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The Crystal Structure of 5*H*,8*H*-Dibenzo[*d*,*f*] [1,2]-dithiocin-1,1-dioxide

BY GEORGE H. WAHL, JR AND JON BORDNER
Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607, *U.S.A.*
AND DAVID N. HARPP AND JOHN G. GLEASON
Department of Chemistry, McGill University, Montreal 101, *Quebec, Canada*

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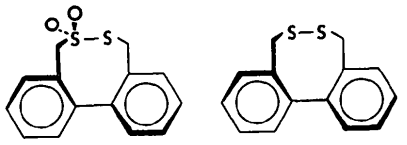
The crystal structure of 5*H*,8*H*-dibenzo[*d*,*f*] [1,2]dithiocin-1,1-dioxide, $C_{14}H_{12}S_2O_2$, has been determined by direct methods. The bridged biphenyl crystallizes in the triclinic space group $P\bar{1}$ with $a=7{\cdot}950$ (7), $b=11{\cdot}240$ (9), $c=7{\cdot}945$ (7) Å, $\alpha=91{\cdot}10$ (7), $\beta=117{\cdot}22$ (6), $\gamma=88{\cdot}86$ (7)°, $Z=2$. Intensities were collected with Mo $K\alpha$ radiation on a Syntex $P\bar{1}$ diffractometer to a maximum 2θ value of 42° by the θ–2θ scan technique. Coordinates and anisotropic temperature factors of the non-hydrogen atoms were refined by full-matrix least-squares. The final R was 0·063. The conformation of the eight-membered ring is a 'pseudo-chair'. A significant shortening of 'pseudo-axial' S–O bond lengths is observed.

Introduction

The structure of the title compound, $C_{14}H_{12}S_2O_2$, (I), is of interest as part of a program designed to determine the factors which influence conformational preferences in eight-membered ring bridged biphenyls.



(I) (II)

Previous work (Wahl, Bordner, Harpp & Gleason, 1972) indicated that the parent disulfide (II) existed in an unexpected 'pseudo-chair' conformation.

Experimental

Crystals suitable for X-ray examination were grown by slow evaporation from acetone. A colorless, platelike crystal (0·1 × 0·3 × 0·3 mm) was mounted on a glass fiber in a general orientation. A rotation photograph provided parameters sufficient to determine cell dimensions. These results were confirmed by precession photographs. No systematic absences were observed, and the lack of symmetry in the diffraction pattern indicated a triclinic crystal. Since the compound was chiral and was not resolved, the likely space group was $P\bar{1}$. A density measurement (flotation in aqueous potassium iodide) indicated two molecules in the unit cell.

A 1Å intensity data set (maximum $\sin\theta/\lambda = 0{\cdot}5$) was collected at 22°C on a Syntex $P\bar{1}$ diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The diffractometer was equipped with an incident beam graphite monochromator mounted in the perpendicular mode. Final unit-cell parameters were obtained from a least-squares fit of 14 high-angle reflections. A check reflection was monitored every 30 reflections and remained constant, within counter statistics, throughout the data collection. Details of the crystal and data collection are summarized in Table 1.

Table 1. *Crystal data and data-collection parameters*

Molecular formula	$C_{14}H_{12}O_2S_2$
Molecular weight	276·4
Cell dimensions (22°C)	$a =$ 7·950 (7) Å
	$b =$ 11·240 (9)
	$c =$ 7·945 (7)
	$\alpha =$ 91·10 (7)°
	$\beta =$ 117·22 (6)
	$\gamma =$ 88·86 (7)
	$V =$ 631·2 (9) Å^3
Space group	$P\bar{1}$
Molecules/unit cell	2
Density calculated	1·45 g cm^{-3}
Density observed	1·45 g cm^{-3}
Scan technique	θ–2θ
Scan width	1·2° below $K\alpha_1$; 1·2° above $K\alpha_2$
Scan speed	4° per min in 2θ
Background count time	Half peak scan time on each side of peak
Number of reflections	1430
Non-zero reflections*	1259

* All intensities with a value less than $2\sigma(I)$ were set equal to zero and were assigned zero weight.

The diffractometer output was processed with subroutines of the CRYM system (Duchamp, 1964). The processing included corrections for background, Lorentz and polarization effects. Polarization due to the monochromator was also corrected for (Azaroff, 1955). For each reflection the standard deviation was calculated from

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$$

in which S is the number of counts collected during the scan, B_1 and B_2 are the background counts, d is an empirical constant set at 0·02, and α is the ratio of scan time to total background time.

The data were placed on an approximate absolute scale by Wilson (1942) statistics. Atomic scattering factors for C, O and S were taken from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965). No corrections were made for absorption ($\mu = 4{\cdot}0$ cm^{-1}) or anomalous dispersion.

Phase determination

The structure was solved by a reiterative application of Sayre's (1952) equation with a program written by Long (1965). Normalized structure factors $|E|$ were calculated with an overall temperature factor of 3·5 Å^2. Only those reflections with $|E| \geq 1{\cdot}5$ (160) were used. A single E map revealed a plausible trial structure.

Refinement of the structure

All calculations were performed on an IBM 370/165 computer with the CRYM computer system. The full-matrix least-squares routine minimized $\sum\omega(F_o^2 - F_c^2)^2$. The weights used throughout the refinement were set equal to $1/\sigma^2(F_o^2)$ as based on the variance of the intensity.

Full matrix refinement of C, O and S coordinates and isotropic temperature factors resulted in an R of 0·23, where $R = \sum||F_o| - |F_c||/\sum|F_o|$. However, the oxygen temperature factors became quite large. Attempts at further refinement with anisotropic temperature factors resulted in an R of 0·27. A difference Fourier synthesis without the oxygen atoms revealed significant electron density in the vicinity of both sulfur atoms. Refinement proceeded smoothly to an R of 0·063 when a population factor of 0·5 was included for oxygen at each of the four possible sites. Hydrogen positions were calculated and added to the structure-factor calculations in the later stages of refinement but were not refined. The shifts calculated for the parameters in the final cycle of least-squares refinement were all less than one-tenth of the corresponding standard deviations. A final difference Fourier synthesis revealed no missing or misplaced atoms. The observed and calculated structure factors are listed in Table 2.

The final coordinates and anisotropic temperature factors for the C, O and S atoms with their standard

deviations, calculated from the least-squares residuals and the inverse matrix of the final least-squares cycle, are given in Table 3. The final scale factor was 0·905 (3) and the refined population factors were not significantly different from the original value of 0·50. The coordinates calculated for the hydrogens are given in Table 4.

Table 2. *Observed and calculated structure factors*

Within each group the columns contain k, $10F_o$ and $10F_c$. Reflections marked with an asterisk were assigned zero weight in the final least-square cycles

Table 3. *Heavy-atom Parameters and their standard deviations*

The values have been multiplied by 10^4. The temperature factor is in the form

$$T=\exp\{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\}.$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S(1)	1084 (2)	8351 (1)	5590 (2)	234 (4)	74 (2)	194 (4)	11 (4)	31 (7)	16 (4)
S(2)	583 (2)	6645 (1)	6087 (2)	198 (4)	73 (2)	237 (5)	−26 (4)	31 (7)	−18 (4)
O(3)	82 (10)	6008 (7)	4284 (10)	248 (21)	98 (9)	191 (22)	−75 (21)	32 (35)	−106 (23)
O(4)	−519 (10)	6614 (7)	6969 (11)	161 (20)	132 (11)	269 (24)	12 (21)	212 (39)	−15 (24)
C(5)	2884 (7)	6028 (5)	7646 (8)	155 (13)	57 (6)	234 (16)	12 (13)	99 (24)	−13 (15)
C(6)	3484 (7)	6275 (5)	9705 (8)	131 (12)	58 (6)	187 (15)	37 (14)	120 (24)	71 (15)
C(7)	2703 (7)	5612 (5)	10617 (10)	172 (14)	76 (7)	336 (20)	10 (15)	212 (30)	52 (19)
C(8)	3245 (9)	5774 (6)	12535 (11)	269 (18)	110 (8)	323 (22)	36 (19)	350 (34)	134 (21)
C(9)	4615 (9)	6599 (7)	13542 (9)	299 (10)	120 (8)	210 (17)	101 (20)	263 (32)	96 (20)
C(10)	5409 (7)	7263 (5)	12667 (8)	188 (14)	81 (6)	175 (16)	25 (14)	141 (25)	26 (15)
C(11)	4852 (7)	7134 (5)	10738 (8)	133 (12)	62 (6)	155 (15)	21 (13)	85 (23)	29 (15)
C(12)	5730 (7)	7869 (5)	9849 (7)	163 (14)	58 (6)	132 (13)	−36 (14)	94 (23)	−32 (14)
C(13)	7675 (8)	7739 (5)	10418 (8)	179 (15)	85 (6)	186 (15)	−37 (15)	127 (25)	−28 (15)
C(14)	8540 (8)	8405 (6)	9617 (10)	208 (16)	113 (8)	301 (19)	−102 (18)	260 (32)	−80 (20)
C(15)	7546 (10)	9221 (6)	8259 (10)	315 (20)	113 (8)	283 (19)	−153 (20)	365 (34)	−52 (20)
C(16)	5620 (9)	9386 (5)	7701 (8)	332 (19)	78 (6)	161 (14)	−68 (17)	222 (29)	−13 (15)
C(17)	4708 (7)	8722 (5)	8489 (7)	186 (14)	58 (6)	133 (13)	−66 (14)	113 (24)	−48 (14)
C(18)	2642 (7)	8972 (4)	7894 (7)	227 (15)	56 (6)	150 (13)	9 (13)	88 (23)	−28 (13)
O(19)	1959 (11)	8381 (7)	4479 (10)	285 (22)	129 (10)	171 (20)	10 (22)	215 (38)	−25 (21)
O(20)	−730 (9)	8979 (7)	5070 (11)	210 (20)	91 (9)	264 (22)	95 (20)	63 (35)	47 (21)

Table 4. *Calculated hydrogen coordinates*

These values have been multiplied by 10^4. The isotropic temperature factor was fixed at 3·50 Å^2.

	Atom bearing H	x	y	z
H(21)	7	1611	4963	9804
H(22)	8	2602	5264	13225
H(23)	9	5069	6715	15059
H(24)	10	6479	7911	13489
H(25)	13	8504	7097	11504
H(26)	14	10044	8288	10055
H(27)	15	8246	9751	7642
H(28)	16	4789	10025	6589
H(29)	5	3943	6399	7276
H(30)	5	2875	5067	7409
H(31)	18	2274	8585	8952
H(32)	18	2399	9924	7895

Table 5. *Bond distances* (Å)

S(1)—S(2)	2·048 (2)
S(1)—C(18)	1·812 (5)
S(1)—O(19)	1·352 (9)
S(1)—O(20)	1·475 (8)
S(2)—O(3)	1·474 (8)
S(2)—O(4)	1·350 (9)
S(2)—C(5)	1·808 (6)
C(5)—C(6)	1·501 (8)
C(6)—C(7)	1·384 (9)
C(6)—C(11)	1·409 (8)
C(7)—C(8)	1·391 (11)
C(8)—C(9)	1·378 (11)
C(9)—C(10)	1·371 (10)
C(10)–C(11)	1·393 (8)
C(11)–C(12)	1·471 (8)
C(12)–C(13)	1·404 (9)
C(12)–C(17)	1·397 (7)
C(13)–C(14)	1·370 (10)
C(14)–C(15)	1·363 (10)
C(15)–C(16)	1·396 (12)
C(16)–C(17)	1·389 (9)
C(17)–C(18)	1·508 (9)

Description of the structure

The bond lengths and angles with their standard deviations are given in Tables 5 and 6 respectively. An *ORTEP* stereo plot of the final structure is shown in Fig. 1. A 'pseudo-chair' conformation of the eight-membered central ring closely analogous to that observed for the parent disulfide(II) (Wahl *et al.* 1972), is again found. In Table 7, comparable parameters of I, the parent disulfide (II) and dibenzyl disulfide (III) (Lee & Bryant, 1969) are collocated. As expected the phenyl–phenyl dihedral angles of (I) and (II) are quite similar and larger than those calculated for seven-membered ring bridged biphenyls (Mislow, Glass, Hopps, Simon & Wahl, 1964).

Table 8 lists the least squares planes for the two aromatic rings of (I). In each case, the carbon involved in the φ–φ bond [C(11) and C(12)] is the most removed from the least-squares plane.

A striking feature of the structure of (I) is the very significant difference in sulfur–oxygen bond distances. The 'pseudo-axial' bond [S(2)–O(4) ≃ S(1)–O(19)] is substantially *shorter* than its 'pseudo-equatorial' analog (S(2)–O(3) ≃ S(1)–O(20)] which displays a more 'normal' bond length (1·35 *vs.* 1·47 Å). An analogous difference, albeit not as large has been found for γ-SO_3 (McDonald & Cruickshank, 1967).

One possible explanation of this shortening would be a geometrically dependent 'negative hyperconjugation', or 'no-bond resonance'.

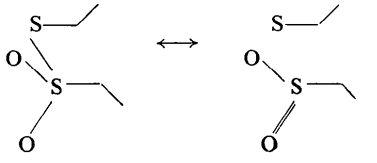
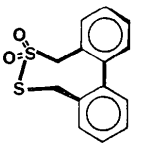
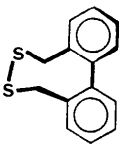
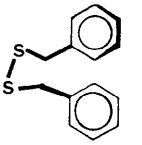
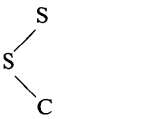
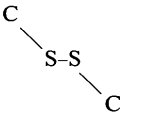


Table 6. *Bond angles* (°)

C(18)–S(1)–S(2)	105·5 (2)
O(19)–S(1)–S(2)	112·0 (4)
O(20)–S(1)–S(2)	103·9 (3)
O(19)–S(1)–C(18)	108·8 (4)
O(20)–S(1)–C(18)	103·7 (4)
O(20)–S(1)–O(19)	121·6 (5)
S(1)—S(2)—O(3)	104·4 (3)
S(1)—S(2)—O(4)	112·0 (4)
O(3)—S(2)—O(4)	122·0 (5)
S(1)—S(2)—C(5)	105·2 (2)
O(3)—S(2)—C(5)	103·2 (4)
O(4)—S(2)—C(5)	108·6 (4)
S(2)—C(5)—C(6)	113·6 (4)
C(5)—C(6)—C(7)	118·7 (5)
C(5)—C(6)—C(11)	121·9 (5)
C(7)—C(6)—C(11)	119·4 (5)
C(6)—C(7)—C(8)	121·3 (6)
C(7)—C(8)—C(9)	118·8 (7)
C(8)—C(9)—C(10)	120·8 (6)
C(9)—C(10)–C(11)	121·3 (6)
C(10)–C(11)–C(6)	118·4 (5)
C(6)—C(11)–C(12)	122·0 (5)
C(10)–C(11)–C(12)	119·6 (5)
C(11)–C(12)–C(13)	119·3 (5)
C(11)–C(12)–C(17)	122·4 (5)
C(13)–C(12)–C(17)	118·4 (5)
C(12)–C(13)–C(14)	120·9 (5)
C(13)–C(14)–C(15)	121·2 (7)
C(14)–C(15)–C(16)	119·0 (7)
C(15)–C(16)–C(17)	121·0 (6)
C(16)–C(17)–C(12)	119·6 (6)
C(12)–C(17)–C(18)	121·7 (5)
C(16)–C(17)–C(18)	118·7 (5)
S(1)—C(18)–C(17)	113·3 (4)

The finding of a longer S–S bond distance for (I) than for (II) (2·035 *vs.* 2·048 Å, see Table 7) is also consistent with such an explanation. However it is not clear why this would be important only in the case of the axial oxygen. Alternatively, the bond shortening could be the result of intramolecular van der Waals repulsion between the aromatic π electrons and those surrounding the axial oxygen. Table 9 lists the closest non-bond-

Table 7. *Comparison of parameters*

	 I	 II	 III*
d_{S-S}	2·048 (2)	2·035 (1)	2·029 (5)
d_{S-C}	1·812 (5) 1·808 (6)	1·835 (3)	1·840 (13)
	105·2 (2) 105·5 (2)	104·3 (1)	102·9 (5)
	47·4 (3)°	56·4 (2)°	92·1 °
φ–φ	65·4 (3)°	67·2 (2)°	–

* Lee & Bryant (1969).

Table 8. *Best planes of* (I)

Comparable data for (II) are given in parentheses.

Atom	Deviation from plane (Å)
C(6)	−0·0058 (0·0077)
C(7)	−0·0044 (0·0014)
C(8)	0·0092 (−0·0059)
C(9)	−0·0035 (0·0011)
C(10)	−0·0069 (0·0081)
C(11)	0·0115 (−0·0124)
C(12)	−0·0125 (0·0124)
C(13)	0·0077 (−0·0080)
C(14)	0·0028 (−0·0012)
C(15)	−0·0083 (0·0060)
C(16)	0·0031 (−0·0014)
C(17)	0·0072 (−0·0077)

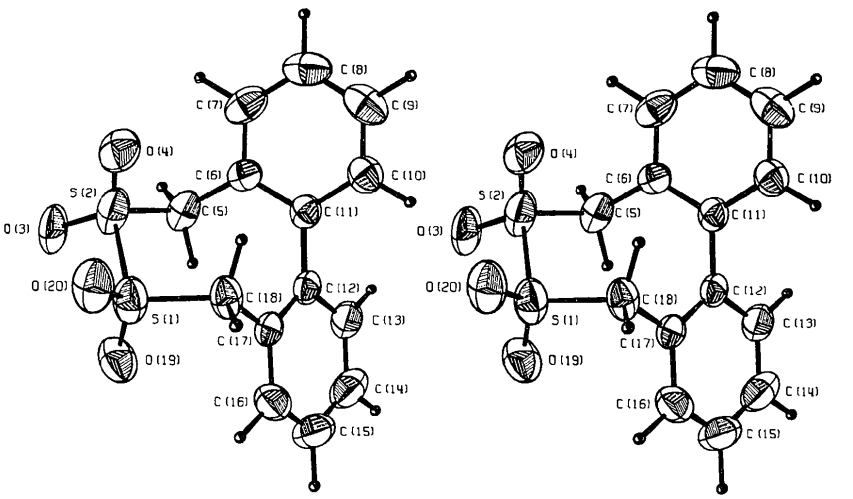


Fig. 1. *ORTEP* stereoscopic view of I. [Although four oxygens are shown, only two are present in any given molecule O(3) and O(4), or O(19) and O(20).]

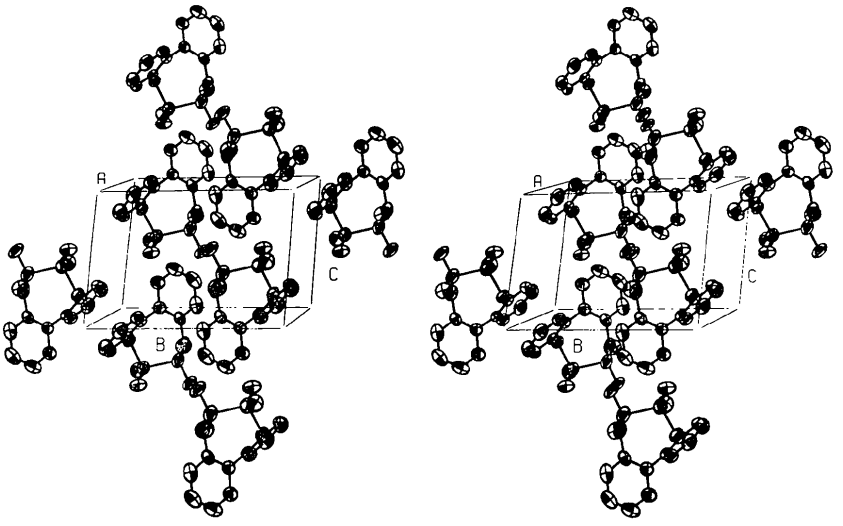


Fig. 2. Stereoscopic view down x showing the packing of the molecules in the unit cell.

ed approaches to the axial oxygen. Both C(6) and C(7) are closer to O(4) than the sum of the oxygen van der Waals radius (1·4 Å) plus one-half of the thickness of an aromatic π cloud (1·7 Å) (Pauling, 1960). This repulsion is also mirrored in the C(5)–S(2)–O(4) angle of 108·6° which is significantly larger than the C(5)–S(2)–O(3) angle (103·2°) (see Table 6).

Table 9. *Intramolecular non-bonded distances* (Å) *of oxygen to proximate atoms*

O(4)—O(3)	2·47
O(19)–O(20)	2·47
O(4)—S(1)	2·85
O(19)–S(2)	2·85
O(4)—C(6) ≃ O(19)–C(17)	2·94
O(4)—C(7) ≃ O(19)–C(16)	3·07
O(4)—C(18) ≃ O(19)–C(5)	3·52

Table 10. *Interatomic distances of close approach*

Atom 1	Atom 2	Distance(Å)	Symmetry operation of atom 1
3(0–eq)	3(0–eq)	2·59	$\bar{x}$ $1-y$ $1-z$
2(S)	3(0–eq)	3·02	$\bar{x}$ $1-y$ $1-z$
1(S)	20(0–eq)	3·04	$\bar{x}$ $2-y$ $1-z$
3(0–eq)	5(C)	3·15	$\bar{x}$ $1-y$ $1-z$
18(C)	20(0–eq)	3·15	$\bar{x}$ $2-y$ $1-z$

A stereo-view of the crystal packing diagram is shown in Fig. 2. Intermolecular distances of close approach ($\leq 3{\cdot}5$ Å) are listed in Table 10. The only close intermolecular contacts (*i.e.* less than the sum of van der Waals radii) are those involving equatorial oxygens.

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