

SHORT STRUCTURAL PAPERS

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Structure of Bis-(2-carboxyphenyl)sulphur Dioxide Dilactone

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Abstract. $(C_7H_4O_2)_2S$, M.W. 272.28, orthorhombic, space group: $F2dd$ (no. 43), $a=4.224$ (8), $b=20.089$ (11), $c=27.830$ (20) Å (from precession photographs), $Z=8$, $D_c=1.531$, $D_x=1.526$ g cm $^{-3}$ (by flotation). The molecules located on twofold axes are held together by weak van der Waals forces which yield the long but very thin (even fibrous) crystals obtained by the method described by Kapovits & Kálmán [*Chem. Commun.* (1971). pp. 649-650].

Introduction. The crystals could not be cut by the usual technique (Kálmán & Argay, 1965) to the dimensions required for the collection of intensities without demolishing their fibrous macro-structure. After numerous fruitless attempts, however, a single crystal (dimensions: 0.03 × 0.03 × 0.30 mm) was found in a branch of crystals grown accidentally on a metal plate from which the compound was sublimed. The thin needle was elongated along the shortest crystal axis a and the equi-inclination Weissenberg arrangement provided by the two-circle Stoe-Güttinger diffractometer (Wölfel, 1968) allowed collection of reflexions only from the layers $0kl-3kl$. Thus 600 independent reflexions were measured with Cu $K\alpha$ (Ni) radiation ($\lambda=1.5418$ Å), 78 of which were unobserved. The structure was determined from a Patterson and two successive Fourier syntheses. A structure-factor calculation based on the positional parameters obtained from the last Fourier map, with an isotropic temperature factor, as given by the Wilson plot of $B=3.30$ Å 2 applied to all the atoms, resulted in an agreement value R of 0.302 for the observed data. The least-squares refinement of the fractional atomic coordinates and four scale factors, together with isotropic (three cycles) and anisotropic (five cycles) vibrational parameters, was terminated at an R value of 0.146 for observed (and 0.172 for all) reflexions because of the very low $h_{max}(=3)$ value (for comparison, $k_{max}=24$, $l_{max}=34$). The effect of the low h_{max} is apparent in the high standard deviations for x coordinates and especially in the quite unreliable B_{11} (as well as in B_{12} and B_{13}) values. A similar phenomenon was described by Kálmán & Cruickshank (1970) for Na_2SeO_4 . Hydrogen

atoms were placed at the calculated positions 1.01 Å from the appropriate carbon atoms, but their coordinates were not refined. The final atomic parameters are given in Table 1. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1962). Fig. 1 shows the bond lengths and angles. A table of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30032.*

Discussion. In spite of the high standard deviations of bond lengths and angles (caused by the very low h_{max} value) the structure determination established the structural formula [Fig. 2(a)] which was drawn up on

* Copies of this table may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

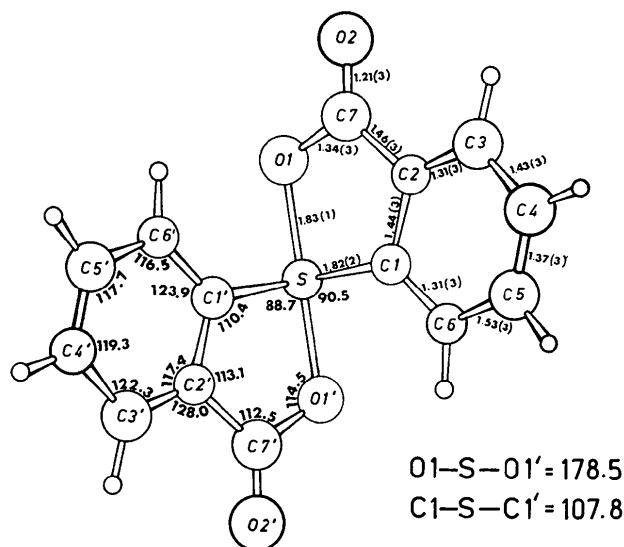


Fig. 1. Molecular conformation observed in the crystal structure of the title compound with bond lengths and angles. The e.s.d.'s for bond angles vary from 0.7 to 2.2°.

the basis of chemical, infrared and n.m.r. studies of the title compound† (Kapovits & Kálmán, 1971). The C_2 molecular symmetry shown by the crystal data had permitted two spatial formulae [Figs. 3(a) and (b)], of which the model with apical oxygen atoms [Fig. 3(a)] proved to be correct. It confirmed our conclusion based on the VSEPR theory of Gillespie (1963) applied to trigonal bipyramidal structures by Muetterties, Mahler, Packer & Schmutzler (1964). The existence of this molecule was predicted earlier by Musher (1969) on theoretical grounds as one of the 'hypervalent molecules' which, however, has been accepted with scepticism by numerous organic chemists.

† It can also be described as a spirodiaryldiacyloxysulphurane.

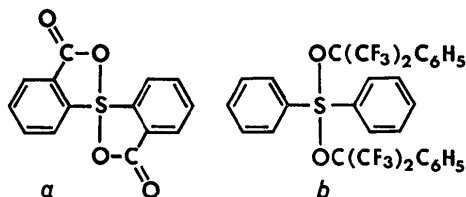


Fig. 2. Chemical formulae of (a) the title compound and (b) a diaryldialkoxysulphurane, Paul *et al.* (1971).

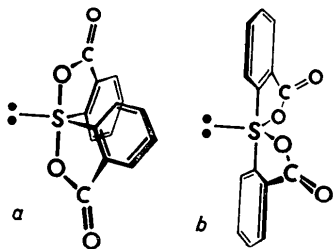


Fig. 3. Spatial formulae for the title compound permitted by the crystal symmetry: $F2dd$. (a) represents the actual structure.

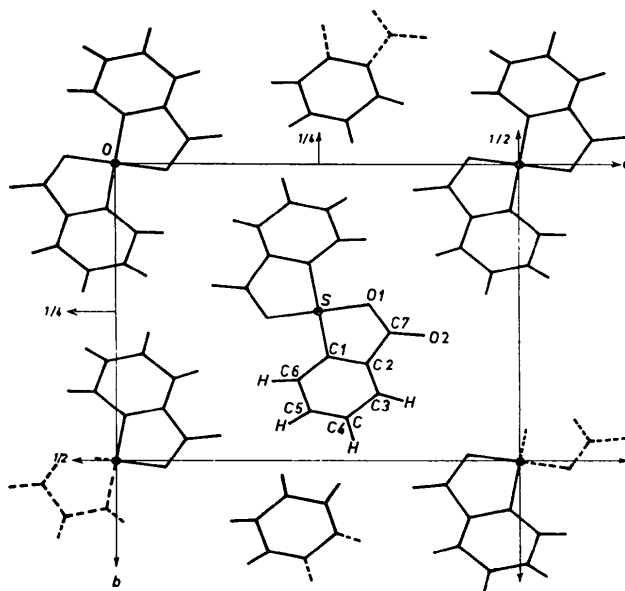


Fig. 4. Packing of molecules of the title compound (a projection).

The spatial arrangement of the molecule is analogous to that of diaryldialkoxysulphurane [hereafter: DDS, Fig. 2(b)], the crystal structure of which was recently determined by Paul, Martin & Perozzi (1971). Both are types of stable organo-sulphur compounds containing a four-coordinate tetravalent sulphur atom and are the first without halogen atom ligands. The S-C bond lengths are, within experimental error, comparable with those found in DDS [1.804 (4) and 1.810 (4) Å]. They are between the theoretical S(IV)-C(sp^2) and S(IV)-C(sp^3) bond distances of 1.80 and 1.83 Å respectively (Truter, 1962), and the experimental values measured *e.g.* in different sulphilimines (*cf.* reference given by Kálmán & Sasvári, 1972). The S-O bond lengths of 1.83 Å are considerably shorter than those of 1.889 (4) and 1.916 (4) Å observed in DDS, but still significantly longer [by 0.13 Å] than the sum

Table 1. Final positional ($\times 10^4$) and vibrational parameters

(Standard deviations for the non-hydrogen atoms are in parentheses.)

The anisotropic vibrational parameters are in the form $\exp[-\frac{1}{2}(B_{11}a^{*2}h^2 + \dots + B_{12}a^*b^*hk + \dots)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	2555 (42)	2357 (6)	3148 (4)	4.45 (0.74)	3.99 (42)	4.31 (43)	0.50 (1.12)	5.97 (0.99)	0.85 (0.78)
O(2)	3955 (96)	2836 (9)	3835 (5)	25.49 (2.41)	7.52 (77)	2.54 (46)	-16.61 (2.24)	3.57 (2.22)	-0.94 (1.00)
C(1)	5036 (56)	3220 (7)	2593 (5)	2.57 (0.96)	2.28 (44)	3.56 (56)	1.18 (1.36)	-2.07 (1.27)	0.92 (0.85)
C(2)	5649 (57)	3313 (7)	3098 (6)	3.92 (0.98)	2.82 (47)	3.66 (56)	3.48 (1.15)	-1.60 (1.41)	0.09 (0.98)
C(3)	7046 (89)	3868 (9)	3228 (8)	9.69 (1.80)	3.41 (58)	4.40 (74)	-5.01 (1.93)	1.84 (2.16)	-0.51 (1.16)
C(4)	8687 (71)	4283 (8)	2894 (7)	7.45 (1.57)	2.66 (56)	5.64 (90)	3.30 (1.63)	5.69 (1.97)	0.69 (1.14)
C(5)	8409 (61)	4159 (8)	2412 (8)	2.67 (0.97)	2.72 (55)	7.00 (84)	0.60 (1.29)	-5.22 (1.50)	0.96 (1.25)
C(6)	6001 (54)	3628 (8)	2259 (7)	1.40 (0.85)	2.68 (47)	6.35 (87)	2.61 (1.05)	-0.32 (1.41)	-0.16 (1.18)
C(7)	3966 (67)	2837 (9)	3402 (7)	4.88 (1.21)	3.58 (61)	3.81 (59)	-3.38 (1.43)	2.82 (1.55)	-1.45 (0.98)
S	2500	2500	2500	3.30 (0.10)					
H(3)	7254	3977	3597	5.09					
H(4)	9999	4648	2986	4.40					
H(5)	9540	4406	2153	5.04					
H(6)	5109	3604	1916	3.32					

of Pauling's covalent radii corrected for the electronegativities (Truter, 1962). The short and long C–C distances [average: 1.40 Å] alternating in the six-membered rings are rather interesting, but this phenomenon can hardly be regarded as significant owing to the large experimental errors. The C(1)–S–C(1'), O(1)–S–O(1') and O(1)–S–C(1) as well as the O(1)–S–C(1') bond angles are also comparable with the corresponding values in DDS. The dihedral angle between the best planes of the benzene rings of the symmetrical parts of the molecule is 106.7°. It is noteworthy that the crystal lattice (Fig. 4) contains enantiomeric pairs of molecules; this is in agreement with the chirality of the structure depicted in Fig. 3(a).

We wish to thank Professor Á. Kucsman for his invaluable advice, Professor J. I. Musher (New York) for providing us with preprints and other data concerning his work on the 'hypervalent molecules' and Mr Cs. Kertész for technical assistance.

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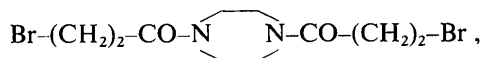
N,N'-Bis-(3-bromopropionyl)piperazine

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Abstract. Monoclinic, $P2_1/c$, $a = 10.58$ (1), $b = 5.81$ (1), $c = 10.83$ (5) Å; $\beta = 100.6$ (1)°; formula $C_{10}H_{16}N_2O_2Br_2$



$Z = 2$, $D_m = 1.81$, $D_x = 1.87$ g cm⁻³. The colorless crystals were recrystallized from water. The space group and cell content imply that the molecule is centrosymmetric. The structure, refined to $R = 0.079$, shows considerable steric strain, which may be connected with the oncolytic activity of the compound.

Introduction. All accessible intensity data from crystals mounted on axes a and c were collected using a Supper–Pace automated diffractometer with Cu $K\alpha$ radiation, Lorentz–polarization corrections applied, and the two axes correlated, giving a total of 1352 reflections. Elimination of reflections less than 4σ as unobserved left 754 unique reflections where σ is defined as

$$\sigma(I) = [(0.05I^2) + N_0 + K^2N_b]^{1/2}$$

[N_0 is gross count, N_b is background count and K is ratio of scan time to background time (Parker, Flynn & Boer, 1968)]. The systematic absences ($h0l$, l odd; $0k0$, k odd) uniquely determine the space group.

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A sharpened Patterson function was used to locate the bromine position. The remaining non-hydrogen atoms were located by electron-density synthesis and a minimum-function map which used the bromine positions as the points of superposition. Hydrogen atoms were located in a difference electron-density map ($F_o - F_c$ synthesis) and their positions optimized to give bond lengths of 1.0 Å. Full-matrix least-squares refinement

Table 1. *Final positions and anisotropic temperature factors*

	x/a	y/b	z/c
Br	0.8485 (1)	0.5633 (0)	0.1352 (2)
C(2)	0.8936 (9)	0.5555 (22)	0.3230 (13)
C(3)	0.7897 (8)	0.4554 (19)	0.3817 (13)
C(4)	0.6758 (7)	0.6164 (15)	0.3691 (11)
O	0.6833 (6)	0.8161 (12)	0.3392 (9)
N	0.5699 (7)	0.5228 (12)	0.4007 (10)
C(7)	0.4606 (8)	0.6742 (16)	0.4066 (12)
C(8)	0.5561 (8)	0.2996 (14)	0.4578 (12)
H(9)	0.633	0.206	0.456
H(10)	0.481	0.221	0.408
H(11)	0.476	0.829	0.372
H(12)	0.383	0.603	0.356
H(13)	0.822	0.424	0.475
H(14)	0.763	0.306	0.338
H(15)	0.911	0.716	0.356
H(16)	0.971	0.459	0.348