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MUTUAL OPTICAL RESOLUTION OF BIS-β-NAPHTHOL AND SULFOXIDES. ABSOLUTE CONFIGURATION AND CRYSTAL STRUCTURE OF A 1:1 MOLECULAR COMPLEX

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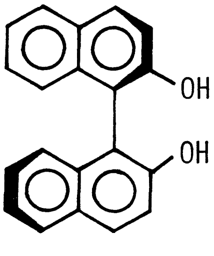
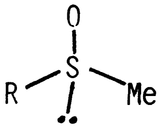
X-Ray analysis of a 1:1 complex of (*R*)-(+)-bis-β-naphthol with (*R*)-(+)-methyl *m*-tolyl sulfoxide has established the absolute configuration and showed that the two molecular components are alternately linked by O-H···O hydrogen bonds to form infinite zigzag chains parallel to the a axis. The bis-β-naphthol molecule adopts a cisoid conformation with a torsion angle of -78.2(2)° about the C-C bond joining the aromatic rings.

Very effective mutual optical resolution of bis-β-naphthol (**1**) and sulfoxides (**2**) through the formation of crystalline adducts was found.1) For example, when a solution of (*R*)-(+)-**1** and (±)-**2c** in benzene was kept at room temperature for 12 h, a 1:1 complex (**3**) of (*R*)-(+)-**1** and (+)-**2c** was formed as colorless prisms. Decomposition of **3** after one recrystallization from benzene gave 100% ee (+)-**2c** ($[\alpha]_D$ +140°) and 100% ee (*R*)-(+)-**1** in 77% yields in both cases. Conversely, **1** was resolved effectively by complexation with optically active sulfoxides. Efficiency of the resolution depends on the molecular shape of the sulfoxide employed; **2a**-**b** were poorly resolved by optically active **1**, and **2d** failed to form crystalline complexes with **1**. High efficiency of the chiral recognition by **2c** is probably due to its straight chain component as depicted in **2c**', since **2e** exhibits a high efficiency for mutual optical resolution, whereas **2g** is not effective and **2f** does not complex with **1** at all. An X-ray analysis of **3**, as described in the present paper, establishes the absolute configuration of the two molecular components and reveals details of the crystal packing.

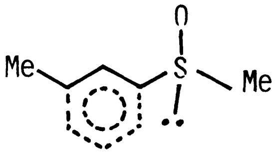


1

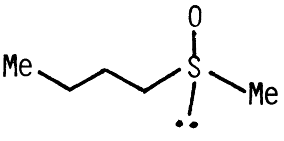


2

a:	R=phenyl
b:	*o*-tolyl
c:	*m*-tolyl
d:	*p*-tolyl
e:	*n*-butyl
f:	*s*-butyl
g:	*i*-butyl



2c'



2e

Crystal data of $C_{28}H_{24}O_3S$ (**3**) (MW = 440.56, mp 152-154 °C, $[\alpha]_D$ +69.7°) are as follows: triclinic, space group P1, a = 7.370(1), b = 8.871(2), c = 9.159(1) Å, α = 100.55(1), β = 96.40(1), γ = 96.77(1)°, V = 579.1(1) Å^3, Z = 1, D_c = 1.263, D_m (flotation in aqueous KI) = 1.26 g cm^{-3}, Mo-Kα radiation (graphite-monochromatized), λ = 0.71069 Å, μ = 2.68 cm^{-1}.

A single crystal (0.52 x 0.48 x 0.36 mm^3) was used for data collection (5727 $\pm h \pm k \pm l$ reflections lying within limiting sphere defined by $2\theta_{max}$ = 50°) on a Nicolet R3m four-circle diffractometer using the ω-2θ scan (2.02-8.37° min^{-1}) technique. The intensities were processed with the learnt-profile procedure[2)] and corrected for Lorentz and polarization factors. Absorption corrections were applied (mean μr = 0.05, transmission factors 0.859-0.918) using a pseudo ellipsoidal treatment of azimuthal scans of selected strong reflections over a range of 2θ values.[3)]

The structure was solved by the direct method based on tangent refinement of random starting phases for all reflections.[4)] In subsequent refinement, all non-hydrogen atoms (Fig. 1) were varied anisotropically. The aromatic H atoms were generated geometrically (C-H fixed at 0.96 Å); after their location from difference Fourier maps, the hydroxy H atoms were held stationary and the methyl H atoms refined as part of a rigid group (C-H = 0.96 Å). Isotopic temperature factors were assigned to all H atoms. Convergence for 5604 observed reflections $[|F_o| > 3\sigma(|F_o|)]$ and 293 variables was reached at $R \equiv \Sigma||F_o|-|F_o||/\Sigma|F_o|$ = 0.032. The chirality parameter η which multiplies all $\Delta f''$ values refined to a value of +0.862(84), attesting to the correctness of the chosen absolute configuration.[5)] Residual extrema in the final difference map lie between +0.45 and −0.44 eÅ^{-3}.

All computations were performed with the SHELXTL[6)] program package on a Nova 3/12 minicomputer. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were used.[7] The weighting scheme employed in the blocked-cascade[8] least-squares refinement was $\omega = [\sigma^2(|F_o| + 0.0008|F_o|^2]^{-1}$.[9]

As shown in Fig. 1, the (+)-bis-β-naphthol molecule has the *R* configuration in conformity with the previous assignment for binaphthyl systems.[10] The molecule adopts a cisoid conformation, and the C(1)-C(11) bond length is intermediate between the corresponding values for transoid (*R*)-(-)-1,1'-binaphthyl [1.511(7) Å][11] and its cisoid racemate conformation (1.475 Å).[12] The exocyclic O-C-C bond angles at C(2) and C(12) exhibit the well established inequality due to the steric influence of the phenolic H atom.[13]

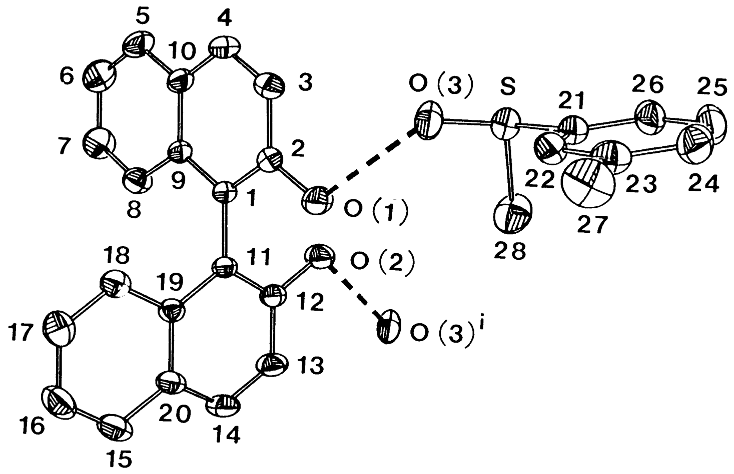


Fig. 1. Perspective view of the absolute configuration of, and hydrogen bonding (broken lines) between, the molecular components of **3**. Selected bond distances (Å) and angles (deg): O(1)-C(2), 1.362(2); O(2)-C(12), 1.362(2); C(1)-C(11), 1.494(2); O(1)-C(2)-C(1), 118.5(1); O(1)-C(2)-C(3), 120.5(1); O(2)-C(12)-C(11), 118.8(1); O(2)-C(12)-C(13), 120.6(1); C(2)-C(1)-C(11)-C(12), -78.2(2); S-O(3), 1.513(1); S-C(21), 1.782(1); S-C(28), 1.791(2); O(3)-S-C(21)-C(22), 14.1(1); O(1)···O(3), 2.758(2); O(2)···O(3)$^{\mathrm{i}}$, 2.781(1); S-O(3)···O(1), 122.0(1); S-O(3)···O(2)$^{\mathrm{ii}}$, 136.2(1); O(1)···O(3)···O(2)$^{\mathrm{ii}}$, 100.9(1). Symmetry transformations: $^{\mathrm{i}}(-1 + x, y, z)$; $^{\mathrm{ii}}(1 + x, y, z)$.

The (+)-sulfoxide has the same absolute configuration as (*R*)-(+)-methyl *p*-tolyl sulfoxide,[14] but the S-O and S-C bonds are slightly lengthened as a result of acceptor hydrogen bonding. The *m*-tolyl ring is oriented such that its methyl group is kept remote from the stereochemically active lone pair.

The two molecular components are linked alternately by O-H···O hydrogen bonds

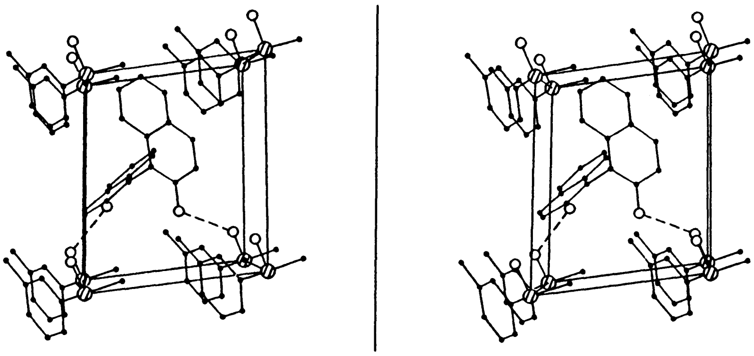


Fig. 2. Stereodrawing of the molecular packing in **3**, with hydrogen bonds represented by broken lines. The origin of the unit cell lies at the upper left corner, with a pointing from left to right, b towards the reader, and c downwards.

to form infinite zigzag chains parallel to the a axis (Fig. 2). Judging from the mode of molecular packing, it is conceivable that replacement of the *m*-tolyl group by a *n*-butyl group in the sulfoxide could yield an analogous structure with a shortened b axis.

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