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CONFORMATION AND ABSOLUTE CONFIGURATION OF CHIRAL 1,1'-BINAPHTHYLS. AN X-RAY DIFFRACTION STUDY OF (R)-$(-)_{546}$-8,8'-(2-THIATRIMETHYLENE)-1,1'-BINAPHTHYL (I)

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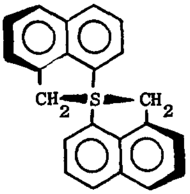
The structure of $(-)_{546}$-8,8'-(2-thiatrimethylene)-1,1-binaphthyl, determined by X-ray diffraction, shows it to have axial chirality R (M helicity): each naphthalene unit is twisted with P helicity. Chirality is thus specified for many synthetically related compounds.

The assignment of absolute configuration to 8,8'-disubstituted 1,1-binaphthyls rests so far on exciton and πSCF calculations of Mason et al.[1] who propose that (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid is (S), and upon the correlation of CD spectra of (+)-1,1'-binaphthyl, (+)-8,8'-dimethyl-1,1'-binaphthyl and (S)-(+)-2,2'-dimethyl-1,1'-binaphthyl[2], valid only if conformations are alike. (+)-8,8'-Dimethyl-1,1'-binaphthyl and (+)-8,8'-(2-thiatrimethylene)-1,1'-binaphthyl are each obtained by a direct synthetic route from (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid and are thus configurationally related to it. We report a structural study of (-)-I[3] in which the molecular conformation and the absolute configuration were determined by the Bijvoet method[4].

A single crystal, M = 312.434, space group $P2_12_12_1$, a = 8.442(7), b = 9.491(3), c = 20.075(9) Å, V = 1608.37 Å^3 $d_c = 1.290$, d_o (flotation in aqueous $ZnBr_2$) = 1.284 gm-cm^{-3}, was mounted on an Enraf-Nonius CAD4 computer-controlled diffractometer, and data (MoKα; $\lambda = 0.71073$ Å) were collected to $2\theta_{max} = 60^o$ (total data used in solution and refinement of the structure: 984 reflections having $I > 3\sigma(I)$). The structure was solved by MULTAN[5] whose first E-map showed most of the heavy atoms of the molecule. Least-squares refinement with anisotropic thermal parameters for the non-hydrogen and isotropic for the hydrogens, led to $R(F) = 0.0233$ and $R_w(F) = 0.0188$. The weights used were $w = [\sigma(|F_o|)]^{-2}$. When the refinement had converged, structure factors for both absolute configurations were computed for CuKα radiation as the source. With the same crystal as for data collection, the 10 reflections showing the largest Bijvoet difference were measured, four times each, on a diffractometer[6] equipped with a Cu tube. The ratios of intensities of all 10 reflections predict that the $(-)_{546}$ enantiomer has the (R) configuration, Fig. 1.



(R) (-) I

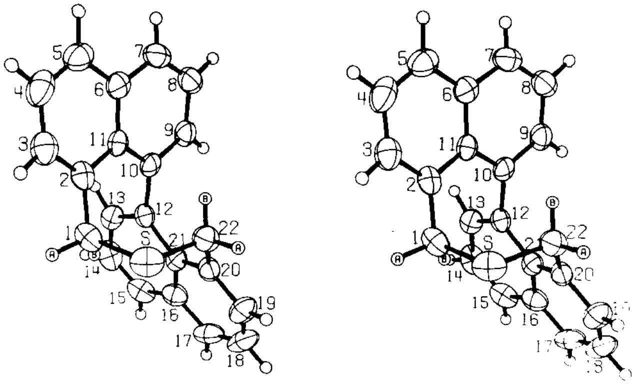


Fig.1. The stereo pair shows the structure determined for (-)-I. According to the convention for designating axial chirality in bridged biphenyls (R.S. Cahn, C.K. Ingold and V. Prelog, *Angew. Chem. internat. Edit.*, 1966, 385) this is the (R)-configuration.

The salient points concerning the structural details are as predicted by chemistry, stereochemistry and spectroscopy[3,6,1,2]. The molecule is badly buckled at the naphthalene rings, and these distortions can be defined in a couple of useful ways: carbons 2,10,12 and 20 (see Fig.1) do not lie on planes defined by the rest of the atoms of their respective naphthalene moieties. In a more quantitative manner, if the carbons 4-8 (see Fig.1) are used to define a plane, C2 and C10 lie 0.129 and -0.213 Å from that plane. Likewise, if C3-C9 are used to define a plane, then C2 and C10 lie 0.105 and -0.168 Å from it. If, now, a plane is defined by C14-C18, C12 and C20 lie 0.244 and -0.135 Å out of that plane. Finally, if the least-squares plane is defined by atoms C13-C19, C12 and C20 lie 0.193 and -0.111 Å away. The two naphthalene rings are nearly orthogonal to each other, the angle of the normals to the planes defined by C4-C8 and C14-C18 being 92.49°. Further details of the molecular parameters will be published elsewhere; meantime, they can be obtained from the authors on request.

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