

Examination of the fused six-membered rings shows that both are in the chair conformation. It is also apparent from Fig. 2 that the stereochemical relationship between the methoxy group and the ester is clearly *cis* and is thus the desired intermediate in the ajugarin (I) synthesis.

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Structure of 5*H*,8*H*-Dibenzo[*d,f*][1,2]oxathiocin 7,7-Dioxide, C₁₄H₁₂O₃S

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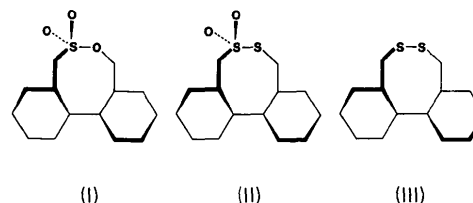
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Abstract. $M_r = 260.31$, monoclinic, $P2_1/c$, $a = 10.672$ (19), $b = 13.780$ (5), $c = 8.354$ (9) Å, $\beta = 99.47$ (10)°, $V = 1211.5$ Å³, $D_m = 1.43$, $D_x = 1.427$ Mg m⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.25$ mm⁻¹, $T = 293$ K. Final $R = 0.040$ for 1442 observed reflections. The structure consists of an eight-membered ring system incorporating a bridged diphenyl. The conformation of the eight-membered ring is 'pseudo-chair'. The two exocyclic S–O bond distances are equal to 1.420 (4) Å while the S–O bond within the eight-membered ring is 1.550 (2) Å. The two phenyl groups are at 63° from each other.

Introduction. The structure determination of the title compound, (I), is part of a project undertaken to establish the possible conformations of eight-membered rings which incorporate a bridged diphenyl unit as part of the cyclic structure. In a previous paper, Wahl, Bordner, Harpp & Gleason (1973) reported that in the dithiocin analog (II), the eight-membered ring adopts a 'pseudo-chair' conformation in the crystalline state. The same conformation was also found to be favored by the related disulfide (III) (Wahl, Bordner, Harpp & Gleason, 1972). However, a totally different ring conformation was observed in the case of the peroxide analog of (III) (Brown, Towns, Kovelan & Andrist, 1976).



Experimental. Preparation of the sultone (I) has been described elsewhere (Steliou, 1978); colorless tabular crystals (from benzene/hexane), D_m by flotation, $0.16 \times 0.45 \times 0.50$ mm, Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, intensity check every hour, orientation verified every 100 reflections, 2131 (hkl , hkl) with $2\theta \leq 50^\circ$, 1442 with $I \geq 1.90\sigma(I)$, 688 unobserved, L_p correction, no absorption correction, direct methods (*MULTAN*, Main, Woolfson, Lessinger, Germain & Declercq, 1978), anisotropic block-diagonal approximation, H (calculated) isotropic, final $R = 0.040$ (observed), $R = 0.072$ (all), $w = 1$, $R_w = 0.037$, final electron density fluctuations -0.34 to $+0.24$ e Å⁻³, maximum (shift/ σ) = 0.95, average (shift/ σ) = 0.15; scattering factors for S, O and C from Cromer & Mann (1968) and from Stewart, Davidson & Simpson (1965) for H, $F(000) = 464$, anomalous dispersion of S (real and imaginary) from Cromer & Liberman (1970); programs used in this work are modified versions of *NRC-2* (data

reduction), *NRC-10* (bond distances and angles) and *NRC-22* (mean planes) (Ahmed, Hall, Pippy & Huber, 1973), *FORDAP* (Fourier and Patterson maps, A. Zalkin), *NUCLS* (least-squares refinement, Doedens & Ibers, 1967), *MULTAN* (Main *et al.*, 1978), *ORTEP* (stereoviews, Johnson, 1965).

Discussion. The final atomic coordinates are given in Table 1.* The molecular structure is represented in Fig. 1. The molecule consists of a biphenyl system bridged

* Lists of structure factors, anisotropic temperature factors, mean planes and a figure showing H-atom distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38184 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and their e.s.d.'s* ($\times 10^4$; for H $\times 10^3$) and U_{eq} ($\times 10^4$ for S, O and C) and U_{iso} ($\times 10^3$ for H)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	$U_{eq}/U_{iso}(\text{\AA}^2)$
S	2418 (1)	270 (1)	842 (1)	652
O(1)	1168 (2)	-231 (2)	1105 (2)	608
O(2)	3058 (2)	-298 (2)	-197 (3)	865
O(3)	2045 (3)	1230 (2)	386 (3)	1023
C(1)	1189 (3)	-1251 (2)	1618 (3)	537
C(2)	3371 (3)	290 (2)	2807 (3)	584
C(11)	1122 (3)	-1291 (2)	3387 (3)	476
C(12)	2212 (3)	-1289 (2)	4570 (3)	450
C(13)	2050 (3)	-1287 (2)	6196 (3)	552
C(14)	863 (3)	-1298 (3)	6630 (4)	661
C(15)	-195 (3)	-1335 (3)	5466 (4)	697
C(16)	-69 (3)	-1326 (2)	3855 (4)	602
C(21)	4055 (3)	-643 (2)	3297 (3)	486
C(22)	3516 (3)	-1354 (2)	4161 (3)	459
C(23)	4241 (3)	-2174 (2)	4678 (4)	579
C(24)	5434 (3)	-2304 (3)	4326 (4)	727
C(25)	5946 (3)	-1612 (3)	3434 (4)	772
C(26)	5261 (3)	-790 (3)	2930 (4)	650
H(11)	45 (2)	-150 (2)	95 (3)	57 (8)
H(12)	190 (2)	-159 (2)	132 (3)	52 (8)
H(13)	280 (2)	-129 (2)	697 (3)	51 (8)
H(14)	84 (3)	-127 (2)	774 (4)	79 (10)
H(15)	-103 (3)	-137 (2)	580 (4)	90 (11)
H(16)	-76 (2)	-133 (2)	299 (3)	59 (8)
H(21)	393 (3)	75 (2)	271 (4)	75 (10)
H(22)	281 (3)	49 (2)	357 (3)	75 (10)
H(23)	385 (2)	-268 (2)	526 (3)	57 (8)
H(24)	594 (3)	-288 (2)	473 (4)	80 (10)
H(25)	671 (3)	-168 (2)	319 (3)	71 (10)
H(26)	558 (2)	-31 (2)	237 (3)	64 (9)

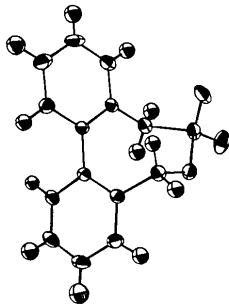


Fig. 1. View of one molecule of 5*H*,8*H*-dibenzo[*d,f*][1,2]oxathiocin 7,7-dioxide.

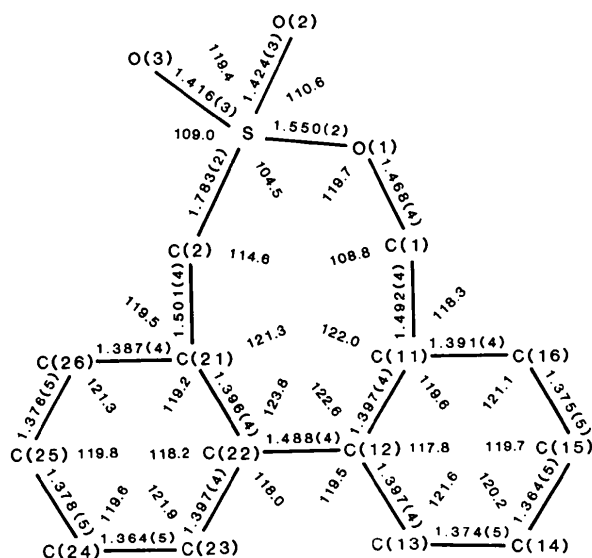


Fig. 2. Bond distances (\AA) and angles ($^\circ$). The e.s.d.'s for the angles are in the range 0.1 to 0.3 $^\circ$.

through an eight-membered ring in a 'pseudo-chair' conformation similar to those reported for the dithiocin analog (II) (Wahl *et al.*, 1973) and the parent disulfide (III) (Wahl *et al.*, 1972). The bond distances, the bond angles and their standard deviations are given in Fig. 2.

The average $C(sp^2)-C(sp^2)$ distance in the phenyl rings is in agreement with recently tabulated values (Brisse & Sygusch, 1974). It should be noted that all four bonds adjacent to that joining the two phenyl rings are significantly longer, 1.397(4) \AA , than the aromatic-ring bond distance of 1.379 \AA . At the same time, the two bond angles $C(11)-C(12)-C(13)$ and $C(21)-C(22)-C(23)$ are significantly smaller [117.8(3) and 118.2(3) $^\circ$ respectively] than the $C(sp^2)-C(sp^2)-C(sp^2)$ bond angle of 120 $^\circ$. In the same manner, $C(11)-C(12)-C(22)$ and $C(21)-C(22)-C(12)$ are larger [122.6(3) and 123.8(3) $^\circ$ respectively], while $C(13)-C(12)-C(22)$ and $C(23)-C(22)-C(12)$ are slightly smaller [119.5(3) and 118.0(3) $^\circ$] than 120 $^\circ$. These effects are characteristic of distortions in bridged biphenyls. The atoms in the phenyl rings are coplanar. Their deviations from their respective mean planes average 3σ , but C(1) and C(22) are significantly displaced by 0.066(3) and -0.135(3) \AA from the mean plane of C(11) to C(16); similarly C(2) and C(12) are displaced by -0.097(3) and 0.049(3) \AA from the mean plane of C(21) to C(26). The bridging of the two phenyl rings keeps them at 63(0.5) $^\circ$ with respect to one another. This dihedral angle compares well to the values of 65 $^\circ$ observed for (II), 67 $^\circ$ reported for (III) and 62 $^\circ$ for the peroxide analog of (III) (Brown *et al.*, 1976).

The conformation of the eight-membered-ring bridged biphenyl can be described as 'pseudo-chair'. The torsion angles characterizing such a conformation are compared in Table 2 to the corresponding angles in the dithiocin analog (Wahl *et al.*, 1973) and those of the peroxide analog of (III) (Brown *et al.*, 1976). The torsion angles in the dithiocin analog of (I) are more symmetrically distributed around the eight-membered ring than those of (I). This, of course, is probably related to the more chemically symmetrical eight-membered ring present in this structure. However, in the peroxide (Brown *et al.*, 1976), the conformation is that of a 'pseudo-boat'. The reported shortening of the 'pseudo-axial' S—O bond in (II) is not observed here. Instead, the two exocyclic S—O bond distances are within 2σ from each other, and compare well to the average of the two S—O bonds in (II). *Ab initio* calculations have been recently carried out (Boyd & Szabo, 1982) on a model of (II) where the shortening effect was noted (Wahl *et al.*, 1973). These calculations predict equal S—O bonds in the gas phase. Thus the authors conclude that the shortening effect is likely associated with crystal-packing forces. However, one should consider this observation with caution since the O atoms in (II) are disordered over four possible sites. The coordination at the S atom is tetrahedral, but the O—S—O bond angles vary within large limits from 104.1 (2) to 119.4 (2)° for the two exocyclic O atoms. The angles O(2)—S—C(2) and O(1)—S—O(3) (not shown in Fig. 2 for clarity purposes) are 108.1 (2) and 104.1 (2)° respectively. The S—O distance in the eight-membered ring with a value of 1.550 (2) Å is very acceptable, as is the S—C bond distance of 1.783 (2) Å. However, the C—O bond distance of 1.468 (4) Å is significantly longer than that observed in either the peroxide analog of (III) (Brown *et al.*, 1976) or the trimeric acetone peroxide (Groth, 1969). Another remarkable quantity is the very large S—O(1)—C(1) angle with a value of 119.7 (2)°. The corresponding value in the peroxide analog of (III) is 112.9° and only 107.4° in the trimeric acetone peroxide.

Table 2. Comparison of the eight-membered-ring torsion angles (°) to those in similar rings with a disulfide or a peroxide bond

	Oxathio ¹	Disulfide ²	Peroxide ³
S—O(1)—C(1)—C(11)	102.6 (2)	86.9	-31.3
O(1)—C(1)—C(11)—C(12)	-90.3 (3)	-104.8	-52.1
C(1)—C(11)—C(12)—C(22)	-6.7 (4)	2.1	3.3
C(11)—C(12)—C(22)—C(21)	64.8 (4)	67.0	64.9
C(12)—C(22)—C(21)—C(2)	4.3 (4)	2.1	3.3
C(22)—C(21)—C(2)—S	-92.1 (3)	-104.8	-52.1
C(21)—C(2)—S—O(1)	81.3 (2)	86.9	-31.3
C(2)—S—O(1)—C(1)	-64.9 (2)	-47.4	119.5
O(1)—C(1)—C(11)—C(16)	89.4 (3)		
S—C(2)—C(21)—C(26)	90.0 (3)		
C(13)—C(12)—C(22)—C(23)	60.5 (4)		

(1) This work; (2) Wahl *et al.* (1973); (3) Brown *et al.* (1976).

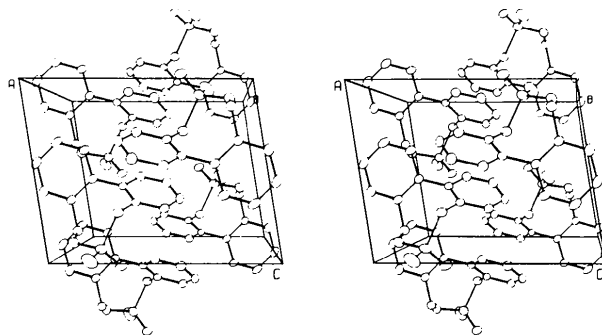


Fig. 3. Packing of the molecules in the unit cell.

A stereoview of the crystal packing is shown in Fig. 3. There is only one relatively short contact between atoms of adjacent molecules, the two O(1) atoms at (xyz) and (x̄yz̄). The O(1)⋯O(1) distance is 2.917 (3) Å. Apart from this there are no other unusually short contacts. Consequently, only van der Waals interactions maintain the molecules together in the crystal.

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