The Crystal Structure, Absolute Configuration, and Circular Dichroism of (*R*)-$(-)_{546}$-8,8′-(2-Thiatrimethylene)-1,1′-binaphthyl

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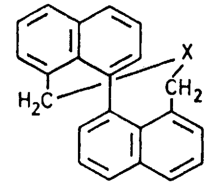
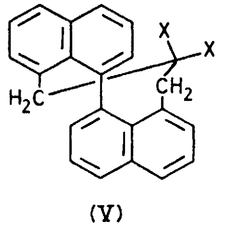
The crystal structure of $(-)_{546}$-(2-thiatrimethylene)-1,1′-binaphthyl has been examined by the Bijvöet *X*-ray method using Cu radiation :† the orthorhombic crystals are of space group $P2_12_12_1$ with four molecules in a unit cell of dimensions a = 8.442(7), b = 9.491(3), c = 20.075(9) Å. The structure was solved using MULTAN, and refined to a final *R* value of 2.3%. The molecules are found to have axial chirality *R* (helicity *M*), while each individual naphthalene unit is twisted with *P* helicity. The angle between the main planes of the naphthalene pairs is 92.5° and they are badly buckled, as predicted earlier on the basis of the low optical stabilities of related but unbridged compounds. The pattern of naphthalene bond lengths is unusual, all bonds adjacent to the strained points of connection of the two naphthalene rings to each other and to the 2-thiatrimethylene bridge being longer than normal. The two six-membered rings adjacent to the 2-thiatrimethylene bridge are more distorted from planarity than the other two. The C–S and C–C bond lengths in the bridge average 1.830 and 1.496 Å, while the naphthyl–naphthyl C–C distance is 1.503 Å. The C–S–C angle is 103.8°. C.d. spectra of this and related compounds are presented, compared, and discussed. Chemical correlation through synthesis extends the assignment of absolute configuration to many other 8,8′-disubstituted 1,1′-binaphthyls.

CRYSTALLOGRAPHIC studies[1–5] have established the absolute configuration of selected 2,2′-di- and 2,2′,3,3′-tetra-substituted 1,1′-binaphthyls, and synthetic routes to and from such substances have led to further assignments of absolute configuration in the 2,2′-disubstituted series. Recently Kuroda and Mason have subjected (—)-1,1′-binaphthyl itself to Bijvöet analysis.[6] However, until now the configurational assignments of the 8,8′-series have rested upon the results of π-SCF calculations[7] which indicated that (—)-1,1′-binaphthyl-8,8′-dicarboxylic acid is *S*. C.d. spectral correlations in the hydrocarbon series[8] extended the list of probable assignments by suggesting that (+)-1,1′-binaphthyl, (+)-2,2′-dimethyl-1,1′binaphthyl, and (+)-8,8′-dimethyl-1,1′-binaphthyl [which is obtained from the above (—)-rotatory dicarboxylic acid by stepwise reduction] are all of *S*-configuration. Using such information, the probable configurations of the (+)-rotatory enantiomers (I)—(IV) were also designated *S*.[9] These assignments have not previously been confirmed by the definitive methods of *X*-ray crystallography (the Bijvöet test).

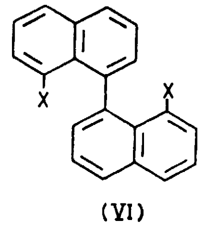
Many years ago Harris and Mellor[10] and Chua Cheung King Ling and Harris[11] ascribed the ease of racemisation of the (+) and (—)-atropisomers of certain 8,8′-disubstituted 1,1′-binaphthyls to favourable distortion of the naphthalene rings consequent upon *peri*-substitution. Crystallographic studies of octamethylnaphthalene[12] and of octachloronaphthalene[13] supported this view. Okaya and Ashida[14] determined the structure of methyl-(α-naphthyl)phenylsilanes in which crowding around the silicon atom causes buckling of the α-naphthyl system such that carbon atoms are displaced out of plane by *ca.* 0.2 Å with the C(1)–C(2) and C(7)–C(8) bonds bent in opposite directions. Despite this distortion, they described the naphthalene rings as, ' more or less normal. The bond distances and angles of the α-naphthyl group are quite similar to the corresponding values in free naphthalene.' There is only one *peri*-substituent in Okaya and Ashida's case, whereas in the 8,8′-disubstituted binaphthyls there are two *peri*-substituents on each naphthalene, making compressions and distortions of greater significance. We have also studied the structural details of naphtho[*b,c*]dicyclobutene and found that annelation causes small deviations in bond length from those found in naphthalene, the largest being



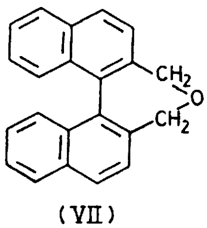
(I) X = O
(II) X = S
(III) X = Se
(IV) X = SO_2



(V)



(VI)



(VII)

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† This structure was briefly described in a preliminary publication, J. D. Korp, I. Bernal, M. M. Harris, and P. K. Patel, *Tetrahedron Lett.*, 1979, 4099.

at C(9)–C(10) ($\Delta = 0.023$ Å) while other differences are negligible.[15] And in a $Re_2Br_2(CO)_6$ complex of 1,8-naphthalene disulphide[16] we found that significant distortions from planarity do not necessarily cause observable changes in bond lengths with respect to the parent naphthalene.[17]

A naphthalene system which is subject to out-of-plane distortion consequent upon *peri*-compressions is necessarily a chiral structure and capable of enantiomerism. Unfortunately, conformational mobility will usually mean that the chirality is not observable; however, in the bridged molecules of the 8,8′-series these conformations are fixed. It is suggested that such twisted naphthalene units may be responsible for c.d. bands in the 280—315 nm region which in the *S*-8,8′-bridged compounds are of opposite sign from the other (*S*)-1,1′-binaphthyls (the chirality of the two naphthyls in any one molecule is the same).[18] This difference in sign is observed similarly in the enantiomeric *R*-series, the 8,8′-bridged compounds falling out of line with the rest.

These considerations have led us to undertake an *X*-ray structural investigation of (−)-8,8′-(2-thiatrimethylene)-1,1′-binaphthyl (II). As an example of an 8,8′-disubstituted 1,1′-binaphthyl it has the advantage of a fixed geometry. The absolute configuration can be found and the effect of strains on the naphthalene rings assessed. Additionally, the c.d. can be studied with the knowledge that the conformation of the molecules is the same in solution as it is in the crystal, an assumption that cannot be made for an unbridged structure such as 1,1′-binaphthyl itself or either of the dimethyl compounds mentioned above.

EXPERIMENTAL

Details of the synthesis have been described previously.[19] The crystal used for the *X*-ray study was a yellowish tabular plate of approximate dimensions 0.25 × 0.25 × 0.35 mm; all measurements were made on an Enraf–Nonius CAD-4 automatic diffractometer using Mo-K_α radiation monochromatized by a dense graphite crystal assumed for all purposes to be ideally imperfect. The lattice parameters used in data collection were obtained from a least squares fit of 25 automatically centred reflections. The final cell constants, as well as other information pertaining to the data collection and refinement, are listed in Table 1. The Laue symmetry is *mmm*, and from the systematic absences noted the space group was unambiguously determined to be $P2_12_12_1$. Intensities were measured using the θ–2θ scan technique, with two standard reflections re-measured periodically to check crystal stability and electronic reliability. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved using MULTAN,[20] and the usual sequence of isotropic and anisotropic refinement was followed. All hydrogens were readily apparent in subsequent difference Fourier syntheses, and they were allowed to refine independently with separate isotropic temperature factors. After all shift : e.s.d. ratios were <0.3, the refinement converged to the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables. The atomic scattering factors for carbon and sulphur were computed from numerical Hartree–Fock wave functions;[21] for hydrogen those of Stewart *et al.*[22] were used. All calculations were made with the SHELX-76 series of programs.[23] The determination of the correct absolute configuration was made from analysis of ten Bijvöet pairs,[24] each having an observed difference of at least 5%, with no counter-indications whatsoever. Since the anomalous dispersion of sulphur is much larger using Cu radiation than using Mo,[25] we made the Bijvöet measurements on a Syntex diffractometer equipped with a Cu target tube.* Final positional and thermal parameters are listed in Table 2, according to the atom labelling scheme of Figure 1. The hydrogens have numbers corresponding to the carbons to which they are bonded. Bond distances, angles, least squares planes, and torsional angles based on these positions are given in Tables 3—6. Structure factors are in Supplementary Publication No. SUP 23163 (8 pp.).†

TABLE 1

Summary of data collection and processing parameters

Space group	$P2_12_12_1$, orthorhombic
Cell constants	$a = 8.442(7)$ Å
	$b = 9.491(3)$
	$c = 20.075(9)$
	$U = 1\,608.5$ Å^3
Molecular formula	$C_{22}H_{16}S$
Molecular weight	312.43
Molecules per cell	4
Density	1.29 g cm^{-3}
Absorption coefficient	1.56 cm^{-1}
Radiation (Mo-K_α)	0.710 73 Å
Collection range	$4° \leq 2\theta \leq 60°$
Scan width	$\Delta\theta = (1.10 + 0.35 \tan\theta)°$
Maximum scan time	300 s
Scan speed range	0.3—3.4° min^{-1}
Total data collected	2 666
Independent data with $I > 3\sigma(I)$	984
Total variables	272
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.023
$R_w = [\Sigma_w(\|F_o\| - \|F_c\|)^2/\Sigma_w\|F_o\|^2]^{\frac{1}{2}}$	0.016
Weights	$W = \sigma(F)^{-2}$

DISCUSSION

Chirality of 8,8′-*Disubstituted* 1,1′-*Binaphthyls*.—This structure is of particular interest to the stereochemist because the configuration and conformation which emerge are in agreement with those arrived at by more speculative methods, providing evidence for their reliability and value when suitable crystals are not available. The position prior to this *X*-ray determination was as follows.

Distorted rings. The optical activity of the 1,1′-binaphthyls is of the biphenyl type, and where there is no bridge configurational inversion takes place if the two vanes can pass each other. 8,8′- and 2,2′-disubstituted compounds are strikingly different in optical stability:[26] for example, (−)-8,8′-dimethyl-1,1′-binaphthyl has a half-life of *ca.* 11 h at 100 °C[8] while 2,2′-dimethyl-1,1′-binaphthyl[27] shows no loss of optical activity when heated at 240 °C for 15 h.[28] Flexibility

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* We thank Dr. F. A. Quiocho, Chemistry Department, W. M. Rice University, Houston, Texas, for allowing us to use his equipment for these measurements.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.

TABLE 2

Atomic co-ordinates and thermal parameters ($\times 10^3$)

Atom	x/a	y/b	x/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0.826 6(2)	0.627 0(1)	0.896 2(1)	51(1)	40(1)	64(1)	−10(1)	−8(1)	5(1)
C(1)	0.648 5(6)	0.588 6(4)	0.944 3(2)	62(3)	34(2)	39(2)	−4(3)	−5(3)	0(2)
C(2)	0.498 3(5)	0.625 9(4)	0.908 4(2)	49(3)	33(2)	36(2)	−3(2)	6(2)	1(2)
C(3)	0.431 8(6)	0.754 6(5)	0.921 3(2)	61(3)	43(3)	53(3)	1(3)	4(3)	−7(2)
C(4)	0.308 0(6)	0.809 3(5)	0.884 2(3)	72(4)	46(3)	69(3)	17(3)	18(3)	0(3)
C(5)	0.253 4(5)	0.739 5(5)	0.830 3(2)	49(3)	60(3)	57(3)	12(3)	8(2)	20(3)
C(6)	0.316 7(5)	0.605 3(4)	0.813 6(2)	38(2)	44(2)	41(2)	−2(3)	8(2)	8(2)
C(7)	0.270 6(5)	0.534 4(5)	0.754 1(2)	37(3)	68(3)	44(3)	−3(3)	−3(2)	14(3)
C(8)	0.330 0(5)	0.407 2(4)	0.737 8(2)	44(3)	70(3)	40(2)	−5(3)	−1(3)	−1(2)
C(9)	0.431 3(5)	0.338 6(4)	0.782 7(2)	41(3)	48(3)	45(3)	0(2)	2(2)	−14(2)
C(10)	0.481 4(4)	0.401 4(4)	0.840 9(2)	24(2)	44(2)	39(2)	−4(2)	7(2)	−1(2)
C(11)	0.433 6(4)	0.542 2(3)	0.855 5(2)	34(2)	35(2)	34(2)	−2(2)	9(2)	0(2)
C(12)	0.565 7(5)	0.305 0(4)	0.888 6(2)	40(2)	29(2)	32(2)	−3(2)	2(2)	−3(2)
C(13)	0.470 9(5)	0.233 5(4)	0.932 1(2)	40(3)	41(3)	48(3)	−5(2)	2(2)	−7(2)
C(14)	0.525 2(6)	0.119 3(5)	0.971 2(2)	69(4)	44(3)	49(3)	−17(3)	9(3)	0(3)
C(15)	0.676 6(7)	0.073 1(4)	0.962 3(2)	69(4)	36(2)	48(3)	−9(3)	−14(3)	5(2)
C(16)	0.782 5(5)	0.144 3(4)	0.919 3(2)	51(3)	37(2)	45(3)	−4(2)	−12(2)	−3(2)
C(17)	0.938 2(6)	0.093 4(5)	0.910 3(2)	50(3)	45(3)	66(3)	11(3)	−24(3)	0(3)
C(18)	1.042 6(6)	0.166 1(5)	0.872 0(2)	32(3)	64(3)	84(4)	5(3)	−13(3)	−10(3)
C(19)	0.999 7(5)	0.296 9(5)	0.844 8(2)	31(3)	54(3)	68(3)	−8(3)	2(3)	−3(2)
C(20)	0.848 1(5)	0.350 5(4)	0.851 4(2)	39(3)	43(3)	32(2)	−2(3)	1(2)	−5(2)
C(21)	0.731 3(4)	0.269 3(4)	0.885 3(2)	37(2)	29(2)	38(2)	−1(2)	−1(2)	−8(2)
C(22)	0.821 1(6)	0.497 8(4)	0.828 2(2)	37(3)	53(3)	43(3)	−8(3)	1(3)	7(2)
H(1A)	0.656(4)	0.653(3)	0.987(1)	49(10)					
H(1B)	0.656(4)	0.490(3)	0.958(1)	39(10)					
H(3)	0.487(4)	0.816(4)	0.954(2)	66(13)					
H(4)	0.259(4)	0.897(3)	0.893(2)	71(14)					
H(5)	0.156(5)	0.771(4)	0.800(2)	81(14)					
H(7)	0.194(4)	0.580(3)	0.729(1)	34(10)					
H(8)	0.281(4)	0.348(3)	0.696(2)	72(13)					
H(9)	0.461(4)	0.242(3)	0.775(1)	37(10)					
H(13)	0.355(5)	0.258(3)	0.929(1)	52(12)					
H(14)	0.448(4)	0.070(3)	1.007(2)	59(12)					
H(15)	0.715(5)	−0.009(3)	0.987(2)	87(15)					
H(17)	0.968(4)	0.006(3)	0.934(2)	49(12)					
H(18)	1.147(4)	0.136(4)	0.866(2)	70(13)					
H(19)	1.079(4)	0.362(4)	0.824(1)	53(12)					
H(22A)	0.912(4)	0.535(3)	0.801(2)	45(13)					
H(22B)	0.726(3)	0.517(3)	0.802(1)	36(10)					

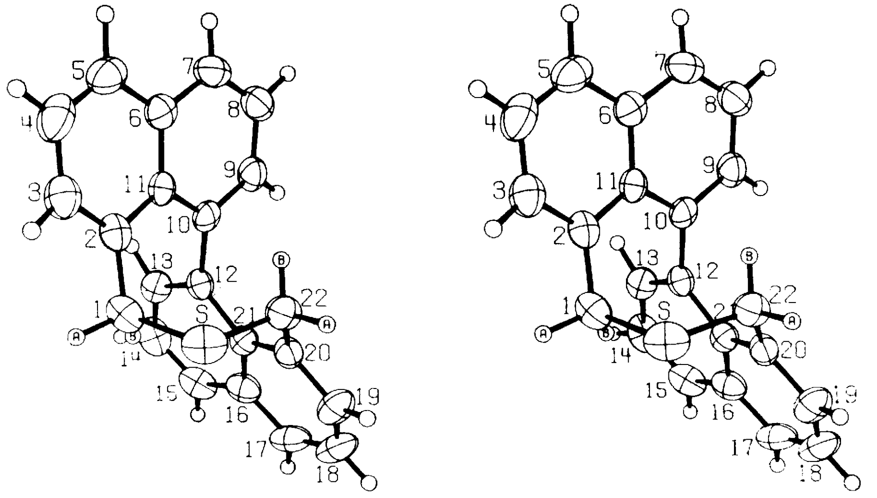


FIGURE 1 Stereoscopic view of the molecule showing the atom labelling scheme. The carbon and sulphur atoms are shown as 50% equiprobability ellipsoids, with hydrogens as spheres of arbitrary diameter. Note the overall *R* axial chirality (*M* helicity), and the *P* helicity of the two naphthalene rings. When a stereopair such as this is used without mechanical aid to see a three-dimensional image deliberate care must be taken to avoid crossing the eyes. In the event of the observer squinting, a ' solid ' image of opposite chirality to that intended by the authors comes into view. As most people find it simpler to achieve the cross-eyed image than the uncrossed one serious errors of understanding can easily arise (A. H. Johnstone, K. M. Letton, and J. C. Speakman, *Educ. Chem.*, 1980, 172)

TABLE 3

Intramolecular bond distances (Å)

S–C(1)	1.824(5)	C(10)–C(12)	1.503(4)
S–C(22)	1.836(4)	C(12)–C(13)	1.365(5)
C(1)–C(2)	1.501(5)	C(12)–C(21)	1.440(4)
C(2)–C(3)	1.369(5)	C(13)–C(14)	1.414(5)
C(2)–C(11)	1.433(5)	C(14)–C(15)	1.363(6)
C(3)–C(4)	1.384(6)	C(15)–C(16)	1.415(6)
C(4)–C(5)	1.349(6)	C(16)–C(17)	1.412(5)
C(5)–C(6)	1.422(5)	C(16)–C(21)	1.435(5)
C(6)–C(7)	1.424(5)	C(17)–C(18)	1.358(6)
C(6)–C(11)	1.429(5)	C(18)–C(19)	1.404(6)
C(7)–C(8)	1.348(5)	C(19)–C(20)	1.384(5)
C(8)–C(9)	1.403(5)	C(20)–C(21)	1.425(5)
C(9)–C(10)	1.379(5)	C(20)–C(22)	1.490(5)
C(10)–C(11)	1.426(5)		
C(1)–H(1A)	1.06(3)	C(13)–H(13)	1.01(4)
C(1)–H(1B)	0.98(3)	C(14)–H(14)	1.08(3)
C(3)–H(3)	1.00(3)	C(15)–H(15)	0.98(4)
C(4)–H(4)	0.94(3)	C(17)–H(17)	0.99(3)
C(5)–H(5)	1.07(4)	C(18)–H(18)	0.93(3)
C(7)–H(7)	0.92(3)	C(19)–H(19)	1.00(3)
C(8)–H(8)	1.09(3)	C(22)–H(22A)	1.00(3)
C(9)–H(9)	0.97(3)	C(22)–H(22B)	0.97(3)

TABLE 4

Intramolecular bond angles (°) *

C(1)–S–C(22)	103.8(2)	C(10)–C(12)–C(13)	115.6(3)
S–C(1)–C(2)	113.2(2)	C(10)–C(12)–C(21)	124.9(4)
C(1)–C(2)–C(3)	117.7(4)	C(13)–C(12)–C(21)	118.8(4)
C(1)–C(2)–C(11)	123.1(4)	C(12)–C(13)–C(14)	123.1(4)
C(3)–C(2)–C(11)	118.6(4)	C(13)–C(14)–C(15)	118.6(4)
C(2)–C(3)–C(4)	122.8(4)	C(14)–C(15)–C(16)	121.2(4)
C(3)–C(4)–C(5)	120.3(4)	C(15)–C(16)–C(17)	120.2(4)
C(4)–C(5)–C(6)	120.1(4)	C(15)–C(16)–C(21)	119.7(4)
C(5)–C(6)–C(7)	121.3(4)	C(17)–C(16)–C(21)	120.1(4)
C(5)–C(6)–C(11)	119.7(4)	C(16)–C(17)–C(18)	120.2(4)
C(7)–C(6)–C(11)	119.0(3)	C(17)–C(18)–C(19)	120.1(4)
C(6)–C(7)–C(8)	121.7(4)	C(18)–C(19)–C(20)	121.8(4)
C(7)–C(8)–C(9)	119.2(4)	C(19)–C(20)–C(21)	119.1(4)
C(8)–C(9)–C(10)	122.0(4)	C(19)–C(20)–C(22)	117.2(4)
C(9)–C(10)–C(11)	119.5(3)	C(21)–C(20)–C(22)	123.4(4)
C(9)–C(10)–C(12)	115.0(3)	C(20)–C(21)–C(12)	124.6(4)
C(11)–C(10)–C(12)	124.9(3)	C(20)–C(21)–C(16)	117.8(3)
C(10)–C(11)–C(2)	124.3(4)	C(12)–C(21)–C(16)	117.7(3)
C(10)–C(11)–C(6)	117.8(3)	C(20)–C(22)–S	113.0(3)
C(2)–C(11)–C(6)	117.8(3)		

* The range of angles involving hydrogens are aromatic (114—124°), aliphatic (98—118°).

and substantial deviation from planarity of the naphthalene systems is invoked to explain this phenomenon. The chirality of the individual naphthalene units [26] in these compounds is probably too labile to contribute to the optical activity. In the compound now examined the chirality of the individual naphthalene units is fixed and is determined by the overall configuration.

The ^{1}H n.m.r. spectra of compounds (I)—(IV) have been studied in detail,[19] and the wide spacing of the signals of the enantiotopic protons of the two methylene groups shows that they are very differently situated with regard to the aromatic rings. The spectra can be interpreted reasonably by recourse to molecular models which allow the necessary degree of distortion.

Carter and Liljefors [29] have applied the molecular mechanics method to compute a minimum enthalpy of activation for racemisation of 1,1′-binaphthyl itself. They comment on the flexibility of the aromatic ring systems, noting that considerable distortion can take

TABLE 5

Equations of least squares planes, deviations (in Å) of atoms from such planes, and dihedral angles between the planes listed

(a) Plane defined by C(4)—C(8)

$$0.7138x + 0.4522y - 0.5348z + 4.192 = 0$$

C(2)	0.129(4)	C(7)	0.020(4)
C(3)	0.143(5)	C(8)	0.008(4)
C(4)	0.029(5)	C(9)	−0.158(4)
C(5)	−0.021(5)	C(10)	−0.213(4)
C(6)	−0.036(4)	C(11)	−0.053(4)
C(1)	0.488(4)	C(12)	−0.631(4)

(b) Plane defined by C(3)—C(9)

$$0.7177x + 0.4285y - 0.5489z + 4.550 = 0$$

C(2)	0.105(4)	C(7)	0.053(4)
C(3)	0.083(5)	C(8)	0.075(5)
C(4)	−0.036(5)	C(9)	−0.084(4)
C(5)	−0.057(5)	C(10)	−0.168(3)
C(6)	−0.034(4)	C(11)	−0.046(4)
C(1)	0.467(5)	C(12)	−0.057(4)

(c) Plane defined by C(14)—C(18)

$$-0.3073x - 0.5387y - 0.7845z + 17.265 = 0$$

C(12)	0.244(4)	C(17)	0.020(4)
C(13)	0.171(4)	C(18)	−0.021(5)
C(14)	−0.001(4)	C(19)	−0.150(4)
C(15)	−0.019(4)	C(20)	−0.135(4)
C(16)	0.021(4)	C(21)	0.051(4)
C(10)	0.722(4)	C(22)	−0.452(4)

(d) Plane defined by C(13)—C(19)

$$-0.2788x - 0.5404y - 0.7938z + 17.251 = 0$$

C(12)	0.193(4)	C(17)	0.058(4)
C(13)	0.090(4)	C(18)	0.049(5)
C(14)	−0.074(4)	C(19)	−0.088(4)
C(15)	−0.053(4)	C(20)	−0.111(4)
C(16)	0.019(4)	C(21)	0.041(4)
C(10)	0.658(4)	C(22)	−0.434(4)

Angles (°) between planes. The labels are the same as those above

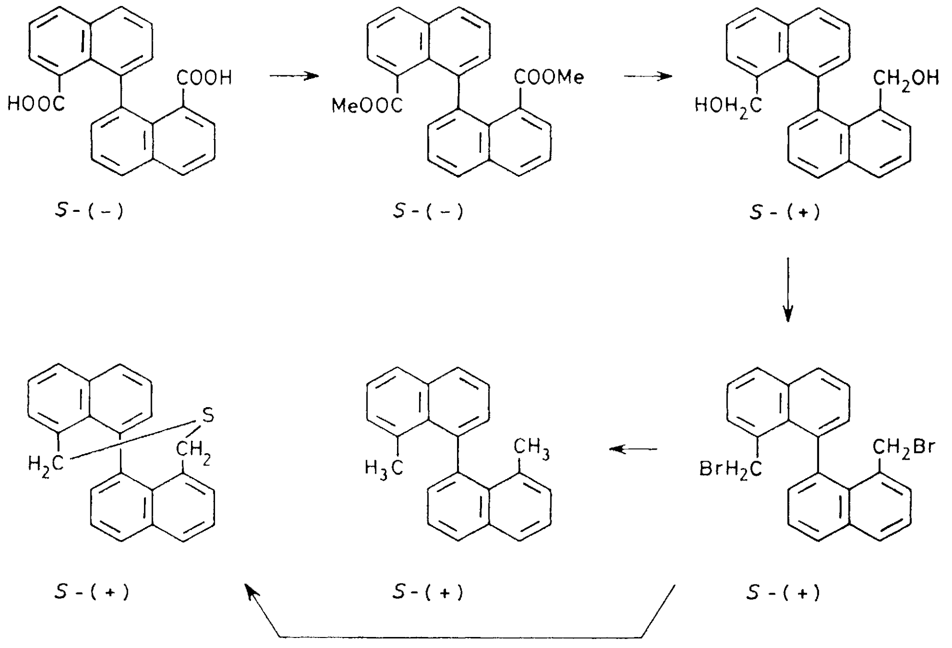
(a)–(b)	1.60	(b)–(c)	91.19
(a)–(c)	92.49	(b)–(d)	89.77
(a)–(d)	91.08	(c)–(d)	1.72

TABLE 6

Selected torsion angles (°)

S–C(1)–C(2)–C(3)	−95.4
S–C(1)–C(2)–C(11)	76.3
S–C(22)–C(20)–C(19)	−98.0
S–C(22)–C(20)–C(21)	75.7
C(1)–S–C(22)–C(20)	−69.0
C(1)–C(2)–C(3)–C(4)	170.0
C(1)–C(2)–C(11)–C(10)	14.6
C(2)–C(1)–S–C(22)	−69.3
C(2)–C(11)–C(6)–C(5)	−8.4
C(2)–C(11)–C(10)–C(9)	−169.3
C(2)–C(11)–C(10)–C(12)	19.7
C(3)–C(2)–C(11)–C(10)	−173.8
C(4)–C(5)–C(6)–C(7)	−174.9
C(5)–C(6)–C(7)–C(8)	180.0
C(7)–C(6)–C(11)–C(10)	−9.1
C(7)–C(8)–C(9)–C(10)	−4.8
C(8)–C(9)–C(10)–C(12)	169.8
C(9)–C(10)–C(12)–C(13)	−87.6
C(10)–C(12)–C(13)–C(14)	167.2
C(10)–C(12)–C(21)–C(20)	21.0
C(11)–C(10)–C(12)–C(13)	83.8
C(12)–C(21)–C(16)–C(15)	−9.3
C(12)–C(21)–C(20)–C(19)	−172.3
C(12)–C(21)–C(20)–C(22)	14.1
C(13)–C(12)–C(21)–C(20)	−168.4
C(14)–C(15)–C(16)–C(17)	−179.1
C(15)–C(16)–C(17)–C(18)	−176.2
C(16)–C(21)–C(20)–C(22)	−164.8
C(18)–C(19)–C(20)–C(22)	172.4

place for very little energy expenditure. The model which gives the minimum value has slightly non-planar naphthalene rings, bent with opposite chirality; it uses the *trans*-passing position. Agreement with experimentally determined values[10] lends credence to their model and to their method. Only 5 kcal mol^{-1} more is required to racemise the molecule with two 8,8′-dimethyl substituents,[10] a figure which would seem absurdly small if it were not that increased out-of-plane distortion raises the ground state energy, and that the distortions are favourable to interconversion of the atropisomers.



Scheme

Although nine-membered carbocyclic rings are notoriously difficult to make in most circumstances, it is easy to prepare them from 8,8′-bisbromomethyl-1,1′-binaphthyl and a reagent which adds one more ring atom.[19,30] If the naphthalene rings were planar the necessary substitutions would be geometrically impossible, as can easily be appreciated by inspection of models. In effect, the strain in these nine-membered rings is taken up at the *peri*-naphthalene positions.

Configuration.—Theoretical treatment of the chromophore[27,31] has proved fruitful: in particular Mason and his collaborators,[7] as a result of exciton and SCF calculations, were led to propose that (—)-1,1′-binaphthyl-8,8′-dicarboxylic acid has the *S*-configuration. It is converted into (+)-8,8′-dimethyl-1,1′-binaphthyl by a straightforward series of chemical reactions in which optical activity is retained. The relationships of sign and configuration in the Scheme therefore derive from Mason's proposal.

Another approach to the absolute chirality of (+)-8,8′-dimethyl-1,1′-binaphthyl (and hence of the bisbromomethyl compounds, precursors of the rings) came through Akimoto's *X*-ray determination which led to the *S*-configuration being derived for (+)-1,1′-binaphthyl and for (+)-2,2′-dimethyl-1,1′-binaphthyl. The c.d.s of these two compounds were then compared with that of (+)-8,8′-dimethyl-1,1′-binaphthyl and they were all found to be closely similar in the region of the 'couplet,' 218—225 nm.[8] This similarity would be expected if they all have the same configuration and also all have conformations in which the dihedral angle between the naphthalene rings is *ca.* 90° or less.[7,27,31] Correlations of this kind had been made previously in the 2,2′-disubstituted series by Mislow.[32] If it is correct to assume that all three dihedral angles lie within these limits in solution, as ^{1}H n.m.r. studies suggest,[28] then the (+)-8,8′-disubstituted compound has the *S*-configuration.

The bridged compound which is the subject of the present study was prepared from optically active (—)-8,8′-bisbromomethyl-1,1′-binaphthyl: it retained its optical activity during the reaction, and therefore its configuration. A large variety of (—)-rotatory rings can be made, carbocyclic,[30] nitrogen-containing,[33] and with O, S, SO$_2$ or Se in the bridge.[19] They must all have the *R*-configuration on the above evidence, and this is confirmed by the *X*-ray determination.

Circular Dichroism.—Table 7 shows the circular dichroism for a set of *R*-(—)$_{546}$-8,8′-bridged 1,1′-binaphthyls. Table 8 illustrates the effect of a bridged or non-bridged structure on the c.d. Points for particular note are as follows.

(a) The couplet in the short wave region,[4,7,8] where a positive extremum of large amplitude is followed by a negative one at longer wavelength. This striking feature is common to all known *R*-confguration 1,1′-binaphthyls, whether they be bridged, unbridged, 2,2′- or 8,8′-disubstituted, or (—)-1,1′-binaphthyl itself. An *R*-

TABLE 7

C.d. in 96% ethanol of (I)—(IV)

Compound								
(I) λ/nm	219	225	232	255	267	281	291	
$10^{-3}[\theta]$	+1 088	0	−1 149	−52	−61	−57	−55	
(II)	228.5	234.5	247		272	283	297.5	312
	+735	0	−511		−32	−44	−54	−32
(III)	232	239.5	255		277		297	
	+717	0	−279		−56		−97	
(IV)	223	228	239	264	273	284	296	304
	+1 149	0	−969	−5	−10	−22.5	−47.5	−49

These compounds all have satisfactory elementary analyses; the specimens used were not tested for optical purity.

configuration molecule in which the 2- and 8′-positions were joined might fall out of line, but such a one has yet to be prepared.

(b) In the region around 295 nm they all have complex negative bands. This leaves these 8,8′-disubstituted ring compounds outside the generalisation made by Mislow[32] in 1962, *viz.* that chiral 1,1′-binaphthyls of *R*-configuration are positive in the 280—315 nm region, a generalisation which we have found to be true for large numbers of 1,1′-binaphthyls,[18] with the exception of the 8,8′-rings.

TABLE 8

C.d. in 96% ethanol of *R*-(−)-(V) and *R*-(+)-(VI)

Compound										
(V; X = CO_2H)	λ/nm 215	221.5	229	257	261.5	287.5	295	301.5	316.5	323
	$10^{-3}[\theta]$(+)707	0.0	(−)719	(−)30	(−)32	(−)9	(−)15	(−)17	(−)2.6	(−)2
(V; X = CO_2Me)	λ/nm 215	220.5	228.5	253.6	261	286.9	294	303	315	
	$10^{-3}[\theta]$(+)600	0.0	(−)1 108	(−)28	(−)31	(+)1	(−)11	(−)14	(−)1.5	
(VI; X = CO_2H)	λ/nm 222.5	231.5	240	252	261.3	274	296—300	312.5	325	
	$10^{-3}[\theta]$(+)565	0.0	(−)342	0.0	(−)39	0.0	(+)79	(+)37	(+)37	
(VI; X = CO_2Me)	λ/nm 221	226.5	236.5	249.5	259	276.5	295	311	329	
	$10^{-3}[\theta]$(+)320	0.0	(−)368	(−)33	(−)67	0.0	(+)47.2	(+)24.8	(+)20	
C.d. in 96% ethanol of *S*-(+)-(VII)										
(VII)	λ/nm 216	222	228		262.3		283.1	300		
	10^{-3}-$[\theta]$(−)2 100	0.0	(+)2 340		(+)151		(−)51	(−)72		

These compounds all have satisfactory elemental analyses; the specimens used were not tested for optical purity.

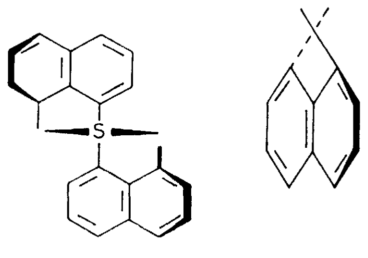
It becomes necessary to find a structural element which is of opposite chirality in the *R*-8,8′-bridged compounds from all the other known types of *R*-1,1′-binaphthyls. Inspection of the structure now determined for the sulphur compound shows that the individual naphthalene rings are each twisted with the same (*P*) helicity; 2,2′-substituted rings of *R*-configuration, on the other hand, are subject to internal repulsions which favour *M* helicity in the twist of the naphthalene rings. This seems to be the case for the unbridged compounds also.

Naphthalene itself has three major u.v. bands, at $\lambda_{\text{max.}}$ 221, 286, and 312 nm. It is tentatively suggested that the c.d. of the 8,8′-bridged 1,1′-binaphthyls falls out of line with all the other 1,1′-binaphthyls investigated because their individual naphthalene units are twisted with opposite chirality from the others and that the difference becomes obvious in the sign of the band around 286 nm. The c.d. of (*S*)-(+)-6-oxa-6,7-dihydro-5*H*-cyclohepta[(1,2-*a*:3,4-*a*′]dinaphthalene (VII) (the *R*-isomer has not yet been investigated) shows a couplet, in 96% ethanol, which mirrors that of the *R*-compounds in Table 7,[18] *i.e.* a negative extremum at the shorter wavelength followed by a positive one, a broad band with a shoulder at 283 nm, and a negative extremum at 300 nm (see Table 8). This compound also shows a positive extremum at 262 nm which lies in the region of a band in the u.v. spectrum attributed to conjugation between the rings.[7,18,27,31] Similar features are present in the u.v.- and c.d. of (*S*)-(+)-9,10-dihydrodibenzo[*c*,*g*]phenanthrene[7,27,31] and the analogous dithiin.[3]

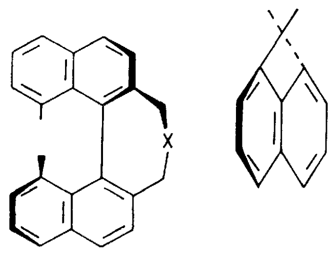
In 1975 Ciardelli and his co-workers studied helical copolymers of α-vinylnaphthalene and (*S*)-oct-1-ene[34] and found c.d. effects which they attributed to chirally perturbed α-naphthyl absorption; the stereoregularity of the polymer causes small c.d. effects to be reinforced. A positive c.d. couplet was observed, very similar to those we report but small in amplitude. They also prepared the monomer (*S*)-(+)-2-(α-naphthyl)butane, which showed very small but detectable c.d.

X-*Ray Structural Results*.—As mentioned above, the absolute configuration of this $(-)_{546}$-8,8′ bridged binaphthyl (see Figure 1) is determined to be *R*, according to the convention for axial chirality in these compounds explained by Cahn *et al.*[35] The angle between the two naphthyl mean planes is *ca.* 92.5°, much closer to orthogonality than the 103° noted in (*R*)-(−)-1,1′-binaphthyl.[6] But the two measurements are not strictly comparable because the 1,1′-binaphthyl molecule is conformationally labile; when it crystallises in 1 : 1 ratio with its enantiomer it has a dihedral angle of only 68°.[36] Two components with relatively ' fixed ' geometry on account of

2,2′-bridging have recently been subjected to Bijvöet structural analysis. These are (*S*)-(+)-9,10-dihydrodibenzo[*c,g*]phenanthrene,[5] crystallising alone or with its enantiomer as a racemate, and (*S*)-(+)-dinaphtho[2,1-*c*:1′,2′-*c*]dithiin:[4] the dihedral angles found are 50, 49, and 56°, respectively.



R axial chirality
P naphthalene helicity



R axial chirality
M naphthalene helicity

In (II), the C–S and C–C bond distances in the bridge average 1.830 and 1.496 Å, respectively, and the C–S–C and S–C–C bond angles are 103.8 and 113.1°. The distances are very nearly what would be expected for pure S–C(sp^3) [37] and C(sp^2)–C(sp^3) [38] single bonds, although the angles are quite obviously distorted from the ideal tetrahedral values of 109.5°. Such compressed C–S–C angles are not unusual in the literature,[39-41] but the S–C–C value indicates that the bridge system is slightly strained, an idea which is supported by the observation of the buckling of the naphthalene rings at the points of connection, C(2) and C(20). The exocyclic bridge bond, C(10)–C(12), is longer than predicted for a C(sp^2)–C(sp^2) single bond,[42] and is almost the same as those noted in similarly crowded binaphthyls,[4,43] and in biphenyls.[44] Interestingly, Mason [6] has observed different lengths in the cisoid and transoid conformations of (+)-1,1′-binaphthyl.

As had been predicted earlier on the basis of optical stabilities,[26] the naphthalene rings are found to be distinctly non-planar. This can be seen quantitatively in Table 5 and visually in Figure 1. If, as suggested by Okaya and Ashida,[14] the mean planes of the two naphthalenes are determined solely from the least strained portion [C(4)—C(8) and C(14)—C(18)], then the strained points of concentration are seen to be significantly removed from the planes in opposed arrangements [C(2) 0.129, C(10) −0.213; C(20) −0.135, C(12) 0.244 Å]. The six-membered rings attached to the sulphur bridge show considerably more distortion than the other two and hence can be considered to be absorbing the bulk of the geometric strain. The reason for this is not at all clear, since there do not appear to be any additional steric constraints on the rings containing the 1,1′-positions which would prevent them from adopting more distorted positions in order to share the strain equally with their neighbours. The nature of the antiplanar distortion is such that *P* helicity is imparted to each naphthalene. Such buckling of the rings is very common in *peri*-substituted naphthalenes,[12,13,45,46] as well as in crowded binaphthyls.[4,5,14] Sometimes there is partial relief by the lateral splaying out of the *peri*-substituents away from each other, giving the C(1)–C(2)–C(11)-type angle a value significantly greater than 120°.[45,46] The effect is also seen in monosubstituted 1-naphthyl compounds where the ligand is bulky.[14] In our case, these exocyclic angles average 123.3° for the sulphur-bridge connection and 124.9° for the binaphthyl bond, despite any tendency for the 2-thiatrimethylene bridge to pull so as to close them up. Another indication of splaying can be found in the non-bonded contacts of the type C(5)–C(7), C(2)–C(10), and C(1)–C(12), for which our values average 2.465, 2.532, and 3.008 Å, respectively. This expansion at the *peri*-ligands is of the same magnitude as found in 1,8-dimethyl [46] and 1,8-diphenyl [45] substituted naphthalenes.

The bond distances in our naphthalene rings show considerable deviation from those of the unsubstituted molecule.[17] There is no longer the symmetric pattern seen in the parent compound, as well as in many derivatives both symmetrically [15] and unsymmetrically substituted [16] with respect to the long axis of the molecule. The basic pattern of long and short bonds remains, with types C(2)–C(3), C(4)–C(5), C(7)–C(8), and C(9)–C(10) significantly shorter than the other seven bonds, however they are not all equal as in naphthalene itself.[17] Instead, the pair adjacent to the bridges [C(2)–C(3) and C(9)–C(10)] are noticeably longer. Bond types C(2)–C(11) and C(10)–C(11) are also seen to be longer than their counterparts, C(5)–C(6) and C(6)–C(7), although the difference is less dramatic. Such aberrations have been seen previously in both binaphthyls [4,5,43] and 1-substituted naphthalenes,[14,47,48] although in these cases only the bonds on one of the six-membered rings were affected. The explanations proposed for this phenomenon involve either steric factors or induction effects,[47] although in our case the latter is not relevant. The central naphthalene bonds [C(6)–C(11) and C(16)–C(21)] are also somewhat longer than in the parent compound,[17] and yet in good agreement with Hückel MO calculations for binaphthyl systems.[49]

Figure 2 shows the nature of the molecular packing in the crystal lattice. There are no close intermolecular contacts, as would be expected for a hydrocarbon of this

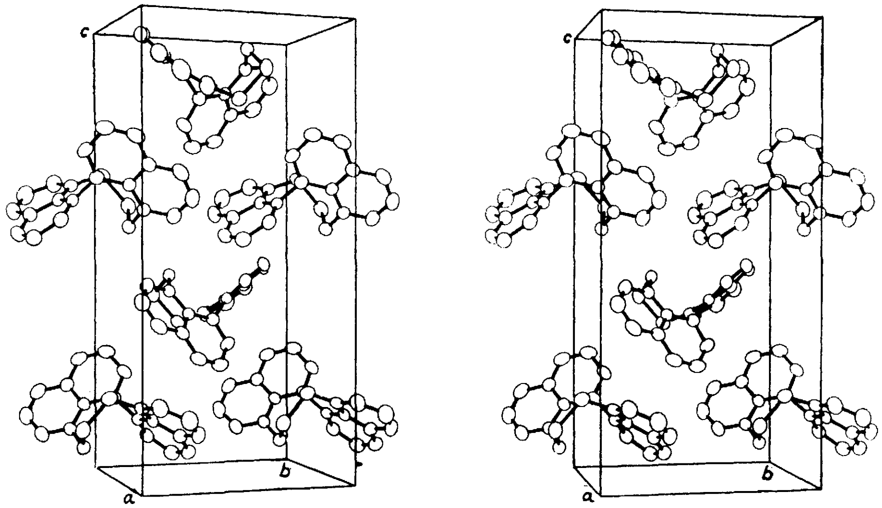


FIGURE 2 Stereoscopic view of the molecular packing in the unit cell, with hydrogens omitted for clarity. There are no abnormally close contacts between molecules, and the packing itself is rather loose

nature. The molecules are arranged so as to optimize packing of the bulky naphthalenes and minimize sulphur–sulphur contacts. Since there are no electrostatic attractions involved, the packing is fairly loose.

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