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THE CIRCULAR DICHROISM, CRYSTAL AND MOLECULAR STRUCTURE, AND ABSOLUTE CONFIGURATION, OF DINAPHTHO[2,1-c,1',2'-e]DITHIIN

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Abstract—The structure of the title compound has been determined by single-crystal X-ray analysis and refined by least-squares methods based on diffractometer data (1388 counter intensities, R 0.035). The crystals are monoclinic, space group $P2_1$, with $Z = 2$, $a = 13.360(2)$, $b = 5.755(1)$, $c = 10.318(1)$ Å and $\beta = 108.32(1)°$. The atoms of each naphthalene nucleus in the molecule are coplanar to within the rms value of 0.087 Å, and the intramolecular dihedral angle between the mean planes of those nuclei is 56°. Both the Bijvoet X-ray method and an analysis of the circular dichroism spectrum indicate that the (+)-isomer has the (S)-configuration, providing a reference for the correlation of configuration in the series of chiral 1,1'-binaphthyl-2,2'-sulphur-substituted derivatives.

The absolute stereochemical configuration of a range of chiral biaryls substituted with elements from the first short period have been determined by chemical correlations[1] based upon a reference enantiomer of known configuration, determined by the Bijvoet X-ray method,[2,3] and by the exciton analysis of the electronic CD and absorption spectra of an isomer of each biaryl considered.[4–6] In the 1,1'-binaphthyl series the CD method is of limited applicability when the dihedral angle between the molecular planes of the naphthalene moieties lies near[5] to 100°, or if the change in the transition–dipole directions of the naphthalene chromophore due to strongly auxochromic substituents is indeterminate. The former ambiguity obtains in the series of 1,1'-binaphthyls with a three-atom bridge between the 8- and the 8'-position.[7] In the case of the 2-thiathrimethylene member of this series the dihedral angle between the mean planes is found to be 92.49°, from an X-ray crystal and molecular structure determination, including the measurement of Bijvoet-pair intensity-differences.[8] The Bijvoet measurements assign the (R)-configuration to the (−)-isomer,[8] providing a reference for the chemical correlation of the configuration of the other members of the series.[7]

The second type of uncertainty connected with the CD assignment of absolute configuration in the biaryl series, strongly auxochromic substituents, is present in (+) - 1,1' - binaphthyl - 2,2' - disulphide (dinaphtho - [2,1 - c,1',2' - e]dithiin) **1** and other chiral derivatives of the enantiomers of 1,1' - binaphthyl - 2,2' - disulphonic acid,[9] which remain unrelated as yet, either chemically or by chiroptical methods, with an enantiomer of known configuration. The disulphide group in the 1,1'-binaphthyl **1** is itself chromophoric, giving the substance a bright yellow colour. Both the disulphide group and the 1,1'-binaphthyl chromophore of the enantiomer **1** are inherently dissymmetric, and correlations between the stereochemical configuration and the CD of a particular electronic transition are available for each chromophore individually.

The weak lowest-energy absorption band of **1** is the analogue of the corresponding $n \to \sigma^*$ band of chiral 1,2-dithianes, and the negative CD of the (+)-isomer **1** at 388 nm indicates, from previously-established correlations,[10–12] that the C–S–S–C bond system has the cisoid form with M-helicity in this isomer (Fig. 1). The assignment is congruent with the inference, from the bisignate CD couplet in the 200–280 region of the CD spectrum of the (+)-isomer **1**, a negative CD band at the higher frequency associated with a positive CD band of comparable magnitude at the lower frequency,[5] that the 1,1'-binaphthyl chromophore has the (*S*)-configuration in this enantiomer (Fig. 1). However, the two dissymmetric chromophores are no longer individual in the isomer **1**, and the interaction between the two chromophores limits the validity of the separate correlations. The 388 nm CD and absorption band of **1** lies at a wavelength longer by ~100 nm than expected for the $n \to \sigma^*$ transition of a cisoid C–S–S–C chromophore with a dihedral angle of ~60° between the two C–S bonds,[11] and the transition giving the 388 nm band of **1** probably has a substantial $n \to \pi^*$ character.

In order to investigate the validity of the spectroscopic CD assignment of the (*S*)-configuration to the (+)-enantiomer **1**, the crystal and molecular structure of **1** has been determined by X-ray diffraction, including the measurement of Bijvoet pairs of reflection intensities. An additional objective was a study of the packing modes of the molecule **1** in the crystal. Like the parent molecule,[13] 1,1'-binaphthyl, the disulphide derivative **1** is expected to spontaneously resolve on crystallisation from the melt (racemate m.p. 214°, enantiomer m.p. 262°)[9] into a conglomerate of crystals which individually contain solely either the (+)- or the (−)-isomer. Spontaneous optical resolution by crystallisation from the melt or from solution is relatively rare, only 250 cases being identified as yet.[14] The principal method for the large-scale optical resolution of racemates is entrainment, the seeding of a melt or supersaturated solution of the racemate with a crystal of one of the enantiomers, and the procedure is confined to the minor class of racemates which spontaneously resolve on crystallisation.[15] The investigation of the molecular packing modes in examples of the minor class of self-resolving racemates is relevant to extensions of the entrainment method which, with other resolution procedures, has enantioselective importance in pharmacological and other biological applications of synthetic racemates.[16]

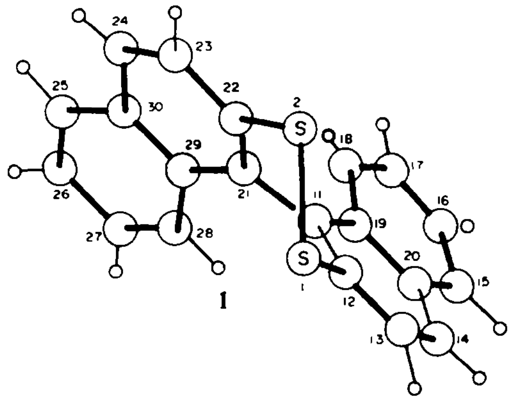

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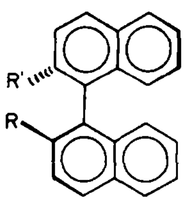
Fig. 1. The absorption (upper curve) and CD spectrum (lower curve) of (S) - (+) - 1,1' - binaphthyl - 2,2' - disulphide 1 in ethanol solution.

EXPERIMENTAL

Materials. Samples of (−)- and (+) - dinaphtho(2,1 - c,1',2' - e]dithiin 1 and of (−) - 4:4 - dimethyldinaphtho[2,1 - b,1',2' - d][1,3]dithiepine 2 were kindly supplied by Dr. W. L. F. Armarego.[9]

Spectra. The absorption and CD spectra of EtOH solns of the (+)-enantiomer 1 (Fig. 1) and the (−)-isomer 2 (Fig. 2) were measured with a Cary 14 and a Jouan CD 185 instrument, respectively.

X-ray study. Yellow needles of 1 were obtained from chloroform soln. The crystal employed for the X-ray diffraction analysis had the dimensions 0.11 × 0.23 × 0.35 mm. Unit cell dimensions were determined from Weissenberg photographs and were subsequently refined on a diffractometer.



2: R, R' = $-S-C(CH_3)_2-S-$
3: R = R' = $-SO_3H$
4: R = R' = $-SO_2Cl$
5: R = R' = $-SH$
6: R,R' = $-S-SO_2$

Fig. 2. The absorption (upper curve) and CD spectrum (lower curve) of (R) - (−) - 4:4 - dimethyldinaphtho[2,1 - b,1',2' - d][1,3] dithiepine 2 in ethanol solution.

Crystal data. $C_{20}H_{12}S_2$, M = 316.41, monoclinic, a = 13.360(2), b = 5.755(1), c = 10.318(1) Å, β = 108.32(1)°, U = 753.11 Å^3, Z = 2, D_m = 1.40, D_c = 1.395 g cm^{-3}, F(000) = 328, CuK$_\alpha$ radiation, λ = 1.54178 Å, μ(CuK$_\alpha$) = 29.8 cm^{-1}, space group P2$_1$.

The intensities were measured with CuK$_\alpha$ radiation on an Enraf–Nonius CAD-4 automated diffractometer operated in the $\theta-2\theta$ scan mode up to $\theta = 60°$. Out of the 1573 unique reflections observed, 1388 with $|F_0| > 3\sigma$ were employed for the refinement. The intensity data were not corrected for absorption.

Structure determination. The structure was solved by the heavy atom method and was subsequently refined employing SHELX 76. All of the H atoms appeared in the difference Fourier map and they were included in the refinement. Isotropic and anisotropic thermal factors were adopted for the H and for the other atoms, respectively. The final R value was 0.035 for the (*S*)-configuration of the enantiomer 1. Structure amplitudes were calculated additionally for the (*R*)-configuration by changing the coordinates from (x, y, z) to (x, $\frac{1}{2}$ − y, z), followed by refinement. Convergence was reached with R = 0.044. The larger R value suggests, but does not establish, that the (+)-isomer 1 has the (*S*)-configuration. Accordingly Bijvoet pairs of related reflections, (hkl) and (h$\bar{k}$l), were compared in the Weissenberg photographs taken about the *a* and the *c* crystal axes. The inequality relations show less ambiguously that the (+)-enantiomer 1 has the (*S*)-configuration (Table 1).

Atomic scattering factors for the H atoms were taken from Ref. 25, and for the S and C atoms, together with Δf' and Δf" for the S atoms, from Ref. 26.

DISCUSSION

Molecular structure. Table 2 lists the final set of atomic coordinates determined for (*S*) - (+) - 1,1' - binaphthyl - 2,2' - disulphide with the atom-numbering scheme of 1. The atoms of each naphthalene ring system are coplanar to within the root mean square deviation of 0.087 Å, which is larger than the corresponding value (0.009 Å) determined for racemic 1,1'-binaphthyl,[17] but less than the displacements from coplanarity, up to 0.213 Å, found[8] in the case of (*R*) - (−) - 8,8' - (2 - thiatrimethylene) - 1,1' - binaphthyl. The atoms of the two individual benzene rings in a given naphthalene residue of 1 show smaller displacements, 0.048 Å for the ring exocyclically bonded and 0.016 Å for its annelated neighbour. The angle between the mean planes of the two benzene rings in a naphthalene residue is 171°. The intramolecular dihedral angle between the mean planes of the two naphthalene ring systems in 1 is 56°, and the corresponding angle for the two C–S bonds of the C–S–S–C residue is 62°. In the disulphide-bridged biphenyl analogue, 5H,8H-dibenzo[d,f][1,2]dithiocin, the dihedral angles are 57° between the aromatic mean planes and 54° between

Table 1. Determination of the absolute configuration. The corresponding structure factors $|F_c(hkl)|^2$ and $|F_c(h\bar{k}l)|^2$ calculated for the (*S*)-configuration and the observed qualitative inequalities

h	k	ℓ	$\|F_c(hk\ell)\|^2$	Obs.	$\|F_c(h\bar{k}\ell)\|^2$
7	1	3	6.8	<	8.4
$\bar{7}$	1	3	18.5	>	14.4
2	4	3	39.7	<	42.3
10	2	3	26.0	>	21.2
1	1	9	16.8	>	13.7
3	5	0	10.2	>	13.0
3	6	0	19.4	>	15.2
$\overline{10}$	1	3	7.8	>	6.8

Table 2. The fractional atomic coordinates ($\times 10^3$ for the hydrogen atoms, and $\times 10^4$ for the carbon and sulphur atoms) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S(1)	3066(1)	1412(5)	1597(1)	C(26)	-1119(3)	4184(10)	-4139(5)
S(2)	3030(1)	4983(5)	1622(1)	C(27)	-406(3)	2394(10)	-4116(5)
C(11)	2717(3)	2471(8)	-1089(4)	C(28)	566(3)	2324(9)	-3124(4)
C(12)	3270(3)	1047(9)	-9(4)	C(29)	855(3)	4044(8)	-2090(4)
C(13)	3993(3)	-647(9)	-134(5)	C(30)	104(3)	5785(9)	-2080(4)
C(14)	4204(3)	-886(9)	-1339(5)	H(13)	434(2)	-189(2)	69(2)
C(15)	4107(3)	702(10)	-3596(5)	H(14)	474(2)	-191(2)	-145(2)
C(16)	3782(4)	2369(11)	5434(5)	H(15)	462(2)	-54(2)	-370(2)
C(17)	3110(3)	4120(10)	5580(4)	H(16)	412(2)	242(2)	-533(2)
C(18)	2743(3)	4192(9)	6685(4)	H(17)	289(2)	537(2)	-502(2)
C(19)	3062(3)	2467(8)	7718(4)	H(18)	223(2)	526(2)	-324(2)
C(20)	3777(3)	725(9)	7583(4)	H(23)	130(2)	817(2)	103(2)
C(21)	1850(3)	3990(8)	-1006(4)	H(24)	-28(2)	845(2)	-94(2)
C(22)	1932(3)	5390(9)	121(4)	H(25)	-146(2)	713(2)	-309(2)
C(23)	1183(4)	7086(9)	144(5)	H(26)	-177(2)	416(2)	511(2)
C(24)	309(4)	7359(9)	-968(5)	H(27)	-55(2)	110(2)	528(2)
C(25)	-879(3)	5848(10)	-3160(5)	H(28)	108(2)	100(2)	-319(2)

the C–S bonds of the C–S–S–C residue.[18] The dithiin ring of 1 has a skew-boat conformation with an angle of 52° between the S–S bond and the exocyclic binaphthyl C(11)–C(21) bond.

The bond lengths and bond angles of 1 are similar to the corresponding values found in analogous molecules (Table 3). The exocyclic C(11)–C(21) bond of 1 has virtually the same length as the corresponding bond (1.475 Å) in racemic 1,1'-binaphthyl,[17] and the S–S bond of 1 is only 1% larger than that (2.035 Å) of the disulphide-bridged biphenyl analogue.[18] The molecule 1 is sterically overcrowded, with short non-bonded intramolecular separations between the atoms, C or H, at the 18- and the 28-positions, or the 19- and 28-positions, and C(19)...C(29) (Table 4).

Crystal packing. The molecule 1 has C_2 symmetry with the two-fold molecular rotation axis nearly parallel to the crystal *c* axis and the S–S bond almost parallel to the crystal *b* axis (Fig. 3). If closely packed, an enantiomer with C_2 symmetry is expected [19] to crystallise in the orthorhombic space group $P2_12_12_1$ whereas the (*S*)-(+)-isomer 1 crystallises in the monoclinic space group $P2_1$. The absence of closest packing in the crystal structure of 1 is connected with a preferred packing mode, found also in the crystal of dibenzyl disulphide,[20] where the S atoms are in intermolecular contact, forming infinite S–S...S–S... chains. In the lattice of 1 the infinite sulphur chains extend along the crystal *b* axis with the van der Waals[21] separation of 3.700 Å, compared with the corresponding distance of 3.634 Å in dibenzyl disulphide.[20] The small intermolecular S...S separation in these lattices suggests a S–S interaction analogous to that of the thiathiophens where non-bonded intramolecular S...S separations are commonly intermediate between the van der Waals contact distance and the single-bond length.[22]

Configurational correlation. The establishment of the (*S*)-configuration for the (+)-isomer 1 provides an absolute reference for the configuration of the enantiomers to which 1 is chemically related.[9] A wider range of enantiomers is chemically correlated[9] with the (*R*)-(−)-antipode of 1, all derived from (−) - 1,1'binaphthyl - 2,2' - disulphonic acid 3, including the corresponding (−)-disulphonyl chloride 4, (−)-dithiol 5 and (−)-thiolsulphonate 6, together with the (−)-*S*,*S*-isopropylidene derivative 2. As Walden inversions are improbable in the reactions employed,[9] all of these (−)-enantiomers are assigned the *R*-configuration. The assignment is supported by the CD spectrum of the (−)-isomer 2 (Fig. 2). The bisignate CD couplet in the 200–250 nm region of the spectrum arises from the coupling of the two long-axis polarized naphthalene ^1B_b transitions, the in-phase coupling giving a right-handed helical charge-displacement along the C_2 molecular axis for the (*R*)-configuration, while the out-of-phase coupling produces a left-handed helical charge displacement along the direction perpendicular to the mean molecular plane for that configuration.[5] The in-phase and the out-of-phase coupling modes lie at the higher and the lower frequency, respectively, so that the observed sign-order of the bisignate CD couplet implies the (*R*)-configuration for the (−)-isomer 2 (Fig. 2).

Table 3. The bond lengths (Å) and bond angles (°) of 1,1-binaphthyl-2,2′-disulphide

Bond	Length (Å)	Bond	Length (Å)
S(1) -C(12)	1.775(4)	S(2) -C(22)	1.782(4)
C(11)-C(21)	1.476(5)	S(1) -S(2)	2.056(2)
C(11)-C(12)	1.393(5)	C(21)-C(22)	1.390(5)
C(11)-C(19)	1.444(5)	C(21)-C(29)	1.442(5)
C(12)-C(13)	1.406(6)	C(22)-C(23)	1.404(6)
C(13)-C(14)	1.365(6)	C(23)-C(24)	1.365(6)
C(14)-C(20)	1.423(6)	C(24)-C(30)	1.419(6)
C(15)-C(20)	1.419(6)	C(25)-C(30)	1.431(6)
C(15)-C(16)	1.355(7)	C(25)-C(26)	1.363(6)
C(16)-C(17)	1.389(7)	C(26)-C(27)	1.398(6)
C(17)-C(18)	1.376(6)	C(27)-C(28)	1.379(6)
C(18)-C(19)	1.421(6)	C(28)-C(29)	1.417(5)
C(19)-C(20)	1.419(6)	C(29)-C(30)	1.420(5)

Bonds	Angle (°)	Bonds	Angle (°)
C(12)-S(1)- S(2)	98.1(2)	C(22)-S(2) -S(1)	97.8(2)
S(1) -C(12)-C(11)	118.6(3)	S(2) -C(22)-C(21)	118.6(3)
C(12)-C(11)-C(21)	122.1(3)	C(22)-C(21)-C(11)	122.3(3)
C(12)-C(11)-C(19)	116.7(4)	C(22)-C(21)-C(29)	116.6(3)
C(19)-C(11)-C(21)	121.1(3)	C(29)-C(21)-C(11)	121.1(3)
S(1) -C(12)-C(13)	118.6(3)	S(2) -C(22)-C(23)	118.2(3)
C(11)-C(12)-C(13)	122.8(4)	C(21)-C(22)-C(23)	123.2(4)
C(12)-C(13)-C(14)	119.8(4)	C(22)-C(23)-C(24)	119.5(4)
C(13)-C(14)-C(20)	120.0(4)	C(23)-C(24)-C(30)	120.2(4)
C(16)-C(15)-C(20)	120.8(4)	C(26)-C(25)-C(30)	120.5(4)
C(15)-C(16)-C(17)	120.1(4)	C(25)-C(26)-C(27)	120.5(4)
C(16)-C(17)-C(18)	121.5(4)	C(26)-C(27)-C(28)	120.8(4)
C(17)-C(18)-C(19)	120.0(4)	C(27)-C(28)-C(29)	120.6(4)
C(18)-C(19)-C(20)	118.1(4)	C(28)-C(29)-C(30)	118.2(4)
C(18)-C(19)-C(11)	122.6(4)	C(28)-C(29)-C(21)	122.3(4)
C(20)-C(19)-C(11)	119.3(4)	C(30)-C(29)-C(21)	119.3(4)
C(19)-C(20)-C(15)	119.4(4)	C(29)-C(30)-C(25)	119.3(4)
C(19)-C(20)-C(14)	120.0(4)	C(29)-C(30)-C(24)	119.9(4)
C(14)-C(20)-C(15)	120.5(4)	C(24)-C(30)-C(25)	120.7(4)

Table 4. Non-bonded intramolecular atomic separations (Å)

Atoms	(Å)	Atoms	(Å)
S(1) ··· C(21)	3.052	S(1) ··· H(13)	2.897
C(11)··· S(2)	3.058	S(2) ··· H(23)	2.863
C(11)··· C(28)	2.980	C(11)··· H(28)	2.687
C(12)··· C(22)	3.105	C(18)··· H(28)	2.917
C(18)··· C(21)	2.981	C(19)··· H(28)	2.625
C(18)··· C(28)	3.165	C(21)··· H(18)	2.611
C(18)··· C(29)	3.155	C(28)··· H(18)	2.824
C(19)··· C(28)	3.171	C(29)··· H(18)	2.574
C(19)··· C(29)	3.156	H(18)··· H(28)	2.902

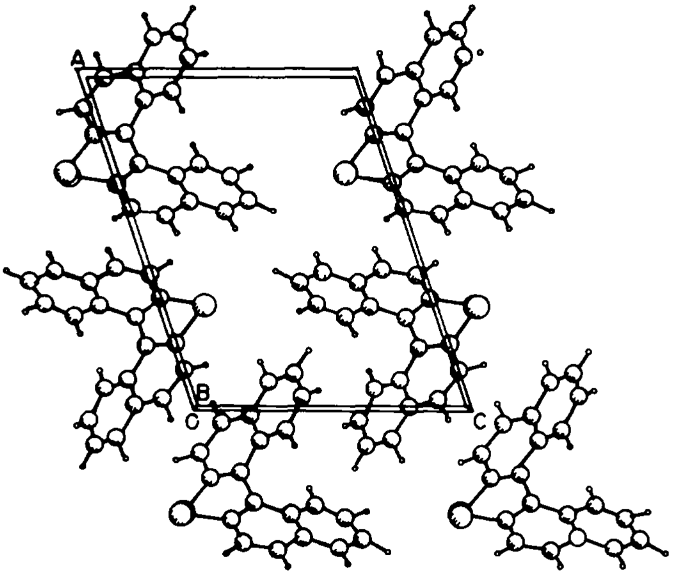


Fig. 3. A projection of the crystal structure of (S) - (+) - 1,1' - binaphthyl - 2,2' - disulphide 1 on the plane perpendicular to the *b*-axis of the crystal.

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