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3-Bromo-2,5-diphenyl-1,4-dithiin 1,1-Dioxide

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Abstract. $C_{16}H_{11}BrO_2S_2$, triclinic $P\bar{1}$, $a = 9.174$ (1), $b = 9.239$ (1), $c = 9.367$ (1) Å, $\alpha = 71.68$ (1), $\beta = 89.29$ (1), $\gamma = 85.04$ (1)°, $V = 750.8$ (2) Å³, $Z = 2$, $D_m = 1.680$ (floatation), $D_c = 1.676$ Mg m⁻³. The molecule has a boat conformation. The mean S–C distances and the C–S–C angles at the two S atoms are similar. The molecule is more nearly planar than other 1,4-dithiin derivatives.

Introduction. The title compound was first obtained as a product of the oxidation of 3-bromo-2,5-diphenyl-1,4-dithiin with H₂O₂ (Parham, Nicholson & Traynelis, 1956) or with peracetic acid (Szmant & Alfonso, 1957), although the regiochemistry of the oxidation (*i.e.* whether the Br was at the 2 or 3 position of the ring) was not established. More recently (Levi, 1979), products believed to be the 2-bromo and 3-bromo isomers of this compound were prepared; however, spectroscopic data again provided no definitive basis for determining the identities of these isomers. Since this information was of importance in the interpretation of the chemistry of these molecules, and since no detailed structural data were available for any dithiin 1,1-dioxide, a crystal structure analysis was undertaken.

Colorless crystals of the title compound were obtained by slow evaporation of a chloroform solution. The crystal used for all X-ray studies was a rectangular prism of dimensions 0.33 × 0.20 × 0.20 mm which had been cut from a larger crystal and mounted on a glass fiber. Data were collected with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on a Syntex $P2_1$ automated diffractometer under the control of a Nova 1200 computer. Refined cell parameters ($T = 295$ K) were based upon the setting angles of 15 reflections with $30^\circ < 2\theta < 35^\circ$. Profiles of 2θ and ω scans of several representative reflections showed symmetrical peak shapes and normal breadths in ω . All independent data with $2^\circ \leq 2\theta \leq 55^\circ$ were collected by the θ - 2θ scan technique in bisecting geometry. Peaks were scanned at a variable rate of 2–8° min⁻¹, depending upon their intensity. The scans ranged from 1.0° in 2θ below the $K\alpha_1$ peak position to 1.2° above the $K\alpha_2$ peak. A stationary background count was

taken at each end of the scan for half the scan time. Four standard reflections were measured after each 50 data. These standards declined in intensity by about 3% during data collection.

Data processing, including correction for Lorentz and polarization effects and for variation of standard reflections, was carried out by use of the locally written program *SYNOU* (Doedens, 1977). The p factor in the expression (Corfield, Doedens & Ibers, 1967) for the standard deviation of the observed intensities was 0.05. No absorption correction was attempted. Of the 3439 independent data collected, 2601 had $F^2 > 3\sigma(F^2)$ and were used in subsequent calculations.

Intensity statistics implied a centrosymmetric structure. The structure solution was achieved in a straight-

Table 1. Positional parameters and equivalent isotropic thermal parameters of the nonhydrogen atoms

	x	y	z	U_{eq} (Å ²)
Br	0.06266 (4)*	0.39511 (4)	0.22221 (4)	0.045†
S(1)	-0.39831 (8)	0.29030 (10)	0.18010 (9)	0.037
S(2)	-0.07537 (8)	0.19390 (9)	0.07911 (9)	0.039
O(1)	-0.3920 (3)	0.1446 (3)	0.2949 (3)	0.053
O(2)	-0.5288 (3)	0.3919 (3)	0.1681 (3)	0.051
C(1)	-0.2441 (3)	0.3837 (4)	0.2062 (3)	0.034
C(2)	-0.1136 (3)	0.3286 (3)	0.1718 (3)	0.033
C(3)	-0.2349 (3)	0.2087 (3)	-0.0279 (3)	0.034
C(4)	-0.3672 (3)	0.2605 (4)	0.0082 (4)	0.039
C(5)	-0.2727 (3)	0.5125 (4)	0.2677 (4)	0.037
C(6)	-0.2667 (4)	0.6626 (4)	0.1743 (4)	0.047
C(7)	-0.2951 (4)	0.7830 (4)	0.2326 (5)	0.057
C(8)	-0.3302 (4)	0.7550 (5)	0.3817 (6)	0.063
C(9)	-0.3372 (5)	0.6080 (5)	0.4738 (5)	0.060
C(10)	-0.3087 (4)	0.4849 (4)	0.4180 (4)	0.050
C(11)	-0.2099 (3)	0.1594 (4)	-0.1623 (4)	0.035
C(12)	-0.0887 (4)	0.2002 (4)	-0.2525 (4)	0.039
C(13)	-0.0689 (4)	0.1547 (4)	-0.3793 (4)	0.044
C(14)	-0.1673 (4)	0.0679 (5)	-0.4172 (4)	0.049
C(15)	-0.2881 (4)	0.0254 (5)	-0.3278 (5)	0.053
C(16)	-0.3086 (4)	0.0707 (4)	-0.2006 (4)	0.047

* Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant figures.

† $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$, where U_{ii} = principal mean-square thermal displacement.

Table 2. Bond distances (Å) and angles (°)

Internal distances and angles for the phenyl rings have been deposited.

C(1)–C(2)	1.336 (4)	S(1)–O(1)	1.432 (3)
C(3)–C(4)	1.344 (4)	S(1)–O(2)	1.439 (3)
S(1)–C(1)	1.777 (3)	C(1)–C(5)	1.480 (4)
S(1)–C(4)	1.733 (3)	C(3)–C(11)	1.477 (4)
S(2)–C(2)	1.738 (3)	C(2)–Br	1.894 (3)
S(2)–C(3)	1.755 (3)		
O(1)–S(1)–O(2)	117.82 (16)	Br–C(2)–S(2)	110.1 (2)
O(1)–S(1)–C(1)	107.61 (15)	Br–C(2)–C(1)	121.6 (2)
O(1)–S(1)–C(4)	108.51 (16)	S(2)–C(2)–C(1)	128.3 (2)
O(2)–S(1)–C(1)	109.40 (15)	S(2)–C(3)–C(4)	123.5 (2)
O(2)–S(1)–C(4)	108.95 (15)	S(2)–C(3)–C(11)	113.5 (2)
C(1)–S(1)–C(4)	103.61 (14)	C(4)–C(3)–C(11)	123.0 (3)
C(2)–S(2)–C(3)	103.53 (14)	S(1)–C(4)–C(3)	121.8 (2)
S(1)–C(1)–C(2)	116.9 (2)	C(1)–C(5)–C(6)	120.1 (3)
S(1)–C(1)–C(5)	116.7 (2)	C(1)–C(5)–C(10)	120.4 (3)
C(2)–C(1)–C(5)	126.4 (3)	C(3)–C(11)–C(12)	121.1 (3)
		C(3)–C(11)–C(16)	119.9 (3)

forward manner by use of the direct-methods program *MULTAN 77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Full-matrix least-squares refinement employed the local program *UCIGLS* (Doedens, 1978). A difference Fourier map calculated during the latter stages of refinement clearly showed peaks due to all 11 H atoms and had no anomalous features. In the final refinement, anisotropic thermal parameters were employed for all non-hydrogen atoms and H atoms were included at their calculated positions (C–C–H angles of 120° and C–C distances of 0.95 Å). At convergence, the conventional *R* factor was 0.037. In all least-squares refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$. Scattering factors (including anomalous terms for Br and S) were taken from *International Tables for X-ray Crystallography* (1974). The final standard deviation of an observation of unit weight was 1.33. Calculation of

structure factors for the 838 data with $F_o^2 < 3\sigma(F_o^2)$ showed only one reflection with $\Delta F/\sigma$ slightly greater than 3.0. Positional parameters of nonhydrogen atoms are listed in Table 1 and selected bond distances and angles are given in Table 2.*

Discussion. An overall view of the molecular structure of 3-bromo-2,5-diphenyl-1,4-dithiin 1,1-dioxide (I) is shown in Fig. 1. The six-membered heterocyclic ring has a boat conformation, as is found for 2,5-diphenyl-1,4-dithiin 1-oxide (II) (Bandoli, Panattoni, Clemente, Tondello, Dondoni & Mangini, 1971), 1,4-dithiin-2,3,5,6-tetracarbonitrile (III) (Dollase, 1965), and the parent 1,4-dithiin (IV) (Howell, Curtis & Lipscomb, 1954). Selected structural parameters for these four molecules, the only 1,4-dithiins for which crystal structure results are available, are listed in Table 3. The observed boat conformation is in contrast to the chair conformation which is found for 1,4-dithiane (Marsh, 1955) and many of its derivatives.

Since this is the first dithiin 1,1-dioxide whose structure has been determined, it is appropriate to compare its structural details with those of structurally characterized 1,4-dithiins and 1,4-dithiin sulfoxides. Such a comparison is somewhat complicated by the differing pattern of substituents in each case; nonetheless, some trends may be noted. The first point of interest is the similarity of the average C–S distances and the C–S–C angles at the oxidized S(1) and the

* Lists of structure factors, anisotropic thermal parameters, H-atom positional parameters and bond distances and angles in the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35162 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Structural comparison of 1,4-dithiin derivatives

	3-Bromo-2,5-diphenyl-1,4-dithiin 1,1-dioxide (I)	2,5-Diphenyl-1,4-dithiin 1-oxide (II)	1,4-Dithiin-2,3,5,6-tetracarbonitrile (III)	1,4-Dithiin (IV)
C–S (Å)	1.738 (3), 1.755 (3)*	1.711 (9)	1.755 (7)	1.78 (4)
C–S _{ox} † (Å)	1.733 (3), 1.777 (3)	1.755 (9)	—	—
C=C–S (°)	123.5 (2), 128.3 (2)	123.8 (7), 128.4 (7)	121.8 (6)	124.5 (20)
C=C–S _{ox} (°)	116.9 (2), 121.8 (2)	120.8 (7), 126.1 (7)	—	—
C–S–C (°)	103.53 (14)	103.3 (4)	97.3 (5)	101.2 (20)
C–S _{ox} –C (°)	103.61 (14)	98.2 (4)	—	—
Fold angle‡ (°)	147	142	124	137
Boat angle(s) (°)	150, 155	146, 165	154, 154	152
S–olefin plane (Å)	0.44, 0.46	0.28, 0.64	0.70, 0.70	0.53
Reference	This work	Bandoli <i>et al.</i> (1971)	Dollase (1965)	Howell, Curtis & Lipscomb (1954)

* Where chemically equivalent distances or angles differ by more than 3σ, individual values are tabulated; otherwise, mean values are listed with the standard deviation of an individual measurement. Molecule (IV) has crystallographic *2mm* symmetry.

† The oxidized S atom in (I) and (II) is denoted as S_{ox}.

‡ The fold angle is defined as the angle between the two S–C=C–S planes. The boat angles are the angles between the C–S–C planes and the plane of the olefinic C atoms.

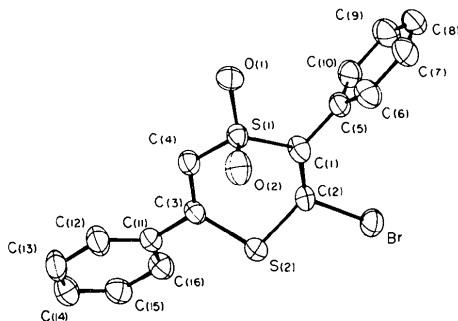


Fig. 1. A view of the molecular structure. Thermal ellipsoids are drawn at the 50% level. H atoms have been omitted for clarity.

unoxidized S(2) in (I). Although there is some variation in the individual C–S distances, the mean values of the C–S(1) and C–S(2) distances differ by only 0.009 Å. Likewise, the two C–S–C angles differ by less than one standard deviation. In contrast, the sulfoxide (II) shows a marginally significant difference of 0.044 (9) Å in mean C–S differences and a marked disparity of 5.1 (4)° in C–S–C angles. The only bond distance or angle of the six-membered heterocyclic ring which falls significantly outside the range of values previously observed in 1,4-dithiin derivatives is the C(2)–C(1)–S angle of 116.9 (2)°. Previously observed values of comparable angles have ranged from 120.8 (7) to 128.4 (7)° (see Table 3 for details). The small value of this angle may well be a consequence of the expansion of the C(2)–C(1)–C(5) angle because of Br⋯phenyl interactions.

The degree of nonplanarity of the six-membered heterocyclic ring may be measured by three inter-related parameters – the fold angle (*i.e.* the angle between the two S–C=C–S planes), the boat angles (*i.e.* the angles between the CSC planes and the plane of the four olefinic C atoms), and the distances of the S atoms to the plane of the four ring C atoms. These parameters are also listed in Table 3. They show that (I) has the largest fold angle (*i.e.* is the most nearly planar) of the four molecules and that its ring conformation is more symmetrical than that of the sulfoxide (II). Thus, the ring conformation and the S–C distances both indicate that the presence of a more highly oxidized S atom in (II) does not result in a lower symmetry for the heterocyclic ring.

Other molecular parameters are much as expected. Both phenyl substituents are twisted significantly with respect to the SCS plane containing the C atom to which they are bound; this twisting is greater for the ring bound to C(1) (75.9°) than for that bound to C(3) (42.1°), presumably because of steric interaction with the Br substituent on C(2). The two S–O distances are equivalent [mean = 1.436 (3) Å] and slightly shorter than the S–O distance of 1.476 (7) Å in the sulfoxide (II).

Note added in proof: In a recent report [Bates, R. B., Kriek, G. R. & Brewer, A. D. (1980). *Acta Cryst.* B36, 736–738] of the structure of a substituted 2,3-dihydro-1,4-dithiin 1,1,4,4-tetroxide long C(vinyl) to S(sulfone) bonds of *ca* 1.78 Å in cyclic vinyl sulfones are attributed to steric interactions involving the carbon substituent. In the absence of such interactions a distance of *ca* 1.73 Å is expected. Our results [C(1)–S(1) = 1.777 (3), C(4)–S(1) = 1.733 (3) Å] are in complete accord with this interpretation.

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