

Acta Cryst. (1968). **B24**, 981

The crystal structure of dibenzothiophene sulfone. By LOUIS R. KRONFELD and RONALD L. SASS, *Department of Chemistry, William Marsh Rice University, Houston, Texas, U.S.A.*

(Received 9 February 1968)

The crystal structure of dibenzothiophene sulfone has been determined. Observed unit cell parameters are $a=10.09(1)$, $b=13.89(3)$, $c=7.22(1)$ Å and $\beta=93.5(4)^\circ$. The space group is $C2/c$. Three-dimensional visual data were collected with Cu $K\alpha$ radiation. The trial structure was obtained by Patterson methods and refined by least squares. The final R was 11%. The S-C bond length is 1.74 ± 0.02 Å. The C-C bond lengths are essentially equal to those found in fluorene.

As part of a study of cyclic sulfones in this laboratory, the crystal and molecular structure of dibenzothiophene 5,5-dioxide (dibenzothiophene sulfone) has been determined. The primary interest of this investigation is to assess the effect of the sulfone group on molecular dimensions and compare this effect with those observed in similar compounds, (Jeffrey, 1951; Desiderato & Sass, 1967).

Crystals of the compound suitable for diffraction studies were grown from the melt by sublimation just below the melting point, 236–238°C. Weissenberg photographs (Cu $K\alpha$, $\lambda=1.5418$ Å) indicated the space group to be either Cc (C_2^1) or $C2/c$ (C_{2h}^2). Systematic absences were hkl absent when $h+k=2n+1$ and $h0l$ absent when $l=2n+1$. Unit-cell dimensions were $a=10.09(1)$, $b=13.89(3)$, $c=7.22(1)$ Å and $\beta=93.5(4)^\circ$. The observed density, measured by flotation, is 1.39 g.cm $^{-3}$; the theoretical density, calculated on the basis of four molecules per cell, is 1.35 g.cm $^{-3}$. Multiple film Weissenberg photographs were taken about the c axis ($l=0-7$) and the primitive [110] axis [$(h-k)/2=0-4$]. Intensities were measured visually. The Lorentz-polarization factor was applied and the data correlated in the usual manner. No corrections were made for extinction or absorption. A total of 605 reflections in the region of reciprocal space considered had detectable intensities.

The trial structure was solved assuming the symmetry to be $C2/c$ (C_{2h}^2). Final refinement indicated this assumption to be correct. Because this space group contains eightfold general positions, the twofold axis of a molecule must coincide with that of the crystallographic unit cell. This information was utilized with the Patterson projection $P(u,v)$ to determine the coordinates of the various atoms. The sulfur atom was quite easily located and the map also contained a moderately well resolved image of the remainder

of the molecule. An electron density projection $\rho(x,y)$ gave a clear image of the molecule lying nearly in the plane of the projection. The rotation of the molecule out of the projection plane was estimated from the shape of the oxygen peaks and packing considerations. The z parameters of all the atoms were subsequently assigned and structure factors were calculated for all 605 reflections. The reliability index, R , for this trial structure was 0.35. A three-dimensional electron density map was synthesized at this point. It was well resolved, showed no spurious peaks and yielded a set of atomic parameters essentially the same as those indicated above. These parameters served as the starting point of the least-squares refinement.

Refinement was carried out with the full matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The R value was lowered to 0.11 with use of individual anisotropic temperature factors on each atom. Hydrogen atoms were included in the final stages of refinement with isotropic temperature factors of 5.9. The hydrogen positions were determined assuming a 0.90 Å C-H bond distance and ideal geometry. No hydrogen parameters were refined. The weighting scheme used was

$$\begin{aligned} \sqrt{w} &= 1/F \text{ for } F > 4 F_{\min} \\ \sqrt{w} &= 1/4F_{\min} \text{ for } F \leq 4F_{\min} \end{aligned}$$

Final atomic parameters and estimated standard deviations are listed in Table 1. A list of observed and calculated structure factors is available from the authors on request.

Bond lengths and angles calculated from the final atomic parameters are shown in Fig. 1. This figure is also the view of the molecule projected down the c axis. On the basis of the estimated standard deviations listed in Table 1, the

Table 1. *Final atomic parameters (e.s.d.'s)*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B^\dagger
S*	0	0.2958 (2)	$\frac{1}{2}$	3.08 (16)	2.70 (15)	3.05 (20)	0.00	0.08 (8)	0.00	3.12 (12)
O	0.9771 (6)	0.2429 (4)	0.4240 (10)	5.84 (32)	4.71 (30)	4.32 (40)	-0.61 (14)	-0.71 (14)	1.01 (16)	5.33 (23)
C(1)	0.1218 (8)	0.3824 (5)	0.2897 (10)	3.61 (32)	3.17 (30)	2.05 (56)	-0.36 (11)	-0.49 (17)	-0.24 (16)	3.34 (23)
C(2)	0.2566 (8)	0.3631 (7)	0.3342 (17)	4.38 (40)	6.25 (46)	4.42 (80)	-0.03 (19)	-0.43 (23)	0.52 (24)	5.24 (30)
C(3)	0.3371 (10)	0.4432 (10)	0.3691 (18)	4.50 (44)	8.88 (77)	4.98 (80)	-1.12 (22)	-0.62 (24)	0.48 (30)	6.09 (37)
C(4)	0.2873 (10)	0.5363 (8)	0.3546 (16)	9.00 (68)	6.87 (69)	2.24 (76)	-1.98 (27)	-0.09 (27)	0.36 (24)	6.91 (39)
C(5)	0.1545 (10)	0.5522 (7)	0.3043 (15)	7.18 (61)	4.71 (46)	3.23 (72)	-0.87 (19)	0.01 (14)	0.12 (20)	5.99 (36)
C(6)	0.0716 (7)	0.4757 (5)	0.2736 (28)	4.30 (28)	3.32 (30)	2.53 (46)	-0.64 (14)	0.13 (16)	0.14 (21)	3.74 (23)
H(1)‡	0.2874	0.3075	0.3653							5.90
H(2)	0.4162	0.4362	0.3963							5.90
H(3)	0.3369	0.5792	0.3681							5.90
H(4)	0.1189	0.6007	0.2919							5.90

* x and z parameters for sulfur were fixed by symmetry at values shown.

† Temperature factors isotropic refinement. The temperature factors are of the form $\exp[-\frac{1}{2}(h^2a^*2B_{11} + k^2b^*2B_{22} + l^2c^*2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$ or $\exp(-B \sin^2\theta/\lambda^2)$.

‡ All parameters for hydrogen were frozen with C-H equal to 0.90 Å and H-C-C angles equal to approximately 120°.

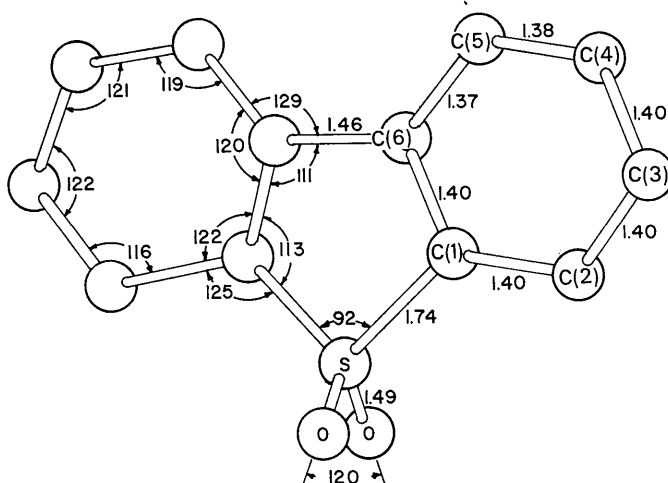


Fig. 1. Molecular dimensions of dibenzothiophene sulfone. The molecular orientation displayed is that of the [001] projection.

largest estimated error in bond length is 0.02 Å and the average error is 0.017 Å.

The molecular packing is quite reasonable with no intermolecular distances shorter than the sum of the normally accepted van der Waals radii.

The sulfur-carbon bond distance reported herein as 1.74 Å is in good agreement with those found in β -isoprene sulfone (Jeffrey, 1951) and *cis*-2-butene episulfone (Desiderato & Sass, 1967). The sulfur-oxygen bond distance of 1.49 Å is in good agreement with the value predicted from the sum of the Pauling double-bond covalent radii but is about 0.05 Å longer than that observed in other sulfones (Desiderato & Sass, 1967). In the remainder of the structure, the bond distances and angles are comparable to the equivalent values found for fluorene (Burns & Iball, 1955). The ring closing C(6)-C(6') distance of 1.46 Å is, within experimental error, equal to the value of 1.48 Å observed

for fluorene. The molecule, within experimental error, possesses C_{2v} symmetry.

This work was supported by grants from the National Aeronautics and Space Administration and the Robert A. Welch Foundation of Houston, Texas. The 7094 computer calculations were done at the Common Research Computer Facility located in the Texas Medical Center and supported by USPH Grant FR-00254.

References

- BURNS, D. M. & IBALL, J. (1955). *Proc. Roy. Soc. A* **227**, 200.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962).
 ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 DESIDERATO, R. & SASS, R. L. (1967). *Acta Cryst.* **23**, 430.
 JEFFREY, G. A. (1951). *Acta Cryst.* **4**, 58.

Acta Cryst. (1968). **B24**, 982

The cation distribution in CoFe_2O_4 . By G. D. RIECK and J. J. M. THIJSEN, *Laboratory of Physical Chemistry, Technological University, Eindhoven, The Netherlands*

(Received 12 February 1968)

The metal ions in CoFe_2O_4 when fired in air, are probably randomly distributed over the cation sites of the spinel structure.

As a part of a programme on the determination of the distribution of the cations in spinel type structures (Rieck & Driessens, 1966), we studied the structure of CoFe_2O_4 with respect to the occupation of the octahedral and tetrahedral sites by Co and Fe ions. If λ is the fraction of the tetrahedral sites occupied by Fe ions, the formula may be written $\text{Co}_{1-\lambda}\text{Fe}_\lambda[\text{Co}_\lambda\text{Fe}_{2-\lambda}]\text{O}_4$, the brackets indicating the ions in octahedral sites.

The spinel structures contain as unknown crystallographic parameter the coordinate (u) of the oxygen ions. The value of u may differ somewhat from its value in an

ideal spinel, *viz.* $\frac{3}{8}$, and both λ and u may change in relation to temperature and oxygen pressure during preparation.

The samples were made from $\alpha\text{-Fe}_2\text{O}_3$ (Merck, p.a.) and Co_3O_4 (Merck, p.a.), mixed according to the stoichiometric composition of CoFe_2O_4 , pressed to tablets, fired for 24 hours in air at 1100°C, then powdered, pressed again and fired for 48–53 hours in air at 1200–1400°C. After this they were either quenched or slowly cooled in air and their cell constants a were measured (Table 1). In order to find λ we used the method of Bertaut (1950). We applied Co $K\alpha$ radiation in order to obtain a (maximum) difference between