Crystal and Molecular Structure of 2,5-Diphenyl-1,4-Dithiin 1-Oxide

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Summary The heterocyclic ring of 2,5-diphenyl-1,4-dithiin 1-oxide is arranged in a boat structure (*X*-ray), the oxygen atom being axial and the sulphoxide group differing in bond distances from the sulphide group.

IN connection with previous studies[1] on organic sulphur compounds, we have investigated the reactivity and the molecular parameters of 1,4-dithiins. The controlled oxidation of 2,5-diphenyl-1,4-dithiin[2] with peroxybenzoic acid in dioxan–water (90 : 10 v/v) at 25° gives the corresponding monosulphoxide, m.p. 110—110·5° (lit.[3] m.p. 109°), pure by t.l.c. (silica, benzene–acetone 9 : 1) after careful[3,4] crystallizations from benzene–light petroleum or from acetone. The i.r. spectrum (Nujol) of the sulphoxide shows a strong band at 1020 cm^{-1} (ν_{SO}) and the n.m.r. spectrum ($CDCl_3$, Me_4Si as internal standard) shows two singlets at τ 2·68 and 2·42 corresponding to the non-equivalent protons of the heterocyclic ring; the lower-field signal, overlapped with the multiplet centred at τ 2·40 due to the phenyl protons, was revealed in the spectrum of the corresponding sulphoxide deuteriated in both the benzene rings.

2,5-Diphenyl-1,4-dithiin 1-oxide crystallizes from acetone in white needles: orthorombic, *Pbca*, $a = 27{\cdot}855$, $b = 12{\cdot}162$, $c = 8{\cdot}089$ Å, $M = 284{\cdot}4$, $U = 2740{\cdot}3$ Å^3, $Z = 8$, $D_m = 1{\cdot}40$, $D_c = 1{\cdot}38$ g. cm^{-3}. The intensity of 782 independent non-zero reflections were taken with a Siemens four-circle diffractometer ($\theta \leqslant 50°$). Absorption corrections were deemed to be unnecessary ($\mu = 32{\cdot}9$ cm^{-1}, $0{\cdot}5 \times 0{\cdot}6 \times 0{\cdot}4$ mm). The crystal structure was solved by direct methods, confirmed by Fourier synthesis (F_0 and ΔF to locate hydrogen atoms) and refined by full-matrix least-squares; hydrogen atoms were excluded, carbon atoms allowed to vibrate isotropically, and the sulphur atoms anisotropically. The R index is 0·06.

The observed structure consists of discrete molecules. The heterocyclic ring is arranged in a boat structure with both the sulphur atoms above the plane of the two C–C bonds, the oxygen being axial; the phenyl rings lie below this plane.

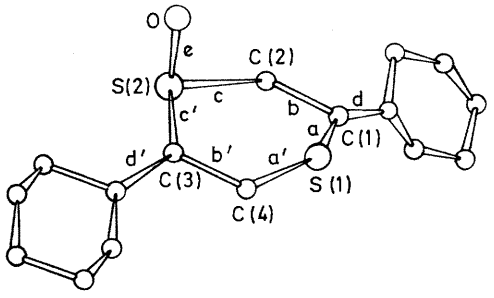

FIGURE. *A perspective view of the molecule*

The C–C and C–H bond distances and the angles within the benzene rings are those normally found in aromatic compounds. The arrangement around the oxidized sulphur is pyramidal, slightly distorted, with the S atom at the apex; the angles O–S(2)–C(2) and O–S(2)–C(3) are close to the normal [5,6] value of 107° and the acute angle (63·5°) between the S(2)–O bond and the bisector of the C(2)–S(2)–C(3) angle is the same as reported for other sulphoxides.[6] In particular, all the structural data of the sulphoxide group are equal, within experimental error, to those found[7] for diphenyl sulphoxide. The b and b' bond distances are 1·32 and 1·34 Å, and hence their mean is in agreement with that of the ethylenic double bond.[8] The C–S bonds show different lengths as the a and a' distances of the unoxidized sulphur are shorter than those, c and c', of the sulphoxide sulphur. Both sets of bond distances have values lower than 1·82 Å, which is considered[7] the normal bond length for a simple C–S bond. Moreover, the S(1) atom is just 0·28 Å above the plane of the C(1)–C(2) and C(3)–C(4) bonds, whereas S(2) is 0·64 Å away from this plane.

The results presented here can be interpreted in terms of different hybridization of the two sulphur atoms or of a different interaction with the neighbouring π-systems. Both of these effects may operate at the same time.

Interatomic distances (Å) *and angles* (*degrees*) *for the heterocyclic ring in* 2,5 *diphenyl*-1,4-*dithiin* 1-*oxide*[a]

Bond lengths			
a	1·721 (9)	$\angle aa'$	103·3 (0·8)
a'	1·701 (9)	$\angle ab$	123·8 (1·0)
b	1·321 (12)	$\angle ad$	114·0 (1·1)
b'	1·347 (11)	$\angle a'b'$	128·4 (1·0)
c	1·745 (8)	$\angle bc$	126·1 (0·9)
c'	1·765 (8)	$\angle bd$	122·1 (1·2)
d	1·498 (13)	$\angle b'c'$	120·8 (1·0)
d'	1·493 (12)	$\angle b'd'$	121·3 (1·2)
e	1·476 (7)	$\angle cc'$	98·2 (0·7)
		$\angle ce$	107·8 (0·7)
		$\angle c'd'$	117·2 (1·2)
		$\angle c'e$	106·1 (0·7)

[a] Estimated standard deviations (in 10^{-3} Å for bond lengths) in parentheses; letters refer to those of the Figure.

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