The Crystal Structure of 5*H*,8*H*-Dibenzo[*d*,*f*][1,2]dithiocin, a Disulphide-bridged Biphenyl

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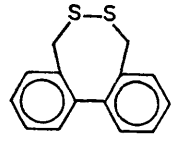
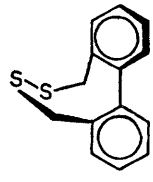
Summary A single-crystal *X*-ray diffraction study of 5*H*,8*H*-dibenzo[*d*,*f*][1,2]dithiocin reveals that the 8-membered ring, bridging the biphenyl moiety, exists in the unexpected pseudo-chair conformation.

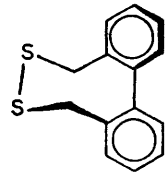
As a prelude to a detailed dynamic n.m.r. study of the conformational interconversions of eight-membered-ring bridged biphenyls it was important to determine unambiguously the ground-state conformation of several typical compounds. To expedite a single-crystal *X*-ray structure determination, a "heavy-atom" derivative was the first compound of choice.



(I)



(II)



(III)

Ph-CH_2-S-S-CH_2-Ph

(IV)

The title compound (I) which can exist in two apparently unstrained conformations (II) and (III)[1] has been resolved by chromatography on cellulose 2·5 acetate and its racemization at 85—100° monitored to obtain activation parameters. The pseudo-tub conformation (II) was considered the most likely[1] since the disulphide dihedral angle in this form (*ca.* 100°) is closer to the ideal value[3] of *ca.* 90°. However, in this conformation the biphenyl dihedral angle is approximately 90° and thus there is virtually no extended phenyl–phenyl conjugation.

The conformation of (I) was unambiguously established by a single-crystal *X*-ray analysis. The results of this study indicate that in the crystalline state, compound (I) exists in the pseudo-chair form (III) rather than the predicted pseudo-tub form (II).[1]

Crystals suitable for an *X*-ray analysis were grown by slow evaporation of an acetone solution. One of these colourless crystals (0·3 × 0·3 × 0·4 mm) was surveyed and one Ångstrom (maximum sin $\theta/\lambda = 0{\cdot}5$) intensity data collected on a Syntex $P\bar{1}$ diffractometer using Mo-K_α radiation ($\lambda = 0{\cdot}71069$). Monochromatic radiation was obtained by the application of a graphite incident beam monochromator.

Crystal data: $C_{14}H_{12}S_2$; monoclinic $C2/c$; $a = 13{\cdot}28(2)$, $b = 8{\cdot}01(1)$, $c = 10{\cdot}93(1)$ Å, $\beta = 91{\cdot}35(5)°$; $V = 1163$ (1) Å^3; $D_m = 1{\cdot}37$ g/cm^3; $D_c = 1{\cdot}39$/cm^3 for $Z = 4$. Non-zero reflections = 594; total unique reflections = 626; scan mode: $\theta/2\theta$; scan rate: 4°/min in 2θ.

The structure was solved using conventional Patterson and Fourier techniques. The first electron-density map revealed the entire structure which refined routinely to an R index of 0·037. The final cycles of full-matrix least-squares refinement contained all the non-hydrogen positions,

their anisotropic temperature factors, and the scale factor in one matrix. While the hydrogen positions were calculated and added to the final structure-factor calculations, their positions were not refined. A final difference Fourier revealed no missing or misplaced atoms in the refined model. Further details of the *X*-ray analysis may be obtained from one of the authors (J.B.). A stereoplot of the final structure is shown in the Figure.

A comparison of selected bond distances and angles obtained in this study with those recently obtained[4] for the open-chain analogue dibenzyl disulphide (IV) is presented in the Table. The longer sulphur–sulphur bond distance for (I) is consistent with the small C–S–S–C dihedral angle which reduces the "double-bond character"[3] of the S–S bond. As indicated in the stereoplot there is a bending of the C(8)–C(8′) bond, away from the disulphide bridge. The C(5)–C(8) axis is 5·9° from linearity with the C(5′)–C(8′) axis.

TABLE. *Comparison of bond lengths and angles of* (I) *and* (IV).

	(I)	(IV) [see ref. 4]
d_{S-S}	2·035 (1)	2·02 ± 0·005
d_{S-C}	1·835 (3)	1·84 ± 0·013
S–S–C angle	103·82°	102·9 ± 0·5°
C–S–S–C Dihedral angle	54·32°	92·1°
ϕ–ϕ Dihedral angle	57·33°	90·9°[a]

[a] In (IV) the phenyl groups are not directly attached to each other.

non-bonded interactions, and crystal forces may be more important than the factors mentioned.

As pointed out earlier,[1] conformational inversion of (III) into its enantiomer requires that (III) is first converted into (II) which then passes through a highly strained, achiral transition state. From the transition state, the mirror image of (II) is formed directly and this in turn must be converted finally into the mirror image of (III). It will be interesting to determine whether other eight-membered-ring bridged biphenyls which racemize much easier than (I) also exist in pseudo-chair-like conformations.

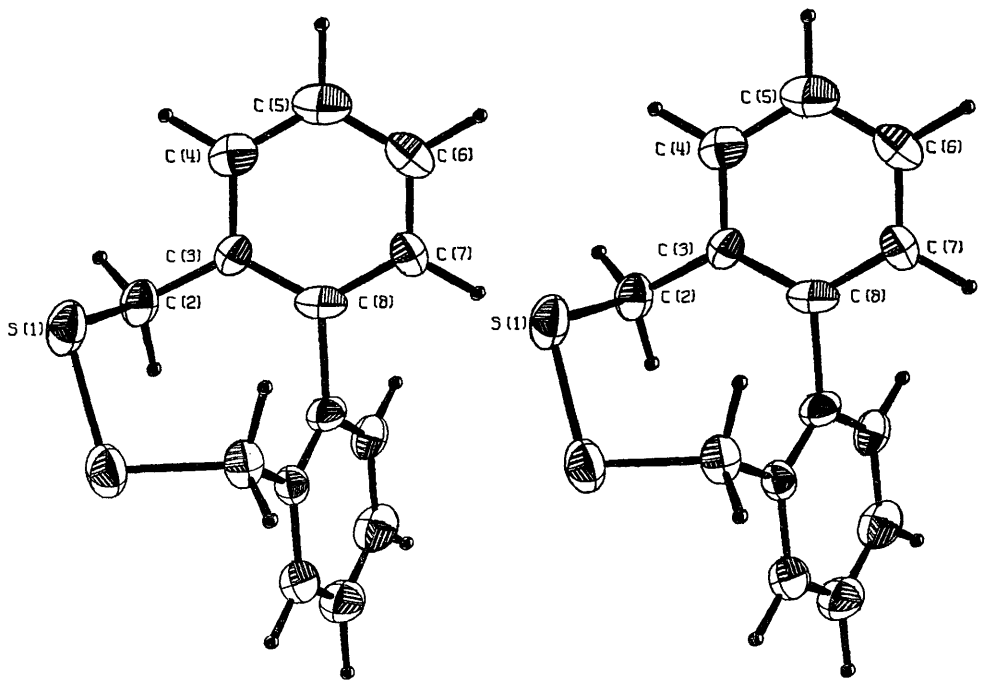


FIGURE. *ORTEP stereoscopic view of* 5H,8H-*dibenzo*[d,f][1,2]-*dithiocin* (I).

From the crystal structure data it is clear that the pseudo-chair conformation is preferred at least in the solid state. Presumably the demands of phenyl–phenyl conjugation outweigh those of sulphur–sulphur lone-pair repulsion. However, although both (II) and (III) appear to be "minimum energy conformations", the effects of torsional strains,

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[4] J. D. Lee and M. W. R. Bryant, *Naturwiss.*, 1969, **56**, 36; *Acta Cryst.*, 1969, **B25**, 2497.