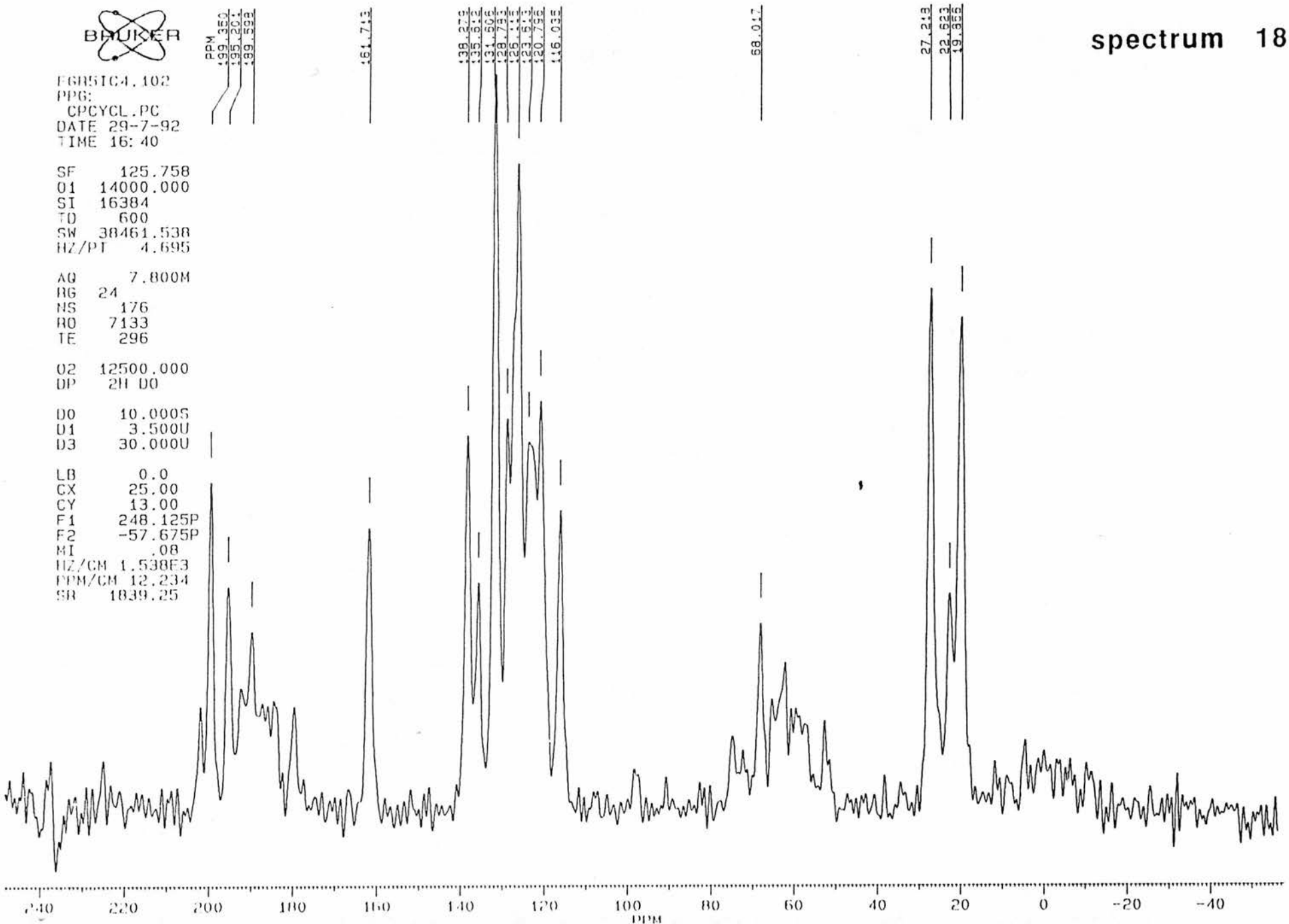
spectrum 16

RECRYSTALLISED INVERSE COUPLED AAA AND AADMCA SPUN AT 7 KHZ

spectrum 17



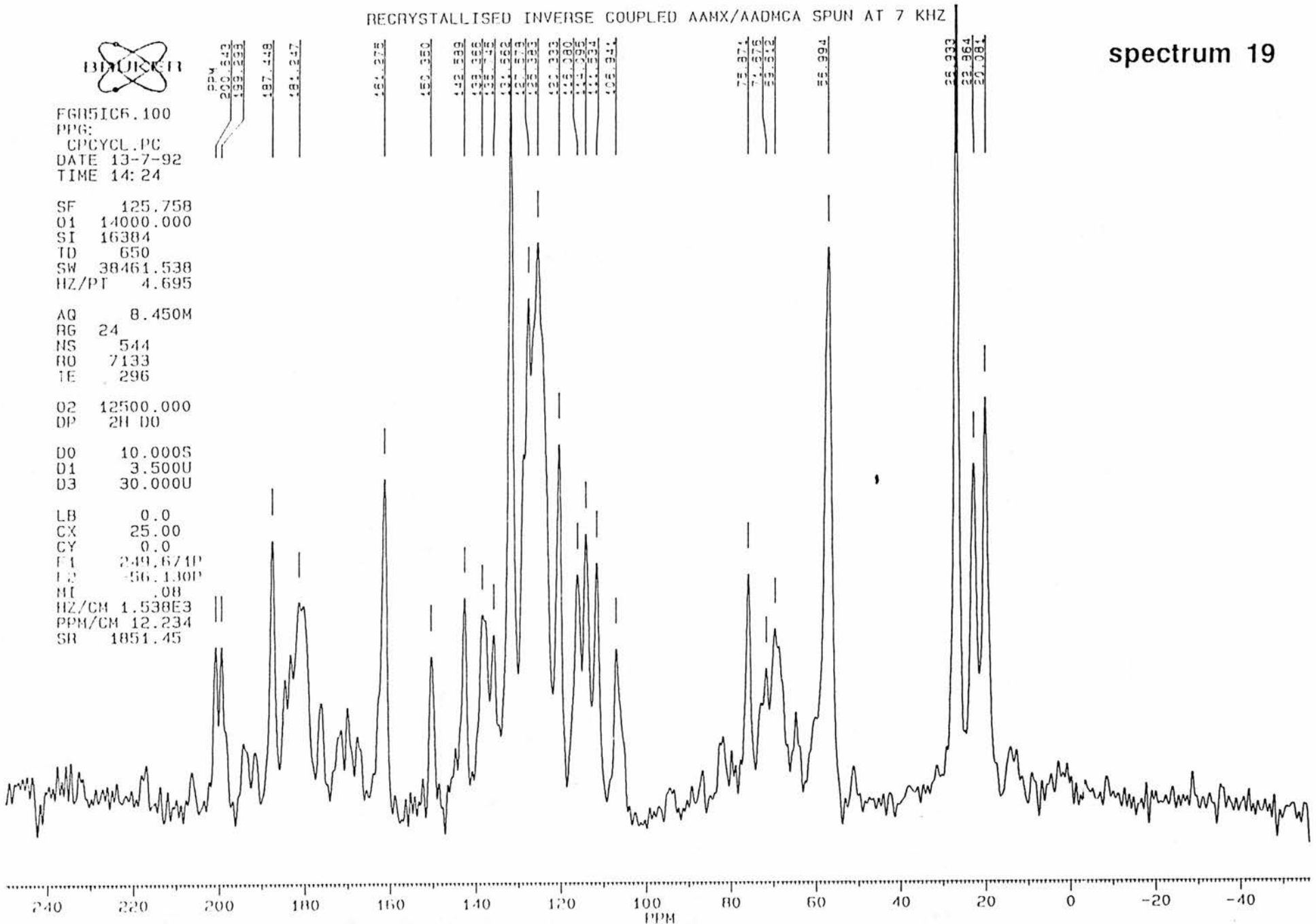
RECRYSTALLISED INVERSE COUPLED AAMX/AAOT SPUN AT 8 KHZ



spectrum 18

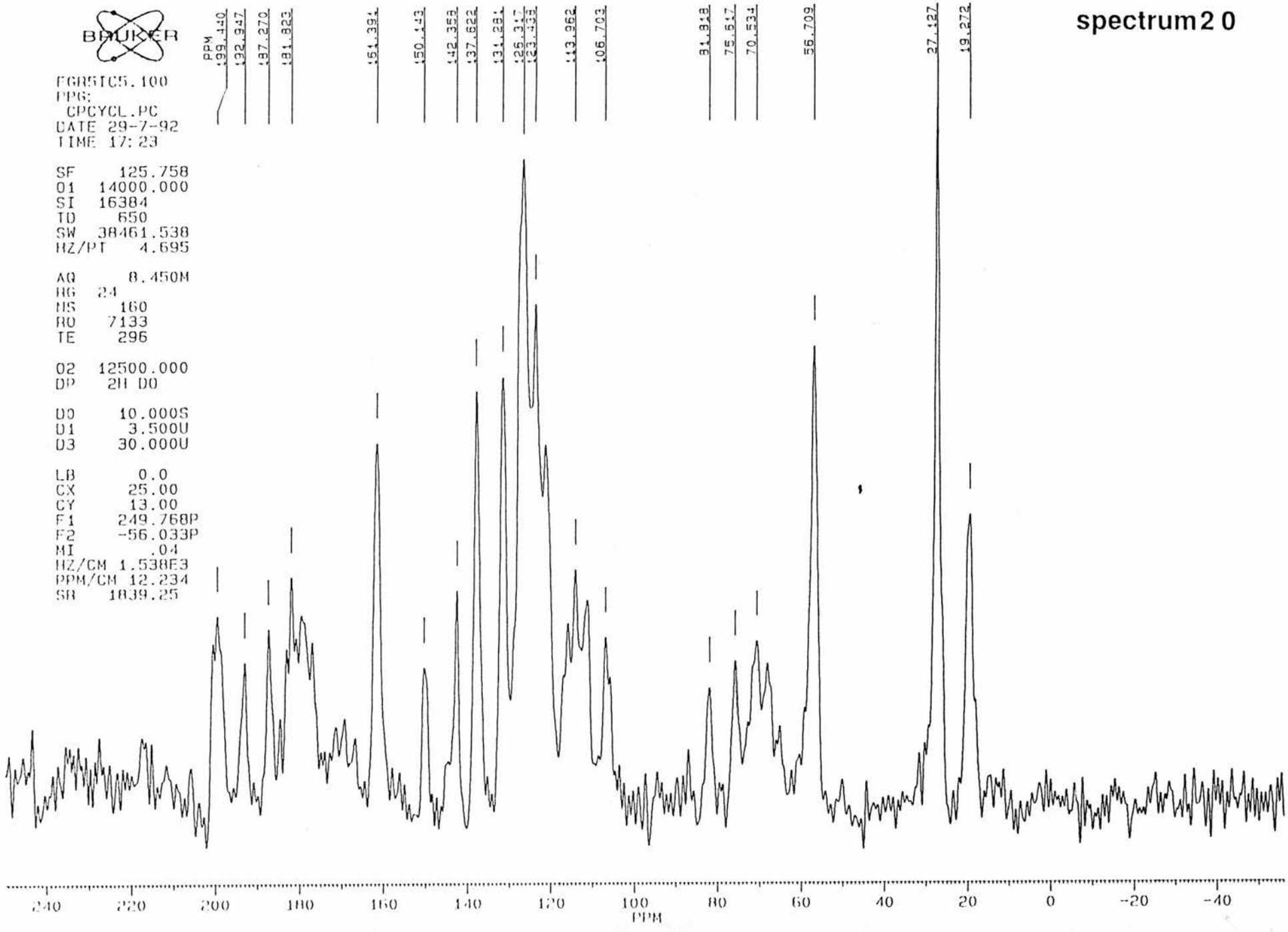
RECRYSTALLISED INVERSE COUPLED AAMX/AADMCA SPUN AT 7 KHZ

spectrum 19



RECRYSTALLISED INVERSE COUPLED AAOT/AADMCA SPUN AT 7 KHZ

spectrum2 0



REFERENCES

1) Ciba-Geigy internal report, Chemistry of Classical Organic Pigments.

2) The Pigment Handbook, 2nd edition, ed. P.A. Lewis, Vol.1, p 535, John Wiley & sons, New York (1988).

3) Dr. I.A. MacPherson, Ciba-Geigy Internal Report, Basic Concepts in Pigment Technology (1979).

4) J.E. Monteith, Ph.D thesis (1990).

5) J.W. Akitt, N.M.R. and Chemistry 2nd edition (1983), Chapman and Hall.

6) Fukushima, E., Roeder, S.B.W., Experimental Pulse N.M.R.: a nuts and bolts approach, Addison-Wesley, London (1981).

7) Ross-Petersen, K.J., Hjeds, H., Dansk Tiddskr. Farm. 43, 1969.

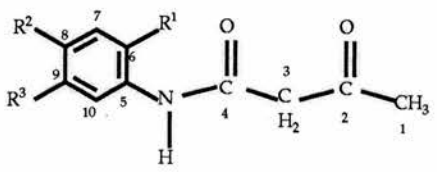
8) Etter, M.C., Reutzel, S.M., and Vojta, G.M., Journal of Molecular Structure, 237 (1990) pp 165-185.

9) Shepherd, T., Smith, D.M., Journal of the Chemical Society Perkin Transactions I, pp 501-504 (1987).

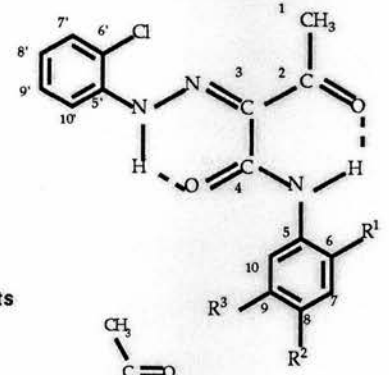
Structures and Numbering Schemes of the Basic Compounds Described in the Text

(1) (2) (3)	AAA Mono 12 P.Y.12	AAMX Mono13 P.Y.13	AAOT Mono14 P.Y.14	AAOA Mono17 P.Y.17	AAPT P.Y.55	AACCA P.Y.63	AADMCA Mono83 P.Y.83
R-1	H	CH_3	CH_3	OCH_3	H	Cl	OCH_3
R-2	H	CH_3	H	H	CH_3	H	Cl
R-3	H	H	H	H	H	H	OCH_3

(1) Coupling Components



(2) Monoazo Compounds



(3) Colour Index Pigments