ligand (1) has been compensated for by an apparently larger thermal vibration in the plane of the ligand.

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Determination of the Crystal Structure and the Absolute Configuration of (+)-2,2'-Dihydroxy-1,1'-Binaphthalene-3,3'-Dicarboxylic Acid Dimethyl Ester Bromobenzene Solvate

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In order to establish the absolute configuration of binaphthyl derivatives, an X-ray diffraction study on the crystal structure of (+)-2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid dimethyl ester bromobenzene solvate has been carried out. The crystals are monoclinic, space group $P2_1$ and the lattice constants are: $a=15{\cdot}78$ Å, $b=9{\cdot}22$, $c=9{\cdot}12$, $\beta=97{\cdot}0°$. The unit cell contains two molecules together with two molecules of bromobenzene. The structure was solved by the heavy atom method using the bromine atoms of the solvate molecules. Refinement was carried out by the block-matrix least-squares method for 1213 observed reflexions including anisotropic temperature factors. The final R value was 0·101.

It was found that the two naphthyl groups are twisted from the exact *cis*-conformation by an angle of 76°38'. The absolute configuration was determined by utilizing the anomalous dispersion effect of the bromine atom for Cu $K\alpha$ radiation, showing that the molecule has the (R)-configuration.

Introduction

It has been shown that the restricted rotation about the single bond joining the two benzene rings in biphenyl derivatives produces a pair of optical enantiomers, where the molecule cannot readily exist in a planar form because of the steric interference of the substituents. The term atropisomerism is often used to denote such kinds of stereoisomerism (Eliel, 1962). In many cases the resolution of the optically active forms is possible provided that the rate of interconversion of the enantiomers is sufficiently slow. The determination of the absolute configuration of this type of compound is very interesting because the optical rotation

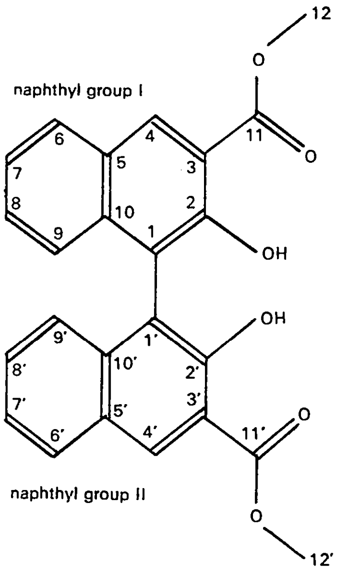

Fig. 1. Chemical structure of 2,2'-dihydroxy-1,1'-binapthalene-3,3'-dicarboxylic acid dimethyl ester.

is merely a result of the three-dimensional conformation of the molecule and not of the asymmetric atoms, so long as the substituents and their arrangement are symmetrical.

Various investigations have been carried out in an attempt to determine the absolute configuration of biaryl compounds. However, their assignments were mostly based on stereochemical mechanisms, optical properties or thermal analysis, and the unequivocal determination of the absolute configuration by X-ray methods has long been desired. The present determination of the absolute configuration of a binaphthyl derivative was undertaken with crystals of optically active (+)-2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid dimethyl ester bromobenzene solvate. The result obtained allowed the assignment of the absolute configurations of some other binaphthyl derivatives by chemical correlations (Akimoto, Shioiri, Iitaka & Yamada, 1968).

Experimental

Optically active (+)-2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid dimethyl ester (Fig. 1) crystallizes in a suitable size for X-ray analysis, containing one equivalent molecule of bromobenzene when recrystallized from bromobenzene solution. The bromine atoms were used as the phase determining heavy atoms as well as the anomalous scatterer. The crystals containing bromobenzene as a solvent of crystallization are monoclinic pale yellow plates with well developed (100) faces. The lattice constants were determined from the 0*kl* and *h*0*l* precession photographs taken with Cu *Kα* radiation. The density was measured by the flotation method in an aqueous solution of sodium iodide.

Crystal data

(*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid dimethyl ester bromobenzene solvate, $C_{24}H_{18}O_6.C_6H_5Br$, mol. wt. 559·4.

Monoclinic,
$a = 15·78 \text{Å} \pm 0·02$, $b = 9·22 \pm 0·01$, $c = 9·12 \pm 0·01$ Å,
$\beta = 97·0° \pm 0·2°$.
$U = 1327$ Å^3.
$D_m = 1·42$ g.cm^{-3},

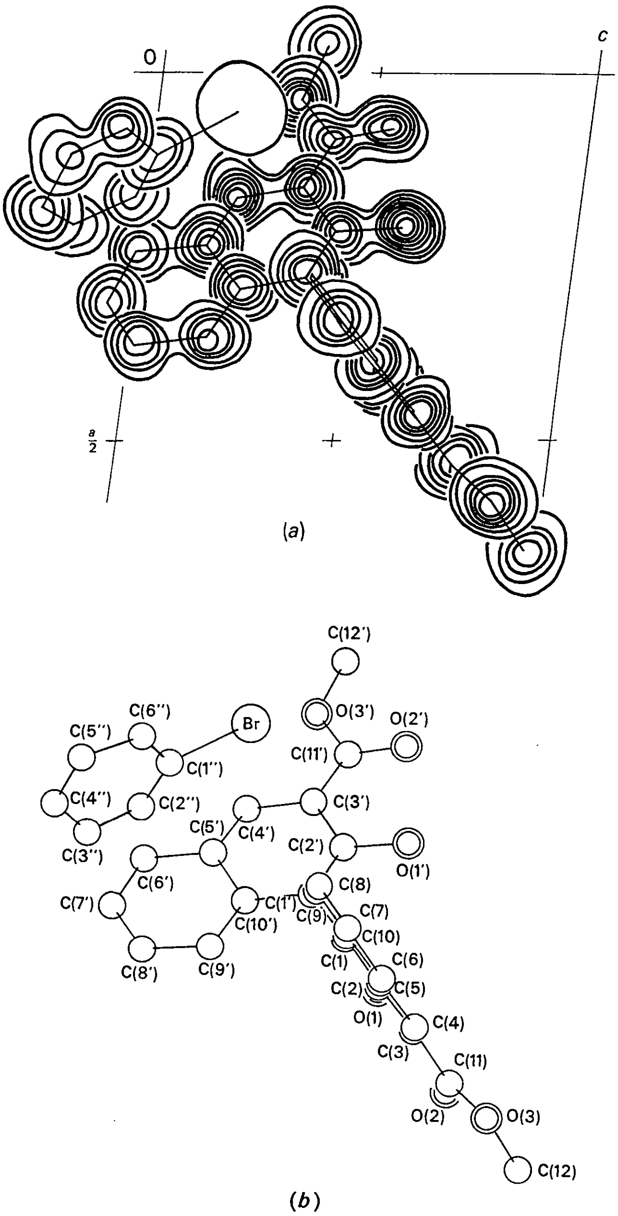

Fig. 2. (*a*) Composite electron density map superimposed on (010). Contours are drawn at intervals of 1 e.Å^{-3} starting from 1 e.Å^{-3}. Those for the bromine atom are omitted. (*b*) The molecular structure deduced from (*a*). The Figure is drawn with correct absolute configuration.

$D_x = 1{\cdot}40$ g.cm^{-3},
$Z = 2$.
Absent spectra, $0k0$ when k is odd.
Space group, $P2_1$.

The intensities were measured visually from the multiple film equi-inclination Weissenberg photographs taken for the layers zero to seven for the c axis and zero to three for the b axis with Cu $K\alpha$ radiation. After correction for Lorentz and polarization factors, the structure factors were put on the same relative scale by correlating the values on various layers. A total of 1213 independent observed structure factors were finally obtained, which correspond to about 70% of the total independent reflexions for $\sin\theta \leq 0{\cdot}83$.

Determination of the structure

The x and z coordinates of the bromine atom were readily determined from the Harker section. A centrosymmetric b axis projection of the electron density map was prepared using the signs of structure factors calculated on the basis of the bromine atom contributions. A gross feature of the structure was revealed on the electron density map, which afforded the approximate x and z coordinates of some of the atoms in the naphthalene nuclei. The two-dimensional analysis was of great help in determining the structure on the three-dimensional electron density map which was calculated by using bromine as phasing atoms ($R = 0{\cdot}41$). Since the latter map had pseudo-symmetry planes through the bromine atoms, the atoms of the two naphthalene nuclei could be located on this electron density map and several subsequent cycles of Fourier and difference-Fourier syntheses revealed the whole structure, together with the molecule of bromobenzene. The R value at this stage was 0·24.

Refinement of the structural parameters was carried out by the method of least-squares for 1213 observed reflexions. Four cycles of the block-diagonal least-

Table 1. *The final atomic parameters and their standard deviations*

x, y and z are the fractional coordinates. The temperature factors are expressed in the form

$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right].$$

The e.s.d.'s given in parentheses are in the units of the least significant digits given for the corresponding parameters. To represent the correct absolute configuration, the parameters should be referred to a right handed set of axes.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·0530 (2)	0·0017 (7)	0·1822 (4)	0·0074 (2)	0·0268 (7)	0·0167 (5)	0·0037 (5)	0·0017 (2)	−0·0042 (8)
O(1)	0·4091 (10)	0·4271 (18)	0·5794 (17)	0·0031 (8)	0·0053 (27)	0·0127 (26)	0·0008 (13)	−0·0004 (11)	0·0005 (23)
O(2)	0·5345 (10)	0·4136 (21)	0·7884 (19)	0·0040 (9)	0·0119 (31)	0·0124 (29)	−0·0014 (15)	−0·0011 (13)	−0·0001 (27)
O(3)	0·5793 (11)	0·1981 (22)	0·8745 (18)	0·0053 (10)	0·0105 (33)	0·0113 (29)	0·0009 (17)	−0·0020 (13)	0·0012 (29)
C(1)	0·3451 (14)	0·2165 (27)	0·4909 (23)	0·0027 (12)	0·0041 (38)	0·0054 (34)	0·0027 (20)	0·0036 (15)	0·0044 (32)
C(2)	0·4068 (14)	0·2811 (27)	0·5834 (25)	0·0029 (12)	0·0036 (37)	0·0095 (37)	−0·0007 (19)	−0·0019 (16)	0·0015 (33)
C(3)	0·4644 (14)	0·1992 (30)	0·6783 (24)	0·0028 (12)	0·0109 (44)	0·0047 (34)	−0·0020 (22)	0·0023 (15)	−0·0028 (36)
C(4)	0·4637 (14)	0·0508 (29)	0·6777 (25)	0·0023 (11)	0·0085 (48)	0·0093 (36)	0·0005 (21)	0·0006 (16)	−0·0018 (37)
C(5)	0·4015 (14)	−0·0216 (31)	0·5858 (23)	0·0033 (12)	0·0030 (38)	0·0091 (34)	0·0007 (22)	0·0013 (15)	−0·0017 (38)
C(6)	0·3947 (18)	−0·1698 (31)	0·5813 (32)	0·0063 (18)	0·0027 (44)	0·0201 (54)	0·0031 (24)	0·0034 (25)	0·0063 (42)
C(7)	0·3312 (18)	−0·2543 (35)	0·4879 (33)	0·0054 (17)	0·0098 (55)	0·0202 (57)	−0·0003 (26)	−0·0035 (24)	0·0015 (49)
C(8)	0·2712 (17)	−0·1632 (34)	0·3980 (30)	0·0051 (17)	0·0096 (51)	0·0130 (48)	0·0009 (26)	0·0012 (22)	−0·0023 (47)
C(9)	0·2749 (14)	−0·0174 (34)	0·3949 (23)	0·0033 (12)	0·0077 (41)	0·0088 (35)	−0·0004 (25)	0·0020 (16)	0·0029 (44)
C(10)	0·3412 (14)	0·0604 (26)	0·4876 (24)	0·0032 (12)	0·0042 (39)	0·0063 (34)	0·0016 (19)	−0·0005 (16)	0·0046 (31)
C(11)	0·5336 (16)	0·2940 (38)	0·7813 (30)	0·0036 (15)	0·0222 (66)	0·0092 (45)	−0·0000 (27)	−0·0005 (20)	0·0058 (47)
C(12)	0·6430 (19)	0·2651 (37)	0·9720 (33)	0·0066 (20)	0·0125 (63)	0·0182 (59)	−0·0058 (30)	−0·0073 (27)	−0·0040 (52)
O(1′)	0·2087 (9)	0·3590 (20)	0·5946 (15)	0·0029 (8)	0·0085 (28)	0·0040 (21)	0·0009 (14)	0·0016 (10)	0·0024 (23)
O(2′)	0·0778 (10)	0·5359 (22)	0·5447 (17)	0·0050 (10)	0·0111 (36)	0·0132 (28)	0·0021 (17)	0·0046 (13)	−0·0004 (28)
O(3′)	0·0370 (11)	0·6095 (22)	0·3259 (19)	0·0055 (10)	0·0135 (34)	0·0101 (28)	0·0019 (16)	0·0034 (14)	−0·0007 (27)

Table 1 (*cont.*)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1′)	0·2829 (15)	0·3029 (28)	0·3895 (25)	0·0037 (14)	0·0080 (43)	0·0059 (36)	−0·0014 (20)	0·0011 (17)	0·0063 (32)
C(2′)	0·2165 (14)	0·3775 (28)	0·4485 (24)	0·0027 (11)	0·0029 (39)	0·0075 (34)	−0·0006 (18)	−0·0003 (15)	0·0007 (32)
C(3′)	0·1566 (13)	0·4638 (27)	0·3572 (24)	0·0022 (11)	0·0059 (45)	0·0086 (34)	0·0003 (18)	−0·0004 (15)	−0·0019 (32)
C(4′)	0·1704 (15)	0·4782 (38)	0·2028 (26)	0·0038 (12)	0·0123 (50)	0·0086 (36)	−0·0017 (24)	0·0011 (16)	−0·0022 (43)
C(5′)	0·2337 (15)	0·4054 (30)	0·1435 (25)	0·0035 (13)	0·0079 (43)	0·0091 (37)	0·0025 (22)	0·0030 (17)	0·0040 (35)
C(6′)	0·2417 (18)	0·4269 (35)	−0·0122 (28)	0·0066 (18)	0·0178 (61)	0·0082 (40)	−0·0026 (27)	0·0035 (20)	0·0054 (41)
C(7′)	0·3070 (17)	0·3474 (37)	−0·0700 (27)	0·0054 (16)	0·0134 (57)	0·0090 (42)	0·0039 (27)	0·0026 (20)	0·0067 (45)
C(8′)	0·3650 (18)	0·2640 (37)	0·0240 (27)	0·0052 (17)	0·0164 (62)	0·0068 (41)	−0·0007 (28)	−0·0016 (20)	0·0002 (43)
C(9′)	0·3608 (15)	0·2407 (31)	0·1772 (26)	0·0023 (13)	0·0092 (48)	0·0120 (40)	0·0027 (21)	0·0053 (17)	−0·0026 (37)
C(10′)	0·2942 (16)	0·3155 (30)	0·2374 (25)	0·0047 (14)	0·0085 (49)	0·0044 (35)	−0·0017 (22)	0·0012 (17)	0·0012 (34)
C(11′)	0·0892 (14)	0·5395 (30)	0·4213 (25)	0·0024 (12)	0·0074 (47)	0·0122 (38)	0·0013 (22)	0·0014 (17)	−0·0037 (39)
C(12′)	−0·0364 (20)	0·6877 (42)	0·3787 (36)	0·0067 (22)	0·0158 (72)	0·0227 (67)	0·0046 (33)	0·0014 (29)	−0·0013 (57)
C(1″)	0·1123 (17)	−0·0434 (36)	0·0097 (29)	0·0046 (15)	0·0210 (76)	0·0088 (44)	0·0030 (26)	0·0003 (20)	0·0065 (47)
C(2″)	0·1720 (19)	0·0410 (44)	−0·0400 (32)	0·0069 (18)	0·0244 (89)	0·0163 (53)	0·0028 (36)	0·0016 (25)	0·0067 (63)
C(3″)	0·2100 (18)	−0·0120 (61)	−0·1550 (33)	0·0040 (17)	0·0650 (122)	0·0237 (56)	0·0047 (49)	0·0039 (24)	0·0405 (88)
C(4″)	0·1730 (18)	−0·1224 (40)	−0·2410 (30)	0·0047 (16)	0·0259 (69)	0·0139 (51)	0·0066 (30)	−0·0017 (23)	−0·0004 (54)
C(5″)	0·1070 (24)	−0·2041 (46)	−0·1970 (43)	0·0106 (27)	0·0237 (87)	0·0372 (83)	−0·0015 (41)	0·0083 (38)	−0·0133 (69)
C(6″)	0·0794 (22)	−0·1718 (39)	−0·0643 (32)	0·0114 (25)	0·0154 (63)	0·0064 (50)	0·0019 (34)	−0·0014 (27)	0·0023 (48)

squares calculations with anisotropic temperature factors for bromine and individual isotropic factors for remaining atoms reduced the R factor to 0·119. Finally, four cycles of the block-matrix least-squares calculations with anisotropic temperature factors for all atoms were carried out by use of the program *HBLS* (Okaya & Ashida, 1967). The R factor reduced to 0·101. In the final calculations, the following weight system was adopted,

$$\sqrt{w}=30\cdot0/F_o \quad \text{when } F_o>30$$
$$\sqrt{w}=1\cdot0 \quad \text{when } 30\ge F_o>5$$
$$\sqrt{w}=0\cdot3 \quad \text{when } 5\ge F_o\,.$$

The atomic scattering factors used were those given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and oxygen atoms and those given by Thomas & Umeda (1957) for bromine atoms. The final atomic parameters and their standard deviations are listed in Table 1, and the list of the observed and calculated structure factors is given in Table 2. A composite electron density map synthesized using the final atomic parameters is shown in Fig. 2.

Absolute configuration

The absolute structure of (+)-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic acid dimethyl ester bromobenzene solvate was established by utilizing the anomalous dispersion effect of the bromine atom for Cu $K\alpha$ radiation. The values of the dispersion correction terms, $\Delta f'=-0\cdot9$ and $\Delta f''=1\cdot5$, were taken from *International Tables for X-ray Crystallography* (1962). Intensities of hkl and $h\bar{k}l$ pairs of reflexions were calculated with the assumption that the atomic coordinates given in Table 1 are referred to a right-handed set of axes and they were compared with the reflexions recorded in the various layers of the c axis Weissenberg photographs. Some of the results used for the establishment of the absolute configuration are shown in Table 3. All Figures shown in the present paper are drawn with the correct absolute configuration.

Discussion of the structure

The present X-ray structure determination has shown the absolute configuration of (+)-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic acid dimethyl ester to be the (*R*)-configuration. The absolute configurations of several other derivatives of the binaphthyl group have now been correlated by chemical methods (Akimoto, Shioiri, Iitaka & Yamada, 1968). These include: (+)-2,2′-dimethoxy-3,3′-diamino-, (+)-2,2′-dihydroxy-, (−)-2,2′-dicarboxylic acid-, (−)-2,2′-diamino-1,1′-binapthyl and (+)-1,1′-binaphthyl, *etc.* The former

Table 2. *Observed and calculated structure factors*

H	K	L	|F(OBS)|	F(CAL)
3	0	0	38.78	35.62
4	0	0	14.75	10.87
5	0	0	20.10	10.92
6	0	0	37.01	37.80
7	0	0	43.38	42.59
8	0	0	44.13	46.26
9	0	0	28.95	25.99
10	0	0	17.38	18.90
11	0	0	7.94	8.50
12	0	0	9.09	9.55
15	0	0	7.35	8.59
16	0	0	16.05	21.57
17	0	0	9.28	11.61
-16	0	1	8.73	9.23
-15	0	1	12.74	15.88
-13	0	1	12.47	11.42
-12	0	1	11.92	9.73
-11	0	1	15.22	14.22
-10	0	1	35.32	32.19
-9	0	1	25.09	24.29
-8	0	1	31.46	26.55
-7	0	1	23.13	24.54
-6	0	1	21.87	21.19
-5	0	1	39.84	40.84
-4	0	1	67.06	70.22
-3	0	1	7.83	1.09
-2	0	1	24.50	27.91
-1	0	1	66.59	84.06
0	0	1	33.31	37.32
1	0	1	3.38	3.91
3	0	1	36.54	40.54
4	0	1	71.58	70.10
5	0	1	56.52	59.05
7	0	1	38.62	42.01
8	0	1	21.12	20.47
9	0	1	26.27	23.80
10	0	1	6.25	6.67
11	0	1	16.99	15.42
13	0	1	14.55	17.71
15	0	1	10.27	16.97
16	0	1	23.24	33.50
17	0	1	7.75	8.54
-16	0	2	8.69	11.11
-12	0	2	8.50	6.85
-10	0	2	27.22	26.53
-9	0	2	30.91	25.34
-8	0	2	25.53	26.15
-7	0	2	6.02	0.41
-6	0	2	36.97	34.24
-5	0	2	59.11	57.61
-4	0	2	91.36	95.36
-3	0	2	129.75	144.99
-2	0	2	93.49	110.04
-1	0	2	20.18	21.87
0	0	2	26.00	17.35
1	0	2	45.27	46.15
2	0	2	27.02	26.50
3	0	2	48.22	52.98
4	0	2	32.01	26.79
5	0	2	39.84	37.95
6	0	2	56.87	57.95
7	0	2	19.04	18.58
8	0	2	25.92	22.21
9	0	2	23.79	23.84
10	0	2	15.85	14.55
11	0	2	5.03	1.18
12	0	2	35.75	41.25
13	0	2	9.16	4.22
14	0	2	14.47	17.42
-12	0	3	18.72	18.05
-11	0	3	11.68	8.00
-10	0	3	14.28	13.79
-9	0	3	16.44	15.31
-8	0	3	17.82	21.37
-7	0	3	30.72	27.03
-6	0	3	21.87	14.02
-5	0	3	21.28	23.64
-4	0	3	27.53	12.95
-3	0	3	82.40	80.89
-2	0	3	8.50	11.78
-1	0	3	36.69	33.18
0	0	3	44.29	48.39
1	0	3	9.44	9.25
2	0	3	29.46	28.78
3	0	3	31.35	24.46
5	0	3	22.38	18.93
6	0	3	32.72	33.30
7	0	3	43.81	45.61
8	0	3	39.37	34.59
9	0	3	13.37	11.60
10	0	3	12.39	11.67
11	0	3	24.35	20.93
12	0	3	27.14	24.40
13	0	3	14.39	11.36
14	0	3	11.52	10.61
15	0	3	9.79	6.62
-16	0	4	9.60	10.70
-13	0	4	12.78	13.15
-12	0	4	12.55	11.06
-11	0	4	22.14	24.17
-10	0	4	10.62	10.97
-9	0	4	12.74	4.27
-8	0	4	23.44	19.52
-7	0	4	65.29	66.20
-6	0	4	51.05	45.10
-5	0	4	65.01	67.06
-4	0	4	53.10	60.01
-3	0	4	5.03	2.02
-2	0	4	25.33	27.32
-1	0	4	38.66	32.29
0	0	4	9.40	8.42
1	0	4	13.02	14.47
2	0	4	9.68	10.53
3	0	4	8.14	6.92
4	0	4	15.26	16.68
5	0	4	16.32	13.85
6	0	4	20.61	22.44
7	0	4	17.58	20.22
8	0	4	12.98	12.44
9	0	4	28.99	30.78
10	0	4	28.36	22.95
11	0	4	7.67	2.18
-12	0	5	7.39	3.6[illegible]
-11	0	5	12.55	12.82
-10	0	5	8.61	5.92
-9	0	5	22.58	21.90
-8	0	5	30.68	33.12
-6	0	5	55.46	54.00
-5	0	5	8.57	4.32
-4	0	5	11.41	8.16
-3	0	5	31.39	28.53
-2	0	5	26.35	14.25
-1	0	5	6.69	4.63
0	0	5	69.54	76.63
1	0	5	38.46	40.39
2	0	5	17.27	18.39
3	0	5	20.10	21.21
4	0	5	10.34	12.46
5	0	5	22.46	22.45
6	0	5	6.17	3.25
7	0	5	10.54	7.39
8	0	5	23.56	20.64
9	0	5	36.34	34.05
10	0	5	10.78	6.06
11	0	5	11.92	12.25
12	0	5	13.61	14.94
-13	0	6	12.51	8.52
-10	0	6	57.66	64.68
-9	0	6	15.26	13.70
-7	0	6	18.72	13.80
-6	0	6	13.45	9.18
-5	0	6	5.86	5.08
-4	0	6	15.06	16.26
-3	0	6	32.53	32.65
-2	0	6	25.33	26.61
-1	0	6	28.87	30.30
0	0	6	16.83	17.81
1	0	6	15.38	17.19
2	0	6	16.95	15.24
3	0	6	5.98	4.39
4	0	6	11.72	10.36
5	0	6	16.24	17.49
6	0	6	23.95	23.73
7	0	6	27.41	27.95
8	0	6	5.86	7.76
-11	0	7	10.30	11.51
-10	0	7	25.56	27.99
-9	0	7	10.46	6.94
-8	0	7	17.23	13.37
-7	0	7	5.15	11.20
-6	0	7	14.36	13.82
-5	0	7	19.39	19.55
-4	0	7	7.00	8.43
-3	0	7	15.54	16.02
1	0	7	12.15	11.89
2	0	7	12.27	11.61
3	0	7	18.29	21.11
4	0	7	11.48	12.21
5	0	7	22.02	18.31
6	0	7	49.60	57.64
7	0	7	7.39	7.61
8	0	7	13.65	7.57
-14	0	8	7.63	7.82
-13	0	8	9.48	11.85
-12	0	8	12.90	13.48
-9	0	8	14.47	12.15
-8	0	8	10.38	7.63
-4	0	8	19.51	16.02
-2	0	8	18.76	18.39
-1	0	8	16.44	17.66
0	0	8	12.74	14.16
2	0	8	25.09	27.55
4	0	8	18.80	17.07
7	0	8	13.96	13.54
8	0	8	8.18	9.47
-3	0	9	17.74	16.39
-2	0	9	10.27	9.70
0	0	9	7.24	3.67
1	0	9	12.43	12.58
2	0	9	19.47	23.20
3	0	9	14.83	13.65
4	0	9	11.84	12.65
5	0	9	10.46	9.56
7	0	9	7.32	8.66
1	1	0	38.82	38.04
2	1	0	35.55	33.96
3	1	0	76.69	76.13
4	1	0	36.34	36.60
5	1	0	37.36	33.93
6	1	0	23.17	19.96
7	1	0	41.38	39.92
9	1	0	24.70	23.15
10	1	0	21.63	19.85
12	1	0	8.42	6.23
13	1	0	14.91	13.21
14	1	0	20.57	21.07
15	1	0	13.77	15.28
-16	1	1	9.75	8.29
-12	1	1	5.51	8.22
-11	1	1	17.34	15.39
-10	1	1	19.43	20.33
-9	1	1	17.58	15.07
-8	1	1	13.33	12.76
-7	1	1	31.19	31.84
-6	1	1	49.95	50.22
-5	1	1	48.53	45.98
-4	1	1	61.08	54.21
-3	1	1	41.49	37.71
-2	1	1	68.67	65.56
-1	1	1	43.97	45.47
0	1	1	20.14	18.41
1	1	1	43.54	41.46
2	1	1	137.93	147.44
3	1	1	107.49	101.94
4	1	1	31.19	27.46
5	1	1	25.41	22.01
6	1	1	4.13	2.11
7	1	1	19.67	16.61
8	1	1	26.74	24.26
9	1	1	31.74	31.84
10	1	1	20.88	18.95
11	1	1	10.03	9.55
12	1	1	13.96	13.38
13	1	1	11.52	14.08
14	1	1	16.95	17.88
15	1	1	18.13	21.87
16	1	1	9.52	5.75
-14	1	2	14.39	13.14
-13	1	2	5.78	5.56
-12	1	2	27.85	28.89
-11	1	2	12.98	11.87
-10	1	2	33.04	31.39
-9	1	2	25.21	22.26
-8	1	2	37.68	30.20
-7	1	2	29.62	24.90
-6	1	2	36.42	30.82
-5	1	2	48.85	47.87
-4	1	2	40.08	37.12
-3	1	2	50.58	57.13
-2	1	2	93.49	93.23
-1	1	2	51.17	50.61
0	1	2	48.61	48.54
1	1	2	50.34	45.70
2	1	2	60.21	51.22
3	1	2	8.18	4.80
4	1	2	26.98	17.20
5	1	2	78.35	74.02
6	1	2	12.15	13.27
7	1	2	29.46	25.97
8	1	2	4.60	1.08
9	1	2	14.39	13.59
10	1	2	15.34	15.03
11	1	2	9.79	10.52
13	1	2	16.16	12.36
14	1	2	9.40	8.85
-15	1	3	8.18	6.92
-14	1	3	11.76	9.84
-13	1	3	17.50	18.40
-10	1	3	18.96	15.22
-9	1	3	17.34	15.09
-8	1	3	15.93	13.44
-7	1	3	50.15	47.55
-6	1	3	56.71	52.31
-5	1	3	39.88	40.60
-4	1	3	55.85	57.02
-3	1	3	37.13	34.98
-2	1	3	36.38	29.58
-1	1	3	10.23	5.34
0	1	3	28.40	24.08
1	1	3	20.81	22.82
2	1	3	47.27	49.20
3	1	3	20.73	21.02
4	1	3	40.79	40.65
5	1	3	24.86	24.46
6	1	3	35.51	35.33
7	1	3	20.65	18.34
8	1	3	19.27	15.52
9	1	3	9.12	9.06
10	1	3	15.85	13.11
11	1	3	18.05	17.12
12	1	3	14.04	13.29
13	1	3	11.80	10.91
14	1	3	10.86	10.72
-15	1	4	11.37	12.32
-12	1	4	11.56	8.19
-11	1	4	13.77	10.26
-10	1	4	20.88	20.25
-9	1	4	22.69	23.84
-8	1	4	38.54	38.54
-7	1	4	19.70	18.82
-6	1	4	17.58	18.08
-5	1	4	36.97	28.84
-4	1	4	10.19	2.93
-3	1	4	33.39	32.05
-2	1	4	69.81	66.26
-1	1	4	39.72	38.94
0	1	4	52.94	58.79
1	1	4	16.91	18.41
2	1	4	47.83	49.82
3	1	4	9.52	12.50
4	1	4	30.91	30.06
5	1	4	9.95	6.18
6	1	4	14.16	12.61
7	1	4	18.01	18.48
8	1	4	14.32	14.08
9	1	4	17.93	19.19
10	1	4	25.96	27.23
11	1	4	7.98	7.52
12	1	4	12.03	11.80
-13	1	5	14.36	12.95
-12	1	5	14.39	10.89
-10	1	5	9.32	5.56
-9	1	5	12.98	11.55
-8	1	5	25.72	22.99
-7	1	5	9.48	9.82
-6	1	5	28.40	24.23
-5	1	5	32.37	31.24
-4	1	5	32.49	30.13
-3	1	5	37.84	35.02
-2	1	5	22.65	21.65
-1	1	5	20.77	22.10
0	1	5	12.39	8.28
1	1	5	23.56	19.95
2	1	5	11.64	13.73
3	1	5	16.75	15.84
4	1	5	23.24	24.99
5	1	5	24.15	24.35
6	1	5	15.73	16.29
7	1	5	16.56	13.74
8	1	5	20.25	19.61
9	1	5	19.74	18.12
10	1	5	12.35	8.28
12	1	5	6.49	3.42
-12	1	6	10.15	9.49
-11	1	6	16.64	13.10
-10	1	6	16.52	18.77
-9	1	6	27.10	22.07
-8	1	6	15.10	11.79
-7	1	6	24.50	23.98
-6	1	6	20.84	23.64
-5	1	6	16.32	15.55
-4	1	6	13.65	7.24
-3	1	6	19.74	18.14
-2	1	6	11.48	7.43
-1	1	6	15.46	12.28
0	1	6	17.58	16.29
1	1	6	8.93	[illegible]
2	1	6	16.39	17.51
3	1	6	24.94	26.26
4	1	6	29.89	32.23
5	1	6	8.18	10.69
6	1	6	7.71	3.82
7	1	6	13.49	10.09
8	1	6	18.41	14.46
9	1	6	8.42	6.4[illegible]
11	1	6	8.18	5.94
12	1	6	11.68	10.79
-11	1	7	12.90	11.66
-10	1	7	5.86	3.64
-9	1	7	11.76	10.57
-8	1	7	25.56	24.49
-7	1	7	17.42	13.72
-6	1	7	9.95	11.68
-5	1	7	5.66	6.91
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-3	1	7	21.59	22.16
-2	1	7	13.61	14.10
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1	1	7	9.71	12.47
2	1	7	15.02	18.16
3	1	7	11.48	10.46
4	1	7	17.42	15.76
5	1	7	21.95	23.86
6	1	7	11.76	11.30
-12	1	8	11.37	13.01
-10	1	8	7.91	6.68
-9	1	8	8.10	4.46
-7	1	8	8.30	11.87
-5	1	8	17.66	18.89
-4	1	8	13.14	12.37
-3	1	8	8.30	8.28
2	1	8	13.18	12.79
3	1	8	8.30	8.93
4	1	8	11.72	12.42
5	1	8	11.56	9.81
-2	1	9	8.14	5.64
1	1	9	12.70	13.52
4	1	9	7.63	12.85
0	2	0	94.71	98.06
1	2	0	105.48	115.00
2	2	0	78.74	79.80
3	2	0	60.61	50.04
4	2	0	30.24	28.00
5	2	0	20.65	14.88
6	2	0	36.38	32.99
7	2	0	22.34	17.99
8	2	0	32.13	30.32
9	2	0	31.15	29.88
10	2	0	26.04	26.95
11	2	0	13.29	13.69
12	2	0	9.24	7.86
13	2	0	9.56	8.41
14	2	0	8.14	7.72
-12	2	1	18.60	19.05
-11	2	1	22.73	23.89
-10	2	1	29.62	31.63
-9	2	1	33.67	35.30
-8	2	1	14.04	10.01
-7	2	1	23.40	24.22
-6	2	1	42.59	43.91
-5	2	1	43.89	44.08
-4	2	1	77.87	74.16
-3	2	1	33.59	34.76
-2	2	1	58.56	59.57
-1	2	1	50.42	49.30
0	2	1	11.00	9.95
1	2	1	37.17	32.32
2	2	1	92.66	87.67
3	2	1	70.28	61.85
5	2	1	67.33	61.92
6	2	1	51.76	47.73
7	2	1	43.[illegible]	37.26
8	2	1	27.22	23.28
9	2	1	14.91	12.84
10	2	1	7.94	5.82
11	2	1	4.84	2.92
12	2	1	8.77	7.41
13	2	1	5.19	6.[illegible]8
14	2	1	13.77	14.37
15	2	1	8.77	10.41
16	2	1	6.73	5.92
17	2	1	4.29	10.05
-11	2	2	7.00	7.53
-10	2	2	22.42	22.56
-9	2	2	9.79	10.96
-8	2	2	24.23	25.38
-7	2	2	26.71	30.9[illegible]
-6	2	2	14.16	3.43
-5	2	2	21.51	18.05
-4	2	2	42.75	41.08
-3	2	2	26.31	21.65
-2	2	2	22.02	15.63
-1	2	2	13.88	14.02
0	2	2	30.80	28.69
1	2	2	4.60	8.38
2	2	2	45.47	39.89
3	2	2	51.29	49.33
4	2	2	51.52	47.90
5	2	2	51.44	46.84
6	2	2	57.19	50.51
7	2	2	12.82	9.07
8	2	2	13.02	11.35
9	2	2	17.31	15.16
10	2	2	22.46	20.89
11	2	2	19.23	21.29
12	2	2	14.04	14.58
13	2	2	9.32	7.62
14	2	2	7.51	6.12
-11	2	3	18.33	17.16
-10	2	3	13.18	12.69
-9	2	3	26.71	28.38
-8	2	3	18.41	17.52
-7	2	3	25.53	27.79
-6	2	3	7.16	6.28
-5	2	3	19.19	21.54
-4	2	3	27.33	22.10
-3	2	3	47.75	44.53
-2	2	3	37.25	31.45
-1	2	3	54.31	50.94
0	2	3	36.07	32.33
1	2	3	39.33	35.27
2	2	3	59.62	57.66
3	2	3	48.57	42.32
4	2	3	49.48	38.19
6	2	3	31.58	25.71
7	2	3	33.78	29.94
8	2	3	27.49	26.53
9	2	3	21.12	20.55
10	2	3	9.91	10.03
11	2	3	7.24	7.52
12	2	3	7.39	8.32
-11	2	4	9.09	7.76
-10	2	4	8.69	8.94
-9	2	4	8.26	10.21
-8	2	4	16.24	12.88
-7	2	4	12.70	11.38
-6	2	4	32.21	31.37
-5	2	4	35.79	30.14
-4	2	4	28.04	23.69
-3	2	4	35.51	35.60
-2	2	4	30.28	25.49
-1	2	4	6.17	4.38
0	2	4	13.21	7.72
1	2	4	15.14	15.73
2	2	4	44.91	42.30
3	2	4	26.23	19.72
4	2	4	33.63	32.06
5	2	4	22.73	23.90
6	2	4	10.82	9.58
7	2	4	26.55	22.46
8	2	4	8.57	7.65
9	2	4	12.70	8.45
11	2	4	10.93	5.10
13	2	4	7.51	5.76
-10	2	5	6.29	4.51
-9	2	5	17.11	17.00
-8	2	5	24.38	28.57
-7	2	5	19.59	18.64
-6	2	5	23.76	21.91
-5	2	5	21.00	20.18
-4	2	5	22.50	19.68
-3	2	5	15.26	12.07
-1	2	5	31.82	26.71
0	2	5	59.86	56.46
1	2	5	41.49	36.50
2	2	5	26.47	28.95
3	2	5	14.16	12.39
4	2	5	16.32	16.55
5	2	5	5.47	7.68
6	2	5	5.78	4.27
7	2	5	6.06	5.45
8	2	5	10.97	7.79
10	2	5	12.35	10.22
11	2	5	9.32	11.44
-11	2	6	23.09	18.46
-10	2	6	13.77	11.63
-9	2	6	18.92	20.08
-8	2	6	27.14	25.06
-7	2	6	12.82	10.51
-6	2	6	11.13	9.18
-5	2	6	16.64	14.24
-4	2	6	27.33	24.75
-3	2	6	21.12	18.91
-2	2	6	28.55	28.72
-1	2	6	34.41	33.54
0	2	6	40.16	35.08
1	2	6	21.59	19.06
2	2	6	18.37	11.75
3	2	6	22.97	23.31
4	2	6	10.86	6.15
5	2	6	14.20	13.25
6	2	6	11.21	10.68
7	2	6	8.18	8.57
8	2	6	17.27	15.50
1	3	0	42.32	40.52
2	3	0	12.98	7.46
3	3	0	31.78	26.79
4	3	0	40.47	38.36
5	3	0	41.18	42.03
6	3	0	28.32	29.61
7	3	0	16.91	16.73
8	3	0	22.81	20.63
9	3	0	14.47	12.69
10	3	0	20.29	23.63
11	3	0	18.84	17.98
12	3	0	17.46	14.29
13	3	0	19.51	19.48
14	3	0	11.52	11.99
-13	3	1	10.38	10.67
-12	3	1	12.47	13.41
-11	3	1	4.92	5.23
-10	3	1	13.18	13.05
-9	3	1	17.62	20.95
-8	3	1	24.50	28.73
-7	3	1	18.25	16.89
-6	3	1	28.71	27.62
-5	3	1	21.67	22.88
-4	3	1	29.22	23.39
-3	3	1	21.67	21.38
-2	3	1	42.48	40.15
-1	3	1	32.64	31.58
0	3	1	51.17	50.50
1	3	1	53.02	54.62
2	3	1	53.80	53.25
3	3	1	76.61	78.99
4	3	1	39.53	38.85
5	3	1	31.42	31.36
6	3	1	24.54	21.89
7	3	1	10.58	6.53
8	3	1	16.48	12.67
9	3	1	19.67	20.19
10	3	1	14.32	14.24
11	3	1	21.75	23.41
12	3	1	15.46	17.23
13	3	1	9.05	9.31
14	3	1	5.15	4.83
-12	3	2	9.12	3.35
-11	3	2	17.66	20.27
-10	3	2	14.63	12.74

Table 2 (*cont.*)

-9	3	2	13.06	11.06
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-7	3	2	19.67	20.36
-6	3	2	31.35	28.59
-5	3	2	43.70	39.56
-4	3	2	45.19	46.35
-3	3	2	32.53	31.43
-2	3	2	39.09	37.99
-1	3	2	32.57	28.17
0	3	2	25.96	32.16
1	3	2	37.99	34.97
2	3	2	25.29	22.89
3	3	2	33.51	29.91
4	3	2	54.71	56.29
5	3	2	24.19	25.88
6	3	2	41.22	38.72
7	3	2	25.53	23.10
8	3	2	19.94	18.98
9	3	2	6.84	7.22
10	3	2	11.33	10.91
11	3	2	5.27	3.65
12	3	2	5.35	6.38
13	3	2	7.59	6.67
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3	8	0	5.15	6.41
5	8	0	9.64	10.90
6	8	0	8.10	10.70
7	8	0	13.02	14.42
-6	8	1	9.01	12.23
-5	8	1	10.42	11.32
-4	8	1	5.23	2.41
-3	8	1	15.61	19.43
-2	8	1	12.70	12.91
-1	8	1	5.19	5.12
0	8	1	7.32	6.37
1	8	1	5.19	5.09
4	8	1	7.35	13.33
6	8	1	5.19	7.71
8	8	1	12.23	15.02
9	8	1	6.80	11.07
-6	8	2	5.35	8.52
-5	8	2	7.59	11.19
-4	8	2	13.18	13.29
-3	8	2	5.39	5.40
-1	8	2	10.74	12.64
1	8	2	7.59	12.14
2	8	2	12.03	9.68
-6	8	3	8.89	11.42
-4	8	3	7.35	6.40
0	8	3	10.46	9.87
1	8	3	10.46	10.97
5	8	3	7.24	6.57
-6	8	4	7.39	8.66
6	8	4	8.69	6.15
-7	8	5	10.97	13.99
-3	8	6	12.59	13.29
-2	8	6	10.11	9.45
4	8	6	6.06	6.22
4	9	0	9.99	11.10
-5	9	1	4.96	8.13
-4	9	1	8.69	11.35
-3	9	1	11.33	16.43
-2	9	1	12.51	18.81
-1	9	1	7.24	8.38
0	9	1	5.11	7.03
-6	9	2	6.96	2.76
-4	9	2	8.89	4.64
-6	9	3	6.57	7.94
-5	9	3	8.26	10.81
3	9	3	4.84	8.38
4	9	3	8.18	9.20
-8	9	5	7.79	11.06
-7	9	5	6.84	7.35
-6	9	5	5.07	7.34
-5	9	5	8.38	9.14

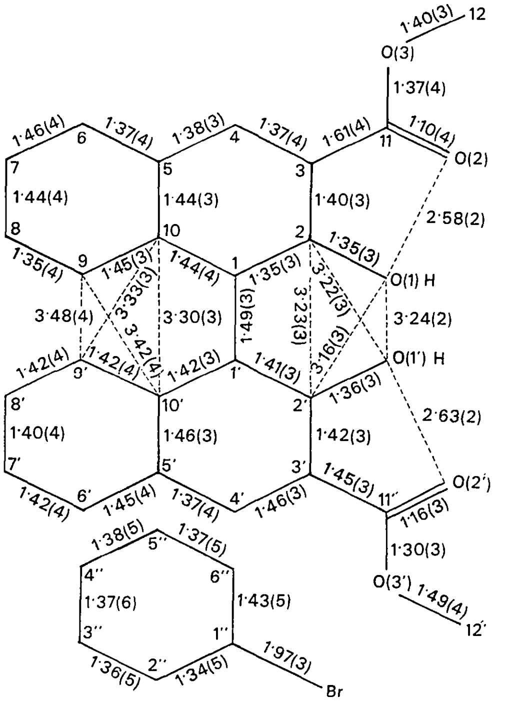

Fig. 3. Bond lengths (Å) and their standard deviations. The e.s.d.'s are given in parentheses denoting the least significant digits in the bond lengths. Some of the shortest intramolecular contacts are also shown.

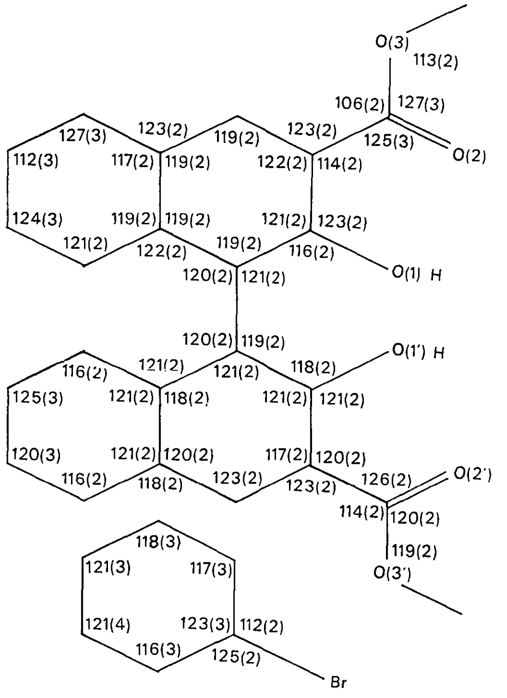

Fig. 4. Bond angles (°) and their standard deviations. The e.s.d.'s are given in parentheses denoting the least significant digits in the bond angles.

Table 3. *Comparison of the calculated and observed intensity ratios of the Friedel's pair of reflexions used for the establishment of absolute configuration*

Indices are referred to a right handed set of axes.

h	k	l	$\lvert F_c(hkl)\rvert^2/\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert^2$	$I_o(hkl)/I_o(\bar{h}\bar{k}\bar{l})$
6	1	0	1·49	> 1
12	1	0	1·67	> 1
13	1	0	1·18	> 1
5	1	1	0·88	< 1
7	1	1	1·12	> 1
8	1	1	0·88	< 1
11	1	1	0·81	< 1
4	1	2	1·27	> 1
6	1	2	0·83	< 1
9	1	2	0·90	< 1
14	1	2	0·88	< 1
10	2	0	1·17	> 1
7	2	1	0·87	< 1
8	2	1	1·11	> 1
9	2	1	0·88	< 1
11	3	0	1·13	> 1
12	3	0	1·13	> 1
8	3	1	0·88	< 1
12	3	1	0·90	< 1
7	3	2	0·80	< 1
8	3	2	1·11	> 1
9	3	2	0·65	< 1

two proved to have the (*R*)-configuration while the latter three had the (*S*)-configuration. These results are consistent with those proposed by Mislow (1958), who worked on the absolute configurations of (*S*)-(−)-1,1'-binaphthalene-2,2'-dicarboxylic acid and its derivatives by means of chemical methods.

Bond lengths and angles found in the molecules are shown in Figs. 3 and 4 together with their standard deviations. Since the main aim of the present determination was in finding out the absolute configuration of the binaphthyl groups, it was not attempted to refine the structure in greater detail. The average bond lengths and angles found within the naphthyl groups are 1·40 Å and 120° for the group I [C(1)∼C(10)] and 1·42 Å and 120° for the group II [C(1')∼C(10')]. Although the individual bond lengths and angles vary from 1·35 Å to 1·46 Å and from 112° to 127°, respectively, and some significant differences are observed between the corresponding values in both napthyl groups, the average values are in agreement with those found in naphthalene and its derivatives. In napthalene, the average values are 1·399 Å and 120° (Cruickshank, 1957) and in β-napthol they are 1·396 Å and 120° (Watson & Hargreaves, 1958).

Least-squares planes through various groups of atoms and the deviations of the atoms from each plane are shown in Table 4. Each of the two naphthyl groups I and II, is almost planar within the limit of experimental error. Group I is twisted with respect to the plane of group II at an angle of 76°36', defining the twist angle of the *cis* conformation to be 0°. As in the case of biphenyl (Hargreaves & Hasan Rizvi, 1962) and 1,3,5-triphenylbenzene (Farag, 1954), the bond connecting the two aryl groups is long enough for it to be concluded that there is no conjugation between them. It should be noted that in biphenyl the molecules are found to take a planar form in the crystalline state, despite the fact that the two phenyl rings are twisted at an angle of 42° in the vapour phase (Almenningen & Bastiansen, 1958). In 1,3,5-triphenylbenzene, on the other hand, the molecules are found to take a twisted form in the crystalline state, the three phenyl rings being twisted out of the plane of the central ring through angles of 24°, 27° and 34°, respectively. It was then assumed that the bonds connecting the two phenyl groups were not the conjugated ones and that the planarity of the biphenyl molecule in the crystal should be attributed to the intermolecular interactions, which would produce a gain in energy greater than that attributable to steric repulsions between *ortho* hydrogen atoms (Hargreaves & Hasan Rizvi, 1962). In the present structure, however, strong intramolecular steric repulsions should be responsible for the large twist angle of the naphthyl groups. Intramolecular short contracts found between the naphthyl groups I and II are shown in Fig. 3.

The two C–OH distances, 1·35 Å for C(2)–O(1)H and 1·36 Å for C(2′)–O(1′)H, are close to the values of 1·347 Å in salicyclic acid (Cochran, 1953), 1·36 Å in α- and β-resorcinol (Robertson, 1936; Robertson & Ubbelohde, 1938), 1·40 Å in α-naphthol (Robinson & Hargreaves, 1964) and 1·39 Å in β-naphthol (Watson & Hargreaves, 1958). These hydroxyl groups are hydrogen bonded to the carbonyl oxygen atoms of the same ring forming rather strong intramolecular hydrogen bonds of length 2·58 Å and 2·63 Å in naphthyl groups I and II, respectively. Similar hydrogen bonds are observed in salicylic acid (Cochran, 1953) and 4-aminosalicylic acid (Bertinotti, Giacomello & Liquori, 1954), in which the lengths of the O–H···O bonds are found to be 2·57 Å and 2·62 Å, respectively.

Table 4. *Least-squares planes and the deviations of the atoms*

The planes are of the form $AX+BY+CZ=P$, where X, Y, Z and P are in Å unit relative to the axes a^*, b and c.

Best planes through napthyl groups

Naphthyl group I		Naphthyl group II	
$-0{\cdot}606X+0{\cdot}030Y+0{\cdot}795Z=-0{\cdot}178$		$0{\cdot}600X+0{\cdot}788Y+0{\cdot}137Z=5{\cdot}269$	
C(1)	−0·008 Å	C(1′)	0·000 Å
C(2)	0·000	C(2′)	0·010
C(3)	0·030	C(3′)	−0·023
C(4)	−0·007	C(4′)	0·015
C(5)	−0·007	C(5′)	−0·010
C(6)	−0·005	C(6′)	0·025
C(7)	−0·006	C(7′)	−0·028
C(8)	0·029	C(8′)	0·012
C(9)	0·005	C(9′)	−0·005
C(10)	−0·031	C(10′)	0·005

Distances from the above planes

O(1)	−0·015 Å	O(1′)	−0·014 Å
C(11)	0·041	C(11′)	−0·008
O(2)	0·115	C(2′)	0·015
O(3)	0·186	O(3′)	−0·096
C(12)	0·208	C(12′)	−0·132

Best planes through ester groups

$-0{\cdot}656X+0{\cdot}038Y+0{\cdot}754Z=-0{\cdot}722$		$0{\cdot}578X+0{\cdot}810Y+0{\cdot}093Z=5{\cdot}164$	
C(3)	0·014 Å	C(3″)	−0·005 Å
C(11)	−0·055	C(11″)	0·017
O(2)	0·025	O(2″)	−0·007
O(3)	0·017	O(3″)	−0·005

Distances from the above planes

C(12)	−0·036 Å	C(12″)	−0·028 Å

Best plane through bromobenzene

$-0{\cdot}667X+0{\cdot}577Y-0{\cdot}472Z=-1{\cdot}312$

C(1″)	−0·031 Å
C(2″)	0·063
C(3″)	−0·086
C(4″)	0·050
C(5″)	0·055
C(6″)	−0·082
Br	0·031

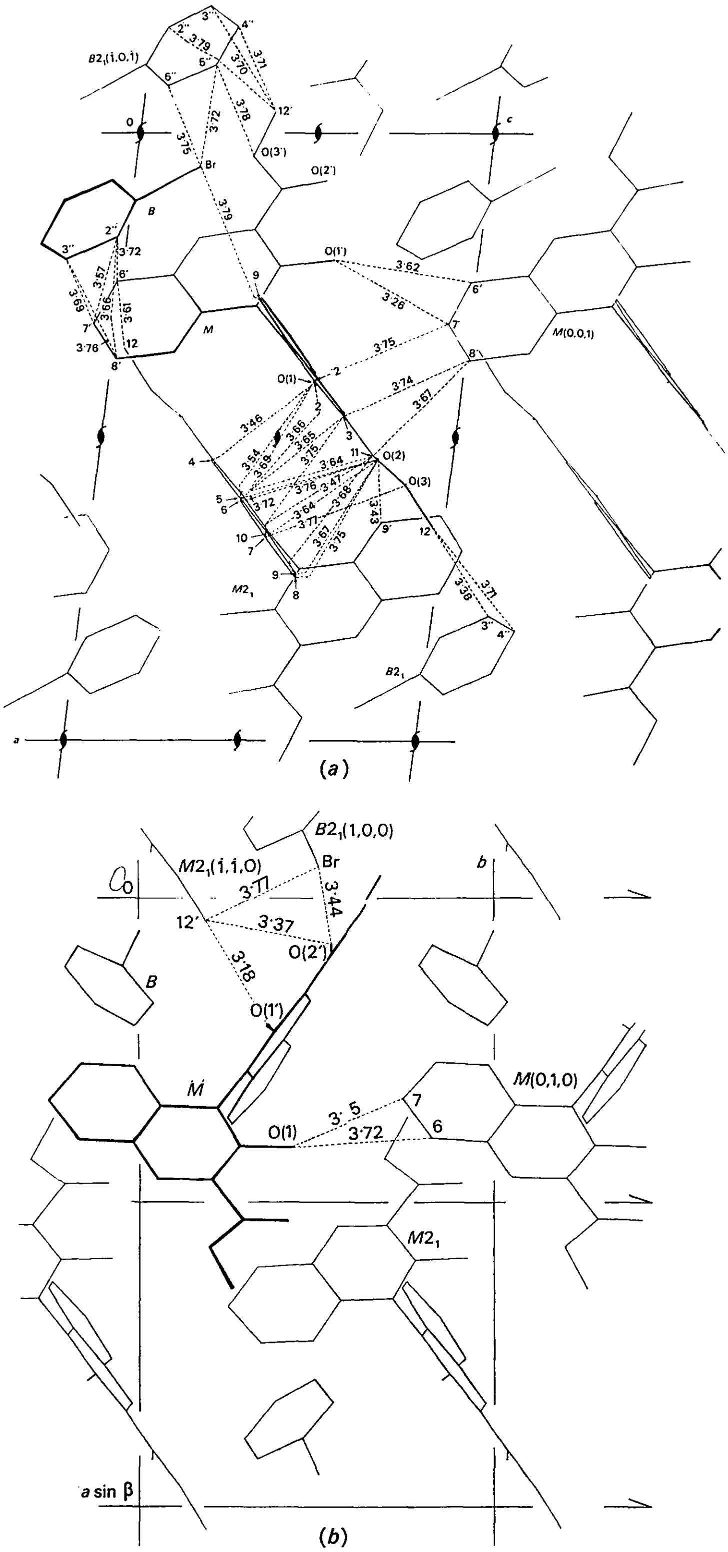

Fig. 5. (*a*) Projection of the crystal structure along the *b* axis. (*b*) Projection of the crystal structure along the *c* axis. To represent the correct absolute configuration, the axes should be taken in the right handed system. Intermolecular short contacts of less than 3·8 Å are shown in the Figure. *M* and *B* represent the molecules of the binaphthyl derivative and bromobenzene given in Table 1, and $M2_1$ and $B2_1$ are their symmetry equivalents at $(1-x, \frac{1}{2}-y, 1-z)$. The translations are denoted in parentheses.

The fact that these hydroxyl groups do not form hydrogen bonds between the naphthyl groups I and II, should be responsible for the repulsive forces between them, which, together with the repulsions between C(9)H and C(9′)H, would account for the larger twist angle between the two groups.

Two projections of the crystal structure along the *b* axis and the *c* axis are shown in Figs. 5(*a*) and (*b*). In these Figures, intermolecular short distances of less than 3·8 Å are shown. It is seen that the closest contacts of the molecules take place mainly between the atoms in the substituents (hydroxyl and methoxycarbonyl groups) and those in the naphthyl groups of the neighbouring molecules related by a twofold screw axis. The shortest distances are, 3·18 Å between C(12′) (methyl carbon) and O(1′) (hydroxyl oxygen), 3·25 Å between C(7) (ring carbon) and O(1) (hydroxyl oxygen) and 3·26 Å between C(7′) and O(1′).

The binaphthyl groups are packed together chiefly through these contacts to form a sheet parallel to (100). The packing of the sheets is conditioned mainly by the interactions among the methoxycarbonyl groups of the group II and those between the atoms of bromobenzene and group II. The molecules of bromobenzene are enclosed in the structure as a solvent of crystallization. It is seen in Fig. 5(*a*) that these molecules are arranged mutually antiparallel along the twofold screw axis and fill up the spaces between the sheets of the binaphthyl groups. Several close contacts of about 3·7 Å hold the bromobenzene molecules in their positions, the shortest distance being 3·38 Å which is found between C(3″) and C(12) (methyl carbon).

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Proton Magnetic Resonance Study of Zinc Benzenesulphonate Hexahydrate

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The lengths and orientations of the interproton vectors of the water molecules in a single crystal of zinc benzenesulphonate hexahydrate have been determined by the Pake (*J. Chem. Phys.* (1948) **16**, 237) method with use of proton magnetic resonance. The proton–proton distance in all the water molecules is 1·61 ± 0·03 Å. An attempt has been made to locate the protons by use of the hydrogen-bonding schemes suggested by the X-ray workers Broomhead & Nicol (*Acta Cryst.* (1948) **1**, 88), but the interproton vectors and the lines joining the acceptor oxygen atoms are not found to be parallel, though the bonds are of normal length. Alternative hydrogen-bonding schemes considered have acceptor oxygen atoms such that the bond lengths are too large, though the parallelism is reasonably good. A refinement of the crystal structure is probably necessary to fix the correct hydrogen bonding schemes.

Introduction

Water molecules in hydrated crystals are typical two-spin systems, in which the intramolecular proton–proton vector can be unambiguously determined, by use of the Pake (1948) method. Following Pake, the splitting of the resonance lines due to the dipolar interaction between the protons is given by:

$$\Delta H = 2\alpha[3\cos^2\delta\cos^2(\varphi-\varphi_0)-1]\,. \tag{1}$$