

# The X-ray Structures of (*R*)-2,2'-Dimethyl-1,1'-binaphthyl and (±)-2-Bromomethyl-2'-dibromomethyl-1,1'-binaphthyl

R. Alan Aitken<sup>1</sup> · Ryan A. Inwood<sup>1</sup> · Alexandra M. Z. Slawin<sup>1</sup>

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✉ R. Alan Aitken  
raa@st-and.ac.uk

<sup>1</sup> EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, U.K.

# The X-ray Structures of (*R*)-2,2'-Dimethyl-1,1'-binaphthyl and (±)-2-Bromomethyl-2'-dibromomethyl-1,1'-binaphthyl

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**Abstract** Molecular structures of (*R*)-2,2'-dimethyl-1,1'-binaphthyl [monoclinic,  $a = 11.24420$  (11),  $b = 10.56190$  (9),  $c = 13.27180$  (13) Å,  $\beta = 90.7041$  (9)°, space group  $P2_1$ ] and (±)-2-bromomethyl-2'-dibromomethyl-1,1'-binaphthyl [triclinic,  $a = 9.4637$  (14),  $b = 9.9721$  (18),  $c = 9.9922$  (19) Å,  $\alpha = 100.093$  (5),  $\beta = 97.141$  (5),  $\gamma = 92.585$  (4)°, space group  $P-1$ ] are reported and compared with those of other simple 2,2'-disubstituted-1,1'-binaphthyls.

**Keywords:** Binaphthyl; Torsion angle; Inter-ring bond length

## Introduction

Although the 2,2'-disubstituted-1,1'-binaphthyl structure has emerged as one of the most powerful and useful molecular frameworks for asymmetric catalysis, most famously in the Nobel prize-winning work of Noyori involving the bis(phosphine) BINAP [1], there are a number of simple derivatives that have not so far been characterised by X-ray diffraction. In the course of recent work to synthesise a chiral diamine ligand containing this structure [2,3], we came across two such compounds that, for different reasons, had not been subject to previous X-ray structure determination. The dimethyl compound **1** has frequently been reported as a non-crystalline oil, resin or glass both in racemic [4–7] and enantiomerically pure [8,9] form. However when we prepared it by reaction of methymagnesium iodide with the bis(triflate) derived from (*R*)-BINOL in the presence of  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$  [8], the product was obtained as colourless crystals that proved to be suitable for X-ray diffraction. The next stage in the synthesis involved bromination of **1** with *N*-bromosuccinimide to form dibromide **2** and, in our hands, this was always accompanied by a small quantity of the tribromide **3** which could be separated from **2** chromatographically, although with difficulty. The formation of this minor byproduct has been noted in several previous papers [6,10] and patents [11–13] but it has never been fully characterised and the only reported data seems to be  $^1\text{H}$  NMR shifts for the aliphatic protons [14]. By subjecting the pure racemic dibromide **2** to further bromination and chromatographic separation we were able to isolate **3** in pure form and characterise it by melting point,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and X-ray diffraction. The resulting structures of (*R*)-**1** and (±)-**3** are compared with those of other simple symmetrical and unsymmetrical 2,2'-disubstituted-1,1'-binaphthyls.

## Experimental

(*R*)-(1,1'-binaphthyl)-2,2'-diylbis(trifluoromethanesulfonate) was prepared from (*R*)-BINOL (Fluorochem) using the published method [14]. (±)-2,2'-Bis(bromomethyl)-1,1'-binaphthyl **2** was prepared [4] by NBS bromination of (±)-2,2'-dimethyl-1,1'-binaphthyl, itself obtained by Grignard mediated coupling [5] of 1-bromo-2-methylnaphthalene [15].

### (*R*)-2,2'-Dimethyl-1,1'-binaphthyl **1**

Following a modified literature procedure [8], a mixture of magnesium turnings (4.75 g, 194.8 mmol) in dry  $\text{Et}_2\text{O}$  (60  $\text{cm}^3$ ) was placed under an  $\text{N}_2$  atmosphere and a single iodine crystal was added. Methyl iodide (11.0  $\text{cm}^3$ , 177.1 mmol) was added dropwise with occasional heating using a heat gun to maintain reaction. Once the addition was complete (ca. 10 min) the mixture was allowed to stir with occasional heating until no further reaction was

observed. The resulting 3 M solution of MeMgI was transferred portionwise *via* cannula over 5 min to a stirred solution of (*R*)-(1,1'-binaphthyl)-2,2'-diylbis(trifluoromethanesulfonate) (22.15 g, 40.2 mmol) and Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (1.32 g, 2.0 mmol) in Et<sub>2</sub>O (160 cm<sup>3</sup>) under N<sub>2</sub> at 0 °C. Once the addition was complete the reaction was stirred overnight at rt and then diluted with EtOAc (100 cm<sup>3</sup>). The mixture was cooled to 0 °C and quenched by careful dropwise addition of 1 M HCl solution before being filtered through Celite. The layers were separated, and the aqueous layer extracted with EtOAc (x 3). The combined organic layers were dried and evaporated and the residue was purified by flash column chromatography on SiO<sub>2</sub> eluting with hexanes to give an orange oil which slowly crystallised to give the title compound (8.40 g, 74 %) as faintly yellow crystals. m.p. 67–70 °C (lit. [5] 67–71 °C); [α]<sub>D</sub> = –38.2 (*c* 1.008, CHCl<sub>3</sub>), (lit. [16] –35.6 (*c* 1.0, CHCl<sub>3</sub>)). The <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data was in accordance with that previously reported [7].

### (±)-2-(Bromomethyl)-2'-(dibromomethyl)-1,1'-binaphthyl 3

To a stirred solution of (±)-2,2'-bis(bromomethyl)-1,1'-binaphthyl **2** (500 mg, 1.14 mmol) in CHCl<sub>3</sub> (10 cm<sup>3</sup>), was added AIBN (37 mg, 0.23 mmol) and NBS (243 mg, 1.37 mmol) and the solution heated under reflux for 3 h. The reaction mixture was cooled to rt and filtered through a silica plug, washing with hexane. The resulting filtrate was concentrated *in vacuo*. The crude residue was purified by flash column chromatography (SiO<sub>2</sub>, hexanes), to give at R<sub>f</sub> 0.19 the title compound (100 mg, 17%) as colourless crystals, m.p. 183–185 °C; δ<sub>H</sub> (Bruker AV400, 400 MHz, CDCl<sub>3</sub>) 8.21 (1 H, d, *J* 8.8, ArH), 8.12 (1 H, d, *J* 8.8, ArH), 8.06 (1 H, d, *J* 8.6, ArH), 7.96–7.92 (2 H, m, ArH), 7.79 (1 H, d, *J* 8.6, ArH), 7.54–7.48 (2 H, m, ArH), 7.32–7.26 (2 H, m, ArH), 7.06–7.00 (2 H, m, ArH), 6.22 (1 H, s, CHBr<sub>2</sub>), 4.33 and 4.14 (2 H, AB pattern, *J*<sub>AB</sub> 10.4, CH<sub>2</sub>Br); δ<sub>C</sub> (125 MHz) 137.6 (C), 134.5 (C), 133.7 (C), 133.2 (C), 132.14 (C), 132.06 (C), 131.2 (C), 130.2 (CH), 129.8 (CH), 129.6 (C), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.61 (CH), 127.59 (CH), 127.25 (CH), 127.16 (CH), 127.0 (CH), 126.7 (CH), 126.1 (CH), 39.8 (CHBr<sub>2</sub>) and 31.6 (CH<sub>2</sub>Br).

X-Ray diffraction data were collected using a Rigaku XtalLAB P200 (confocal optics) with Cu-Kα radiation at 125K for **1** and Mo-Kα radiation at 173K for **3** (data were integrated using CrysAlis Pro for **1** and CrystalClear for **3**). All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. The structures were solved by direct methods and refined by full-matrix least-squares against *F*<sup>2</sup> (SHELXTL [17]). Carbon-bound hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised geometries. Table 1 summarises the X-ray data.

**Table 1** Crystal data and structure refinement details for (*R*)-**1** and (±)-**3**

CCDC deposit no.	2010797	2010798
Empirical formula	C <sub>22</sub> H <sub>18</sub>	C <sub>22</sub> H <sub>15</sub> Br <sub>3</sub>
Formula weight	282.38	519.07
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> (No. 4)	<i>P</i> -1 (No. 2)
Temperature (K)	125	173
Crystal form	colourless prism	colourless prism
	0.20 × 0.20 × 0.20 mm	0.10 × 0.10 × 0.10 mm
Unit cell dimensions	<i>a</i> = 11.24420(11) Å	<i>a</i> = 9.4637(14) Å

	$b = 10.56190(9) \text{ \AA}$	$b = 9.9721(18) \text{ \AA}$
	$c = 13.27180(13) \text{ \AA}$	$c = 9.9922(19) \text{ \AA}$
	$\beta = 90.7041(9)^\circ$	$\alpha = 100.093(5)^\circ$
		$\beta = 97.141(5)^\circ$
		$\gamma = 92.585(4)^\circ$
Volume ( $\text{\AA}^3$ )	1576.04(3)	919.0(3)
$Z$	4	2
$D_c$ ( $\text{g cm}^{-3}$ )	1.190	1.876
Absorption coefficient	$0.505 \text{ mm}^{-1}$	$6.605 \text{ mm}^{-1}$
Radiation type, wavelength	Cu $K\alpha$ , 1.54184 $\text{\AA}$	Mo $K\alpha$ , 0.71075 $\text{\AA}$
$F_{(000)}$	600.0	504.0
$\theta$ range	$3.330\text{--}75.485^\circ$	$2.079\text{--}25.389^\circ$
Limiting indices	$-13 \leq h \leq 13, -12 \leq k \leq 13,$ $-16 \leq l \leq 15$	$-11 \leq h \leq 11, -12 \leq k \leq 12,$ $-12 \leq l \leq 12$
Reflections collected/unique	16327/5990	33694/3349
$R_{\text{int}}$	0.0154	0.0501
Data/restraints/parameters	5990/1/398	3349/0/226
Data with $I > 2\sigma(I)$	5932	2947
Goodness of fit on $F^2$	1.028	1.142
$R_1, wR_2$ (data with $I > 2\sigma(I)$ )	0.0390, 0.1058	0.0566, 0.1829
$R_1, wR_2$ (all data)	0.0411, 0.1097	0.0624, 0.1861
Largest diff. peak/hole ( $\text{e \AA}^{-3}$ )	0.21 and $-0.27$	1.15 and $-2.48$
Flack parameter	0.1(9)	—

## Results and Discussion

Compounds **1** and **3** were prepared using literature methods (Scheme 1) and in each case slow crystallisation of the oil obtained from chromatographic purification led directly to crystals suitable for X-ray diffraction. The structures of **1** and **3** are similar with the naphthyl rings being close to orthogonal in both structures. The crystal structure of (*R*)-**1** showed two closely similar molecules in the unit cell (Figure 1) which differ mainly in the torsion angle between the two naphthalene rings ( $89.6^\circ$  in the former case vs.  $81.9^\circ$  in the latter). For the tribromo compound **3** there was a single molecule in the unit cell (Figure 2) and the large size of the bromine atoms caused this to adopt a definite conformation with the two naphthalene systems at right angles (torsion angle  $87.7^\circ$ ), the  $\text{CHBr}_2$  group oriented to minimise steric interactions with  $\text{C}(19)\text{--H}$  in the plane of the lower ring placing the two bromines as far as possible from the upper ring, and the  $\text{C}(2)\text{--C}(9)$  bond oriented to place the  $\text{CH}_2\text{Br}$  bromine as far as possible away from the  $\text{CHBr}_2$  group.

Figures 3 and 4 illustrate the packing in **1** and **3**. In **1** we did not observe any significant  $\pi\text{--}\pi$  interactions. There are weak  $\text{C--H}\text{--}\pi$  intermolecular contacts:  $\text{H}(9\text{B})$  and  $\text{H}(19\text{B})$  to  $\text{C}(31)\text{--C}(38\text{A})$  mean plane distances are  $2.67(1)$  and  $2.83(1) \text{ \AA}$  respectively;  $\text{H}(29\text{B})$  and  $\text{H}(39\text{B})$  to  $\text{C}(11)\text{--C}(18\text{A})$  mean plane distances are  $3.00(1)$  and  $2.84(1) \text{ \AA}$  respectively.

In **3** the packing (Figure 4) is dominated by the intermolecular  $\text{Br}\dots\text{Br}$  interactions shown more clearly in Figure 5 [ $\text{Br}(19)\dots\text{Br}(9\text{A})$   $3.5353(13) \text{ \AA}$ ]. There are no significant  $\pi\text{--}\pi$  overlaps; the  $\text{C}(7)\dots\text{C}(7\text{A})$  and  $\text{C}(6)\dots\text{C}(7\text{A})$  distances are  $3.221(10)$  and  $3.386(10) \text{ \AA}$  respectively.

By chance these two structures are almost at the extremes of possible 2,2'-disubstituted binaphthyls, one with two equivalent small substituents and one with two unequal very large substituents. We therefore thought it worthwhile to make a systematic comparison with previously reported structures for simple 2,2'-disubstituted binaphthyls focusing particularly on the length of the C(1)–C(1') bond linking the two naphthalene rings and the torsion angle between them (Figure 6, Table 2).

**Table 2** Structural parameters for **1**, **3** and other binaphthyls

Cpd	Ref Code	R <sup>1</sup>	R <sup>2</sup>	length C1–C1' (Å)	torsion angle (°)	Ref
( <i>R</i> )- <b>1</b> <sup>a</sup>		Me	Me	1.494(3) 1.497(3)	81.9 89.6	this work
(±)- <b>3</b>		CHBr <sub>2</sub>	CH <sub>2</sub> Br	1.513(9)	87.7	this work
( <i>S</i> )- <b>2</b>	BRMBNP	CH <sub>2</sub> Br	CH <sub>2</sub> Br	1.4947(3)	88.3	[18]
( <i>R</i> )- <b>4</b>	AJULAS	NH <sub>2</sub>	NH <sub>2</sub>	1.496(3)	68.2	[19]
( <i>R</i> )- <b>4</b>	AJULAS01	NH <sub>2</sub>	NH <sub>2</sub>	1.495(2)	67.6	[20]
(±)- <b>5</b>	BIRKOC01	OH	OH	1.500(3)	89.5	[21]
(±)- <b>5</b>	UKILAC	OH	OH	1.489(3)	78.5	[22]
( <i>S</i> )- <b>5</b>	BUCZIK	OH	OH	1.497(3)	77.3	[23]
( <i>R</i> )- <b>5</b>	WANNII	OH	OH	1.494(3)	78.6	[21]
(±)- <b>6</b>	BUBLIT	OMe	OMe	1.4871(1)	69.0	[24]
( <i>S</i> )- <b>7</b>	LEHLUG	OEt	OEt	1.492(3)	67.9	[25]
( <i>R</i> )- <b>8</b>	DUWGOR	NC	NC	1.497(7)	89.5	[26]
( <i>S</i> )- <b>9</b>	HUZGUE	PPh <sub>2</sub>	PPh <sub>2</sub>	1.504(3)	88.4	[27]
( <i>R</i> )- <b>9</b>	PASRAC	PPh <sub>2</sub>	PPh <sub>2</sub>	1.499(7)	88.3	[28]
(±)- <b>10</b>	ROGMEF	(B(OH) <sub>2</sub> )	B(OH) <sub>2</sub>	1.506(6)	87.1	[29]
(±)- <b>11</b> <sup>a</sup>	ROGLII	SiMe <sub>3</sub>	SiMe <sub>3</sub>	1.509(4) 1.497(4)	88.1 89.6	[29]
(±)- <b>12</b> <sup>a</sup>	ROGLOO	GeMe <sub>3</sub>	GeMe <sub>3</sub>	1.50(2) 1.46(2)	90.0 89.3	[29]
(±)- <b>13</b> <sup>a</sup>	ROGLEE	SnMe <sub>3</sub>	SnMe <sub>3</sub>	1.54(2) 1.47(2)	82.7 86.0	[29]
(±)- <b>14</b>	GIVRIM	OH	NH <sub>2</sub>	1.506(7)	85.9	[30]
( <i>S</i> )- <b>15</b> <sup>a</sup>	KEZYAQ	OH	Me	1.489(3) 1.498(3)	87.0 76.0	[31]

<sup>a</sup> Two molecules in unit cell

It can be seen that the inter-ring bond length varies from 1.46 to 1.54 Å and the torsion angle from 68–90 ° but against this background several trends are obvious. The compounds with the lowest torsion angle are those bearing powerfully electron-donating groups such as NH<sub>2</sub> (**4**), OMe (**6**) and OEt (**7**) which all give values below 70 °. Most of the other compounds have torsion angles over 85 ° but the behaviour we have observed for **1** with two different molecules in the unit cell is also observed for compounds **11**, **12**, **13** and **15** and in the last of these cases there is an 11 ° difference in torsion angle compared to 7.7 ° for **1**. Although having fairly similar torsion angles, the extremes of inter-ring bond length are all observed in compounds **11**–**13** which each have one form with a long bond and one with a short bond. Except for the long-bonded molecule of trimethylstannyl compound **13**, compound **3** exhibits the longest inter-ring bond among such simple compounds at 1.513 Å. This can be compared

with the value of 1.475 Å for 1,1'-binaphthyl itself, which also shows a low torsion angle of 68.1 ° [32]. It might be noted that in many of the structures such as that of BINOL **5** and the boronic acid **10**, there is significant hydrogen bonding which is not possible for either **1** or **3**.

### Conclusion

The dimethyl compound **1** shows two molecules in the unit cell which differ in both inter-ring bond length and torsion angle, a pattern of behaviour previously noted for the group 14-substituted derivatives **11–13** and the methyl hydroxy compound **15**. In contrast the tribromo compound **3** has the its rings nearly orthogonal but with the bromine-containing groups oriented to minimise steric interactions and a very long inter-ring bond.

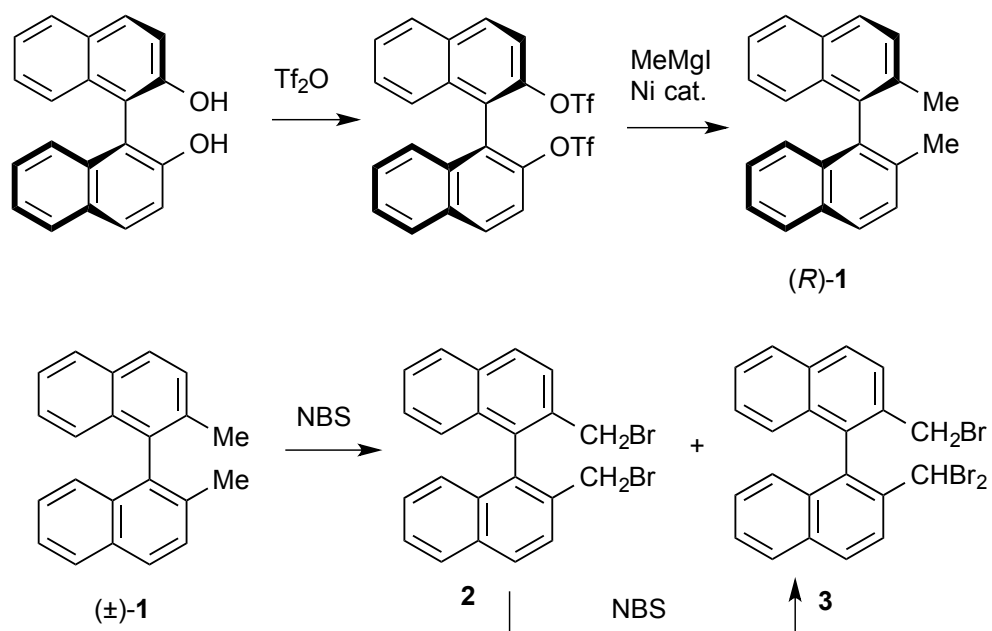
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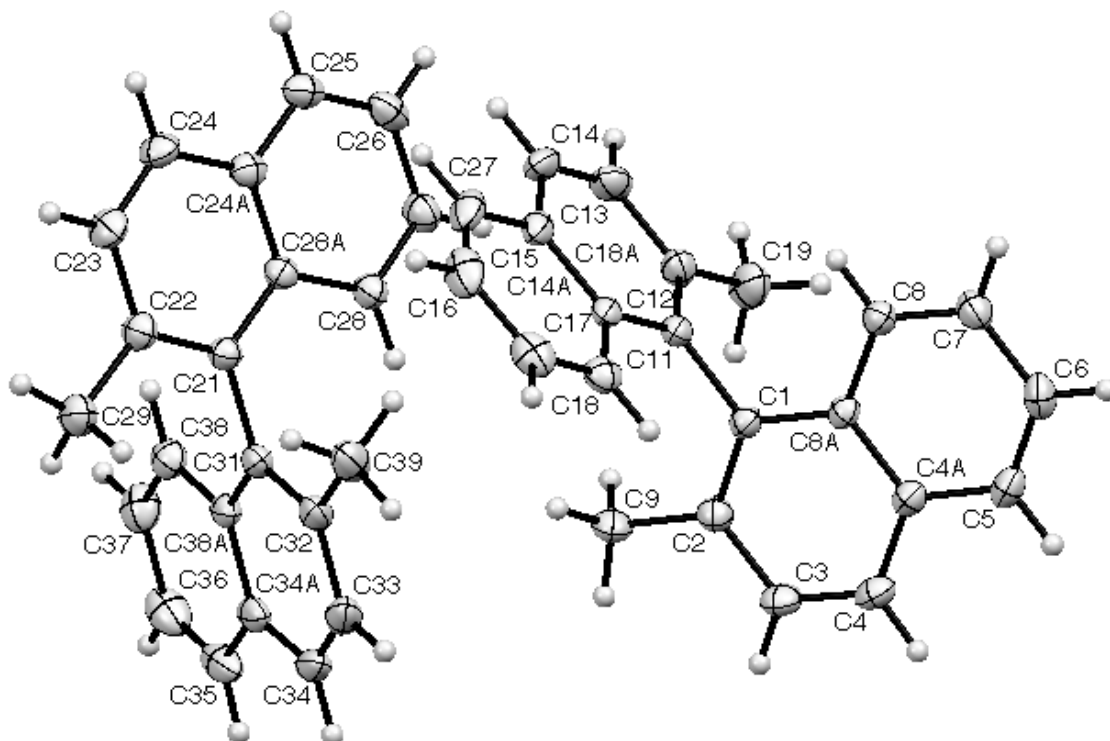
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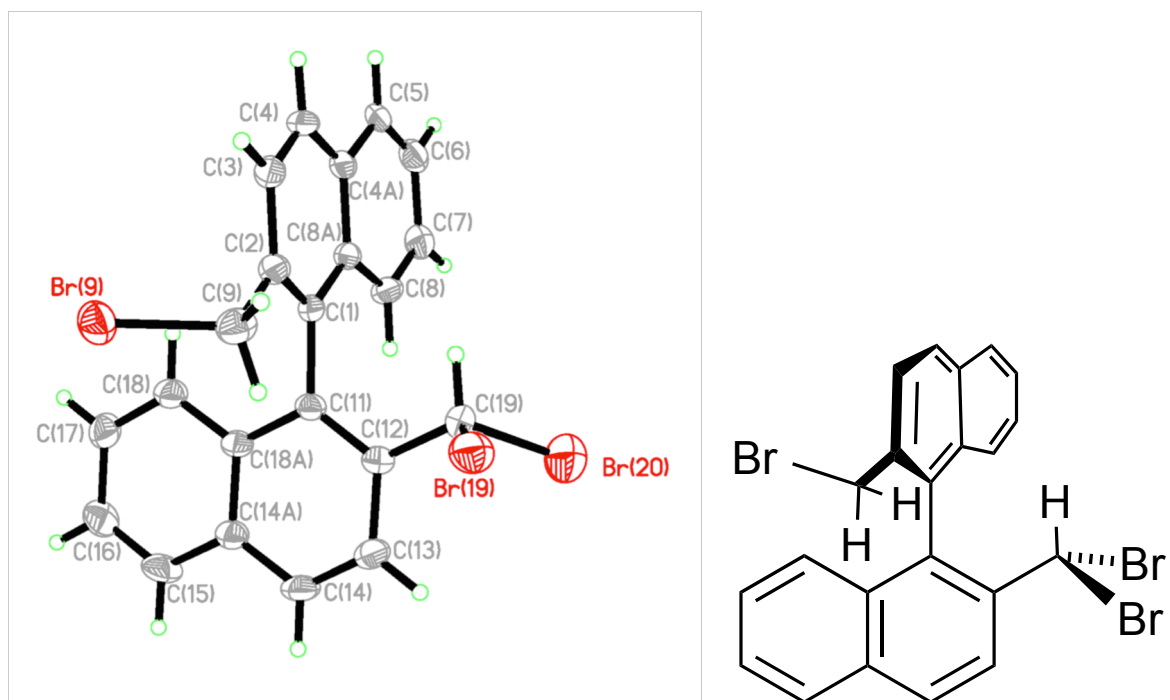


**Scheme 1** Synthetic routes used to obtain compounds 1 and 3.

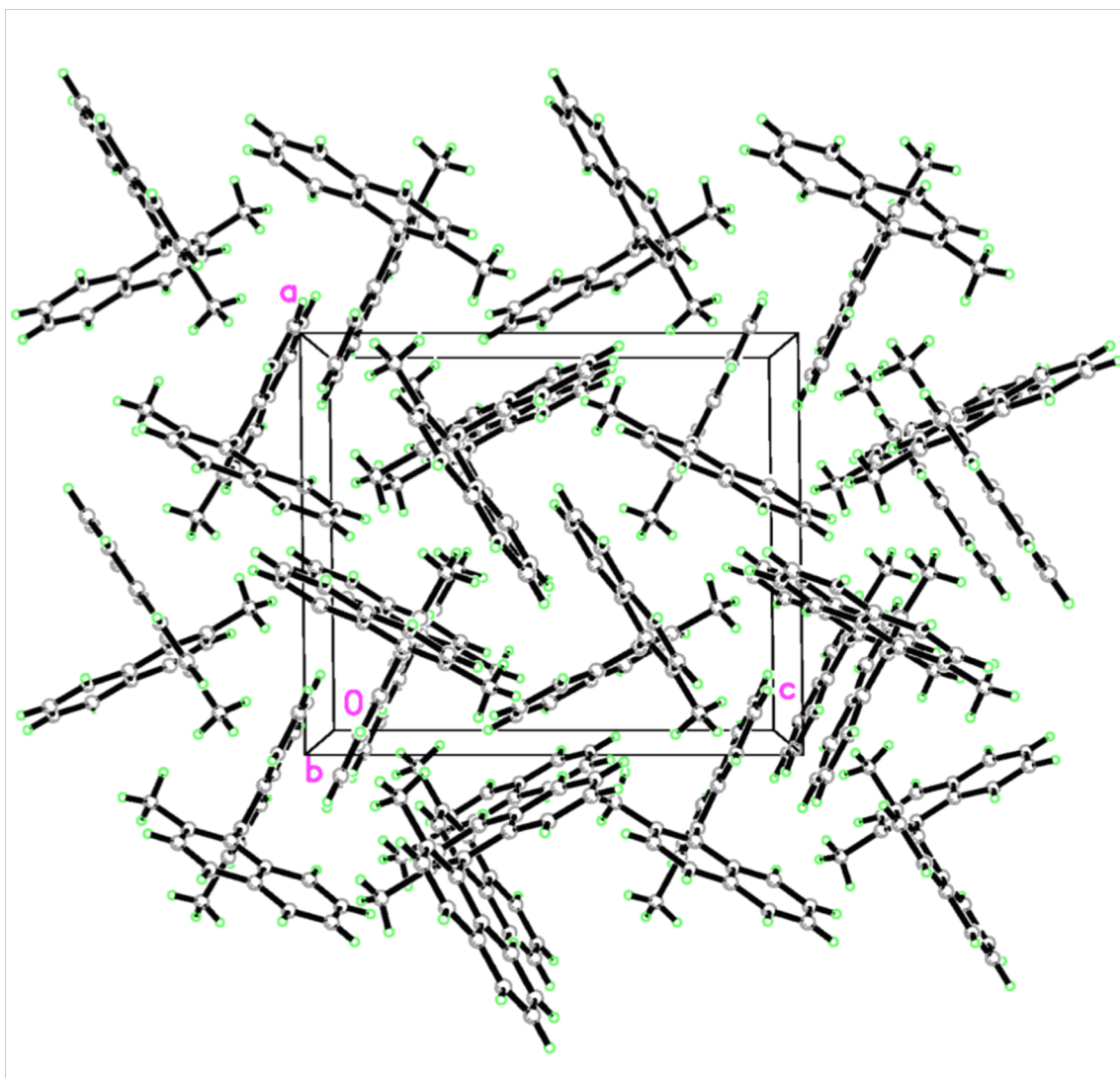


**Fig. 1** The two molecules of 1 showing the numbering system used (ORTEP diagram with ellipsoids at 50% probability level).

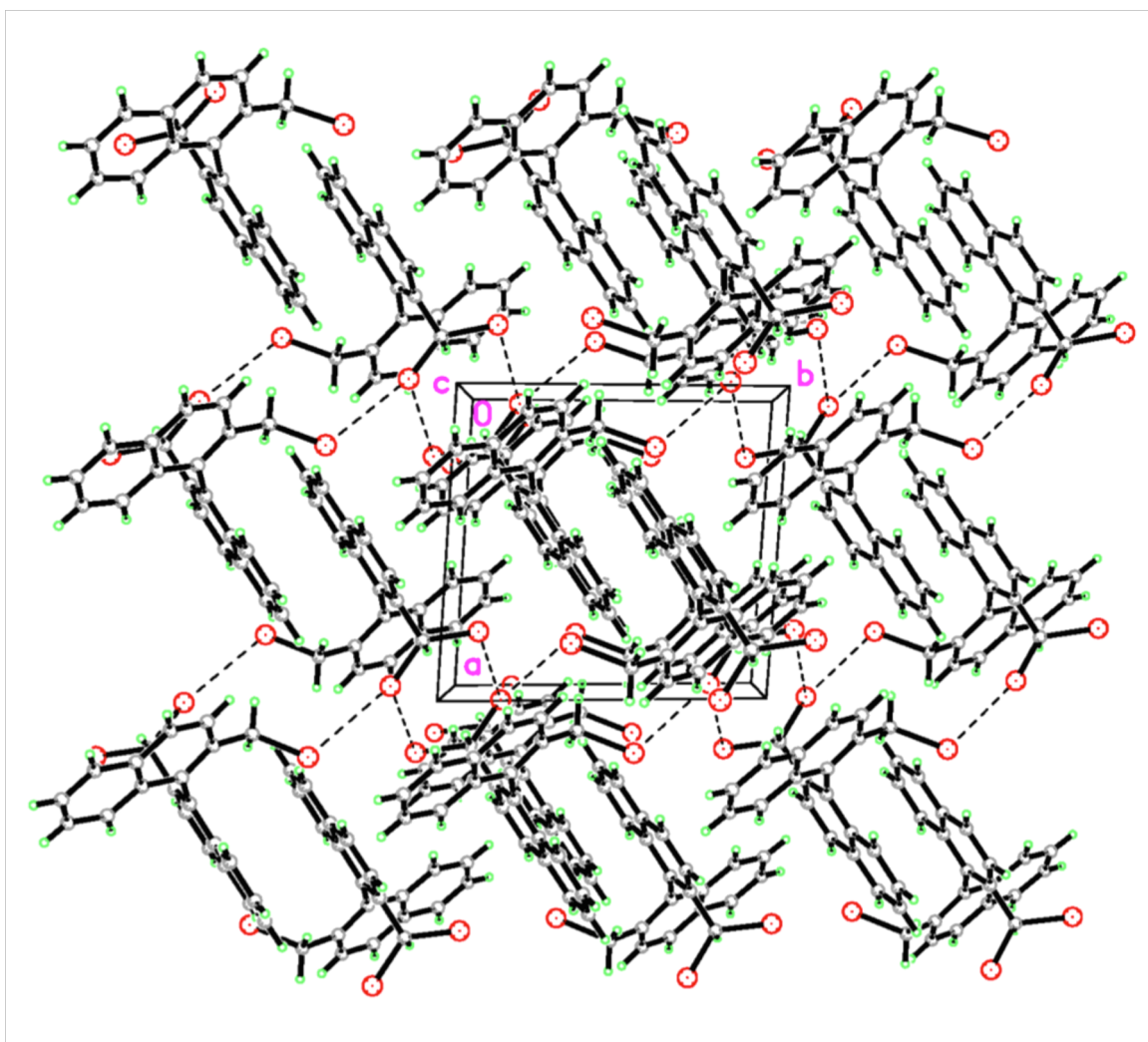




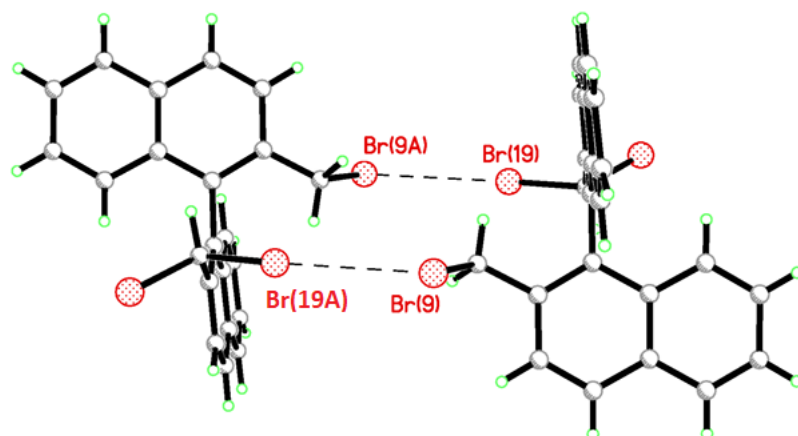
**Fig. 2** Molecular structure of **3** showing the numbering system used (ORTEP diagram with ellipsoids at 50% probability level) and schematic representation.



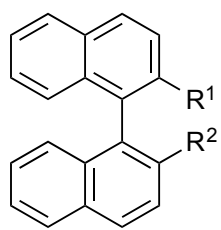
**Fig. 3** Packing of **1** viewed down the *b* axis.



**Fig. 4** Packing of **3** viewed down the *c* axis.



**Fig. 5** Detail of intermolecular Br–Br interactions in **3**



**4-15**

**Fig. 6** General structure of 2,2'-disubstituted-1,1'-binaphthyls