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## The Crystal Structure of Diphenyl Disulphide

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The crystal structure of diphenyl disulphide has been determined by three-dimensional X-ray analysis. Crystals are orthorhombic and belong to the space group  $P2_12_12_1$ . The unit cell has dimensions  $a = 23.78$ ,  $b = 8.13$ ,  $c = 5.64$  Å, and contains four molecules. Positional and temperature factor parameters for the sulphur and carbon atoms have been refined by Fourier and full-matrix least-squares methods on 963 independent reflexions. In the final stages hydrogen atoms were included in fixed positions, the final  $R$  value being 9.0%. The molecule has a non-planar configuration, and the planes of the benzene rings are inclined at an angle of  $77.3^\circ$  to each other. The S-S bond length of 2.03 Å is slightly shorter than the normal single-bond distance, suggesting 15% of double-bond character. The S-C bond lengths of 1.79 and 1.81 Å are close to the normal single bond distance.

### Introduction

Certain organic disulphides are used as additives to lubricating oils, since their presence increases the load bearing properties of the oil, especially at high pressures.

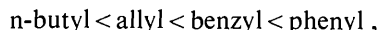
Allum & Ford (1965) have shown that extreme pressure activity of organic disulphides increases along the

series:

phenyl < n-butyl < s-butyl < t-butyl < benzyl,

and suggest that the load bearing properties under these conditions are structural phenomena probably depending on the strength of the sulphur-carbon bond. Furthermore, Allum & Forbes (1967) have shown that the anti-wear properties of organic disulphides in-

crease along the series:



and suggest that the load carrying properties under these conditions are dependent on the ease of cleavage of the sulphur-sulphur bond.

X-ray crystallographic structure determinations of a series of disulphides should give structural information which may be correlated with load carrying activity. As a first step towards this objective an accurate X-ray structural determination has been carried out on diphenyl disulphide.

### Experimental

A sample of diphenyl disulphide was recrystallized from ethanol. Colourless needle shaped crystals elongated in the *c* direction were obtained, and oscillation, zero and higher layer Weissenberg photographs were obtained with the crystal,  $0.3 \times 0.15 \times 0.15$  mm, rotating about the *b* and *c* axes, allowing the observation of 963 independent reflexions. Intensities were measured visually, and Lorentz and polarization corrections applied. No corrections were made for absorption or extinction. Reflexions too weak to be observed were omitted.

#### Crystal data

$(\text{C}_6\text{H}_5)_2\text{S}_2$ ,  $M = 218.34$ .

Orthorhombic,  $a = 23.78 \pm 0.03$ ,  $b = 8.13 \pm 0.02$ ,  $c = 5.64 \pm 0.02$  Å.  $U = 1090.4$  Å<sup>3</sup>,  $z = 4$ ,  $D_m = 1.34$  g.cm<sup>-3</sup>,  $D_c = 1.35$  g.cm<sup>-3</sup>.  $F(000) = 456$ ,  $\text{Cu K}\alpha$ ,  $\lambda = 1.542$  Å,  $\mu = 39.2$  cm<sup>-1</sup>.

Absent reflexions  $h00$  when  $h$  odd,  $0k0$  when  $k$  odd,  $00l$  when  $l$  odd. The space group is thus uniquely determined as  $P2_12_12_1$  ( $D_2^4$ ).

#### Determination of the structure

Since there are four molecules in the unit cell, these must occupy the general positions  $(x, y, z)$ ,  $(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$ ,  $(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z})$ ,  $(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$ . Similarity between the cell parameters and space group of diphenyl disulphide

and diphenyl diselenide, and a Patterson synthesis on the  $hk0$  projection of the disulphide suggested a first trial structure very similar to the diselenide structure. Examination of the latter showed that the origin chosen by Marsh (1952) differed from that shown in *International Tables for X-ray Crystallography* (1952) for this space group, and in order to convert to *International Tables* axes, shifts in atomic parameters of  $+\frac{1}{4}x/a$  and  $-\frac{1}{4}z/c$  were required.

Structure factor calculations were performed by the use of scattering factors of Hanson, Herman, Lea & Skillman (1964) and these initial parameters gave a reliability index,  $R$ , of 35% for the  $hk0$  projection and 43% for  $h0l$  projection. By Fourier techniques the values of  $R$  were reduced to 17% and 20% respectively. Least-squares refinement on three-dimensional data was commenced with a block-diagonal least-squares program written by G.S.D. King (Union Carbide European Research Associates) for the IBM 1620 computer. Five cycles of refinement with unit weights and isotropic temperature factors, rescaling of layers from the sums of the observed and calculated structure factors, followed by three further least-squares cycles, reduced  $R$  to 20%.

A three-dimensional Fourier synthesis showed the sulphur atoms as ellipsoids rather than spheres. The ratio of the major axis to minor axes was approximately 3:2 and the major axis was roughly perpendicular to the sulphur bond direction. This indicated anisotropic thermal motion of the sulphur atoms.

No unaccounted for peaks appeared on the maps. Subsequent refinement was made by a full-matrix least-squares method with the X-ray 63 programs on the S.R.C. Chilton Atlas computer. By the use of unit weights and isotropic temperature factors, refinement stopped after two cycles at  $R = 17\%$ . The weighting scheme was changed to one similar to that used by Hughes (1941) with  $w = 1$  if  $F_{\text{obs}} \leq F^*$  and  $w = F^*/F_{\text{obs}}$  if  $F_{\text{obs}} > F^*$ . From an analysis of the structure factors, the value of  $F^*$  was fixed at 7.5. Anisotropic temperature factors were introduced for sulphur, and the scattering factors for sulphur were corrected for both real and

Table 1. Final coordinates and standard deviations

	$x/a$	$y/b$	$z/c$	$\sigma x/a$	$\sigma y/b$	$\sigma z/c$
S(1)	0.3075	-0.0359	0.1778	0.0001	0.0004	0.0006
S(2)	0.3433	0.0321	-0.1333	0.0001	0.0004	0.0005
C(1)	0.3196	-0.2515	0.2088	0.0004	0.0014	0.0020
C(2)	0.3482	-0.3478	0.0427	0.0005	0.0015	0.0022
C(3)	0.3557	-0.5139	0.0864	0.0005	0.0018	0.0028
C(4)	0.3335	-0.5834	0.2915	0.0005	0.0016	0.0026
C(5)	0.3050	-0.4889	0.4518	0.0005	0.0017	0.0026
C(6)	0.2972	-0.3209	0.4128	0.0004	0.0016	0.0021
C(7)	0.4166	0.0669	-0.0681	0.0004	0.0012	0.0018
C(8)	0.4467	0.1566	-0.2348	0.0005	0.0017	0.0021
C(9)	0.5026	0.1843	-0.2019	0.0007	0.0020	0.0027
C(10)	0.5310	0.1245	-0.0059	0.0005	0.0018	0.0025
C(11)	0.5005	0.0327	0.1659	0.0005	0.0017	0.0020
C(12)	0.4430	0.0083	0.1314	0.0004	0.0014	0.0020

imaginary parts of anomalous dispersion. Refinement continued for three cycles, until  $R=12.2\%$ , and after further agreement analysis a Cruickshank type of weighting scheme was used:

$$w = 1/[2(A) + |F_{\text{obs}}| + (2/B)F_{\text{obs}}^2]$$

with values of  $A=7$ ,  $B=100$ . One further cycle reduced  $R$  to  $11.3\%$ , and the positions of the hydrogen atoms were calculated assuming a C-H bond length of  $1.075\text{\AA}$ . Inclusion of hydrogen atoms with isotropic temperature factors  $B=5.0\text{ \AA}^2$  in fixed positions, followed by refinement of the carbon and sulphur atom parameters gave  $R=9.9\%$ .

New hydrogen atom positions were calculated as before, and the carbon and sulphur atom parameters refined in further cycles of least-squares, when  $R$  dropped to  $9.7\%$ . Finally, anisotropic temperature factors were introduced for carbon atoms, and the parameters of the carbon and sulphur atoms refined for two more cycles, giving a final reliability index of  $R=9.0\%$ .

The final atomic coordinates and temperature factors are given in Tables 1 and 2, and the calculated positions of the hydrogen atoms are given in Table 3. Values of observed and calculated structure factors are listed in Table 4 and an agreement analysis is given in Table 5.

Table 2. Final temperature factor parameters

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
S(1)	3.87	3.86	4.72	0.31	0.97	-0.17
S(2)	4.32	4.77	3.37	-0.26	-0.74	0.57
C(1)	2.51	4.65	3.58	-0.43	0.07	0.28
C(2)	4.16	5.00	3.63	0.93	0.42	-0.46
C(3)	4.59	5.43	6.05	0.73	0.07	-1.03
C(4)	4.25	4.14	6.01	-0.12	-0.64	0.19
C(5)	5.25	5.70	4.70	-0.92	-0.19	0.99
C(6)	3.70	5.02	3.42	0.11	0.30	-0.10
C(7)	4.35	3.22	2.45	-0.13	0.54	0.15
C(8)	4.57	5.25	3.54	0.37	0.22	0.65
C(9)	6.20	6.63	5.20	-1.70	1.89	0.99
C(10)	3.87	5.93	4.77	-0.60	0.07	-0.69
C(11)	4.94	6.00	3.33	-0.78	-0.70	-0.69
C(12)	3.64	4.59	3.18	-0.18	0.16	-0.46

Table 3. Calculated positions of hydrogen atoms

	$x/a$	$y/b$	$z/c$
H(2)	0.3643	-0.2935	-0.1174
H(3)	0.3785	-0.5889	-0.0375
H(4)	0.3388	-0.7127	0.3241
H(5)	0.2884	-0.5446	0.6099
H(6)	0.2744	-0.2469	0.5381
H(8)	0.4258	0.2040	-0.3895
H(9)	0.5254	0.2546	-0.3318
H(10)	0.5752	0.1468	0.0162
H(11)	0.5212	-0.0168	0.3193
H(12)	0.4191	-0.0572	0.2626

All hydrogen atoms were assumed to have an isotropic temperature factor  $B=5.00\text{ \AA}^2$ .

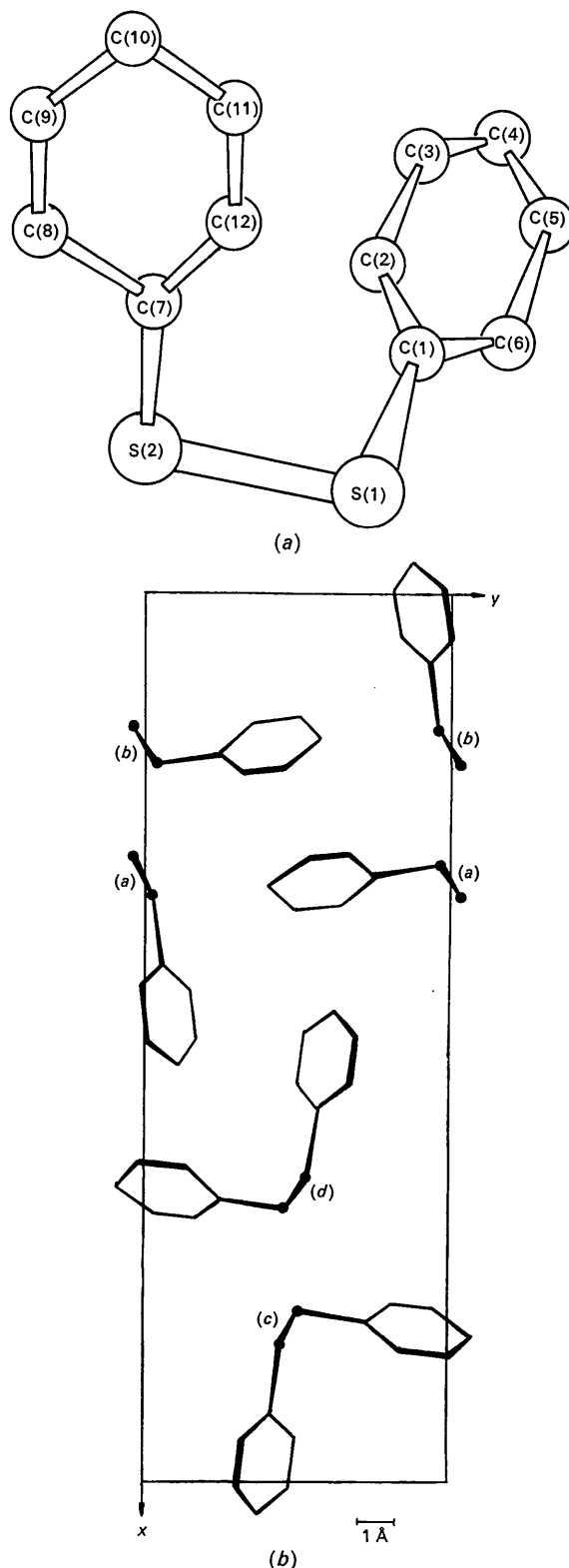


Fig. 1. (a) A view of the molecule. (b) The contents of one unit cell. (The  $z/c$  coordinate for the mid-point of the S-S bond in molecule (a) is 0.0222; molecule (b), 0.5222; molecule (c) -0.0222; molecule (d), 0.4778.)



Table 4 (cont.)

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>					
1	7	2	11.2	10.4	1	2	3	10.6	10.4	8	5	3	15.0	18.5	0	2	4	32.4	33.0	13	6	4	7.8	6.9	18	2	5	4.6	4.8
3	7	2	15.7	15.9	2	2	3	32.9	34.0	9	5	3	7.0	5.7	1	2	4	10.1	8.9	14	6	4	6.1	6.2	19	2	5	4.4	4.8
5	7	2	7.0	6.6	3	2	3	12.4	12.5	10	5	3	13.4	15.9	2	2	4	1.8	2.3	15	6	4	7.2	6.4	0	3	5	8.8	8.6
6	7	2	6.2	7.6	4	2	3	30.9	30.5	11	5	3	7.4	8.3	3	2	4	14.0	12.5	2	7	4	7.2	5.9	1	3	5	7.4	7.8
7	7	2	5.8	5.9	5	2	3	4.6	3.8	12	5	3	7.3	7.5	4	2	4	11.4	11.3	3	7	4	7.4	6.6	2	3	5	6.4	6.8
9	7	2	7.5	7.8	6	2	3	17.4	15.2	13	5	3	5.4	2.8	5	2	4	10.2	8.6	4	7	4	4.0	3.8	3	3	5	10.2	9.6
10	7	2	6.0	4.8	7	2	3	7.1	6.9	14	5	3	7.1	6.6	6	2	4	17.9	17.5	5	7	4	7.7	6.7	4	3	5	5.4	5.9
1	8	2	4.2	3.7	8	2	3	15.2	13.7	15	5	3	7.3	6.7	7	2	4	9.6	8.3	6	7	4	8.6	6.9	5	3	5	10.8	10.1
2	8	2	13.3	12.5	9	2	3	16.7	14.9	16	5	3	9.5	12.0	8	2	4	8.4	7.5	7	7	4	3.8	4.7	6	3	5	11.9	10.1
3	8	2	6.7	7.7	10	2	3	9.9	9.5	17	5	3	6.6	6.9	9	2	4	18.0	17.6	8	7	4	8.4	7.9	7	3	5	8.0	8.0
4	8	2	14.4	15.1	11	2	3	12.0	10.0	24	5	3	3.4	4.0	10	2	4	13.5	14.4	12	7	4	6.5	6.7	8	3	5	13.5	13.3
5	8	2	5.8	5.1	12	2	3	8.4	7.3	0	6	3	7.3	6.8	11	2	4	11.5	10.8	13	7	4	5.5	5.1	11	3	5	5.3	5.1
6	8	2	3.7	4.8	13	2	3	12.8	11.4	1	6	3	10.4	12.2	12	2	4	9.8	9.0	14	7	4	6.5	6.2	11	3	5	4.7	4.3
7	8	2	3.5	3.3	14	2	3	7.3	6.8	2	6	3	7.4	7.5	13	2	4	7.6	7.4	15	7	4	4.2	4.7	12	3	5	11.5	10.7
8	8	2	4.9	5.3	15	2	3	9.1	8.6	3	6	3	7.0	8.5	14	2	4	8.4	8.9	3	8	4	3.4	2.7	13	3	5	7.3	6.6
3	9	2	11.7	10.8	16	2	3	15.4	12.2	4	6	3	9.4	9.0	15	2	4	6.3	7.6	4	8	4	3.0	5.2	14	3	5	11.5	11.2
4	9	2	7.7	6.7	17	2	3	13.5	11.3	5	6	3	7.2	9.0	0	3	4	15.5	16.5	5	8	4	1.6	0.5	15	3	5	7.1	6.2
6	9	2	8.4	6.2	18	2	3	9.4	10.2	6	6	3	4.9	4.1	1	3	4	18.0	18.1	4	0	5	11.2	11.5	16	3	5	5.2	5.3
8	9	2	1.0	0.4	19	2	3	7.2	7.4	7	6	3	5.8	6.6	2	3	4	8.4	8.5	6	0	5	11.9	11.7	19	3	5	3.8	4.2
9	9	2	4.4	4.3	20	2	3	6.6	5.5	8	6	3	3.6	2.6	3	3	4	11.5	10.7	7	0	5	16.4	20.3	0	4	5	6.5	5.3
11	9	2	5.2	1.5	22	2	3	12.6	14.1	9	6	3	11.0	12.8	4	3	4	10.9	10.3	8	0	5	10.5	11.2	1	4	5	11.6	12.3
3	0	3	20.7	21.9	24	2	3	8.1	10.4	10	6	3	10.3	10.9	5	3	4	9.8	8.6	9	0	5	9.7	9.7	2	4	5	7.5	6.7
4	0	3	29.0	31.7	0	3	3	5.1	4.7	11	6	3	13.3	15.0	6	3	4	5.6	5.3	10	0	5	2.7	1.9	3	4	5	4.1	5.1
6	0	3	35.1	33.6	1	3	3	23.3	24.0	12	6	3	5.1	7.3	7	3	4	12.3	12.5	11	0	5	6.8	6.4	4	4	5	5.1	4.2
7	0	3	9.5	8.8	2	3	3	16.6	16.3	13	6	3	9.4	9.0	8	3	4	11.6	12.6	12	0	5	13.4	12.5	5	4	5	2.7	2.9
8	0	3	20.7	16.9	3	3	3	19.1	18.6	16	6	3	6.1	7.9	9	3	4	5.7	4.7	13	0	5	11.1	11.1	6	4	5	8.8	8.5
9	0	3	15.5	13.5	4	3	3	10.2	10.4	17	6	3	10.1	10.6	10	3	4	15.7	15.7	14	0	5	14.4	15.5	7	4	5	9.2	9.0
10	0	3	14.8	12.4	5	3	3	20.4	20.2	2	7	3	5.1	8.0	11	3	4	8.9	8.9	15	0	5	10.5	10.7	8	4	5	5.1	4.2
11	0	3	21.6	20.9	6	3	3	5.8	5.6	4	7	3	7.7	9.5	12	3	4	6.3	5.2	16	0	5	2.7	2.5	9	4	5	8.1	8.3
12	0	3	12.3	11.1	7	3	3	5.0	5.2	6	7	3	5.1	7.1	13	3	4	8.8	10.1	17	0	5	8.0	8.1	10	4	5	4.0	3.5
13	0	3	10.9	9.8	8	3	3	16.6	17.9	8	7	3	8.7	10.1	14	3	4	7.4	7.9	0	1	5	8.4	7.2	11	4	5	2.7	1.8
14	0	3	15.0	14.7	9	3	3	12.9	12.2	10	7	3	12.1	12.8	0	4	4	21.4	23.3	1	1	5	4.5	3.5	12	4	5	10.5	9.9
15	0	3	21.9	22.4	10	3	3	16.3	16.6	12	7	3	7.7	8.5	1	4	4	15.6	15.5	2	1	5	12.9	13.3	13	4	5	3.7	4.2
18	0	3	4.7	3.5	11	3	3	10.8	11.7	16	7	3	6.8	7.8	2	4	4	5.3	4.5	3	1	5	5.4	4.3	15	4	5	4.7	4.2
18	0	3	7.1	5.0	12	3	3	11.9	11.1	18	7	3	5.3	7.5	3	4	4	8.0	7.0	4	1	5	7.6	7.3	0	5	5	14.8	14.7
19	0	3	9.5	8.5	13	3	3	10.3	10.0	3	0	4	12.5	12.8	4	4	4	15.4	14.9	5	1	5	10.7	10.9	1	5	5	9.8	9.6
20	0	3	7.4	7.0	14	3	3	8.7	7.8	4	0	4	13.3	13.0	5	4	4	3.2	1.8	6	1	5	14.8	16.7	2	5	5	4.5	3.4
21	0	3	9.0	7.9	15	3	3	7.2	6.1	5	0	4	10.7	9.5	6	4	4	13.2	12.8	7	1	5	1.7	1.4	4	5	5	3.5	3.6
22	0	3	14.5	12.8	16	3	3	6.3	7.1	6	0	4	12.8	12.8	7	4	4	20.7	17.7	8	1	5	14.7	16.1	5	5	5	8.5	7.7
23	0	3	5.0	3.4	17	3	3	5.9	5.5	7	0	4	12.3	13.4	8	4	4	4.5	3.9	9	1	5	4.1	4.5	8	5	5	10.9	9.8
24	0	3	11.2	9.4	18	3	3	9.0	10.0	9	0	4	32.4	38.0	0	5	4	4.7	4.5	10	1	5	3.9	3.8	7	5	5	9.0	7.6
25	0	3	3.8	2.4	0	4	3	18.5	19.7	10	0	4	6.4	6.5	1	5	4	5.0	4.9	11	1	5	4.7	4.9	8	5	5	9.2	8.5
1	1	3	6.5	5.6	1	4	3	4.5	4.4	11	0	4	19.6	22.1	2	4	4	12.9	11.5	12	1	5	8.5	7.8	9	5	5	4.7	4.4
1	1	3	34.8	35.7	2	4	3	26.4	27.3	12	0	4	6.5	6.5	3	5	4	20.2	18.2	13	1	5	9.7	9.6	11	5	5	4.3	4.1
2	1	3	33.3	33.7	3	4	3	9.6	9.9	13	0	4	5.4	4.8	4	5	4	5.3	4.9	14	1	5	13.7	14.8	12	5	5	5.7	5.3
3	1	3	35.6	39.9	4	4	3	24.2	27.2	14	0	4	11.0	13.3	5	5	4	13.3	11.7	15	1	5	6.2	6.0	13	5	5	3.7	2.5
4	1	3	29.6	29.5	5	4	3	11.9	12.6	15	0	4	12.7	13.6	6	5	4	7.9	8.0	16	1	5	5.5	4.7	14	5	5	7.7	8.6
5	1	3	33.7	34.6	6	4	3	6.2	6.8	16	0	4	5.3	7.1	7	5	4	8.1	7.4	17	1	5	3.6	4.1	15	5	5	3.4	3.6
6	1	3	9.8	7.5	8	4	3	8.1	8.3	17	0	4	16.4	18.9	8	5	4	6.0	6.5	18	1	5	6.2	6.4	0	6	5	8.3	7.4
7	1	3	16.2	15.1	9	4	3	16.9	19.7	0	1	4	22.2	24.0	11	5	4	8.0	7.1	0	2	5	4.6	3.6	1	6	5	6.7	6.9
8	1	3	19.7	16.8	10	4	3	14.3	15.9	1	1	4	22.3	24.7	12	5	4	8.3	7.5	1	2	5	4.4	3.7	2	6	5	6.9	6.5
9	1	3	22.4	18.8	11	4	3	15.2	15.8	2	1	4	7.9	6.2	13	5	4	8.2	8.1	2	2	5	14.4	15.2	3	6	5	7.1	6.2
10	1	3	15.7	12.5	12	4	3	5.1	5.0	3	1	4	10.8	8.9	14	5	4	4.8	4.1	3	2	5	10.4	10.3	5	6	5	5.0	4.5
11	1	3	12.9	11.6	14	4	3	7.5	9.6	4	1	4	6.2	4.8	15	5	4	2.2	1.4	4	2	5	5.7	5.3	6	6	5	6.4	5.8
12	1	3	8.0	6.0	15	4	3	10.4	12.4	5	1	4	20.0	21.6	16	5	4	5.2	5.0	5	2	5	5.5	3.4	7	6	5	5.8	5.1
13	1	3	9.6	8.7	16	4	3	7.1	7.4	6	1	4	9.0	9.4	17	5	4	3.1	2.										

on each atom exceeding that between the bonding pairs of electrons. These angles are close to the value of  $107^\circ$  for *p,p'*-dibromodiphenyl disulphide (Toussaint, 1945) and  $105.4^\circ$  for perfluorodimethyl disulphide (Bowen, 1954). In a review by Abrahams (1956) it is noted that the valency angle for two-bonded sulphur is almost invariably tetrahedral or slightly less.

Table 6. Bond lengths and their standard deviations

Bond	Distance	$\sigma$
S(1)—S(2)	2.03 Å	0.005 Å
S(1)—C(1)	1.79	0.012
S(2)—C(7)	1.81	0.010
C(1)—C(2)	1.40	0.016
C(2)—C(3)	1.39	0.019
C(3)—C(4)	1.40	0.021
C(4)—C(5)	1.37	0.019
C(5)—C(6)	1.40	0.019
C(6)—C(1)	1.39	0.016
C(7)—C(8)	1.39	0.016
C(8)—C(9)	1.37	0.020
C(9)—C(10)	1.39	0.021
C(10)—C(11)	1.42	0.018
C(11)—C(12)	1.39	0.015
C(12)—C(7)	1.38	0.015

Table 7. Bond angles and their standard deviations

	Angle	$\sigma$
C(1)—S(1)—S(2)	$106.5^\circ$	0.4°
C(7)—S(2)—S(1)	105.8	0.4
S(1)—C(1)—C(2)	124.3	0.9
S(1)—C(1)—C(6)	114.7	0.9
C(2)—C(1)—C(6)	121.0	1.1
C(1)—C(2)—C(3)	119.3	1.2
C(2)—C(3)—C(4)	119.7	1.3
C(3)—C(4)—C(5)	120.7	1.2
C(4)—C(5)—C(6)	120.8	1.3
C(5)—C(6)—C(1)	118.5	1.1
S(2)—C(7)—C(8)	116.2	0.8
S(2)—C(7)—C(12)	123.7	0.8
C(8)—C(7)—C(12)	120.1	1.0
C(7)—C(8)—C(9)	119.8	1.2
C(8)—C(9)—C(10)	121.8	1.4
C(9)—C(10)—C(11)	118.7	1.1
C(10)—C(11)—C(12)	118.7	1.1
C(11)—C(12)—C(7)	120.8	1.0

The observed C—S bond lengths of 1.79 and 1.81 Å are in good agreement with the value of 1.812 Å obtained by Cox & Jeffrey (1951) as the mean of eleven molecules containing a formal single bond. The sum of Pauling's (1960) single bond covalent radii for carbon and sulphur is also 1.812 Å.

The bond lengths and angles in the benzene rings are all normal, and the rings are planar to within 0.01 Å.

There are no interatomic distances less than 3.5 Å between atoms in different molecules (except for those involving hydrogen atoms). Disregarding the hydrogen atoms, the intramolecular approaches less than 3.5 Å which are not directly bonded are listed in Table 10. Most of these involve distances across benzene rings and are unavoidable, but the distances C(2)···S(1) = 3.25 Å and C(12)···S(2) = 3.25 Å are of interest. Assuming Pauling's (1960) values for van der Waals radii, S = 1.85 Å and half the thickness of an aromatic ring = 1.70 Å, then these C—S distances are significantly short. It has recently been suggested that the van der Waals radius for sulphur should be 1.72–1.73 Å (Fava Gasparri, Nardelli & Villa, 1967; Nardelli, Fava Gasparri, Giraldi Battistina & Domiano, 1966; Ždanov & Žvonkova, 1950; van der Helm, Lessor & Merritt, 1960).

Even accepting the smaller van der Waals radius the C—S distances remain significantly short. The hydrogen atoms on the aromatic carbon atoms are not favourably placed for hydrogen bonding to the sulphur atoms. Since hydrogen bonding would involve S···H···C bonds bent to about  $110^\circ$ , and the H···S distance is 2.70 Å, this possibility is precluded. The three bond angles round C(1) and C(7) add up to  $360.0^\circ$ , indicating that the bonds round these atoms are planar, as required by  $sp^2$  hybridization. However, the bond angles S(1)—C(1)—C(2) =  $124.3^\circ$  and S(2)—C(7)—C(12) =  $123.7^\circ$  are significantly greater than the theoretical  $120^\circ$ . It would seem that the close approaches between C and S result in the whole benzene ring bending away so that these two angles are increased and the angles S(1)—C(1)—C(6) and S(2)—C(7)—C(8) are reduced from  $120^\circ$  to  $114.7^\circ$  and  $116.2^\circ$  respectively, but that the ring itself is not distorted.

Table 8. Best least-squares planes

Atoms in plane	Equation
C(1), C(2), C(3), C(4), C(5), C(6)	$20.37X + 1.55Y + 2.71Z = 6.68$
C(7), C(8), C(9), C(10), C(11), C(12)	$-4.90X + 6.88Y + 2.77Z = -1.76$

*X*, *Y* and *Z* refer to the unit-cell axes *a*, *b* and *c*.  
Angle between these two planes =  $77.3^\circ$ .

Distances of atoms from planes			
C(1)	-0.007 Å	C(7)	0.008 Å
C(2)	0.008	C(8)	0.001
C(3)	-0.005	C(9)	-0.007
C(4)	0.001	C(10)	0.003
C(5)	0.000	C(11)	0.006
C(6)	0.003	C(12)	-0.012

Table 9. *Some sulphur(II) – sulphur(II) bond lengths*

Compound	S–S Bond length	Dihedral angle	Reference
<i>p,p'</i> -Dibromodiphenyl disulphide	2.15	–	Toussaint (1945)
1,2-Dithiolane-4-carboxylic acid	2.096 ± 0.007 Å	27° ± 1°	Foss & Tjomsland (1958); Foss, Hordvik & Sletten (1966).
Rhombohedral sulphur S <sub>6</sub>	2.057 ± 0.018	74.5 ± 2.5	Donohue, Caron & Goldish (1961).
Perfluorodimethyl disulphide	2.053 ± 0.019	–	Bowen (1954)
Hydrogen disulphide	2.05 ± 0.02	<i>ca.</i> 90°	Stevenson & Beach (1938)
Orthorhombic sulphur S <sub>8</sub>	2.048 ± 0.002	98.7 ± 0.5	Wilson & Badger (1949)
2-(2-Pyridylmethylthio)- benzoic acid	2.046 ± 0.01	99.1	Cooper, Bond & Abrahams (1961)
L-Cystine dihydrochloride	2.044 ± 0.01	79.2 ± 2	Karle, Karle & Mitchell (1969)
Formamidinium disulphide dibromide monohydrate	2.044 ± 0.01	89.2 ± 2	Steinrauf, Peterson & Jensen (1958)
Formamidinium disulphide di-iodide monohydrate	2.044 ± 0.02	104.8 ± 3	Foss, Johnsen & Tvedten (1958)
Dimethyl disulphide	2.04 ± 0.03	–	Foss, Johnsen & Tvedten (1958)
<i>N,N'</i> -Diglycyl-L-cystine dihydrate	2.04 ± 0.005	101 ± 2	Stevenson & Beach (1938)
Potassium barium hexathionate	{ 2.05 ± 0.02 2.04 ± 0.02 2.04 ± 0.02	{ 108 ± 2 105 ± 2 89 ± 2	Yakel & Hughes (1954)
Perchlorodimethyl trisulphide	{ 2.037 ± 0.010 2.032 ± 0.010	{ 95 ± 2 93 ± 3	Foss & Johnsen (1965)
L-Cystine	2.032 ± 0.004	106 ± 1	Berthold (1961)
Diphenyl disulphide	2.03 ± 0.005	96.2 ± 1	Oughton & Harrison (1959)
L-Cystine dihydrobromide	2.024 ± 0.014	90 ± 2	Present work
Tetraethylthiuram disulphide	2.00	96.4	Peterson, Steinrauf & Jensen (1960)
<i>t</i> -Butyl <i>N,N</i> -dimethyltri- thioper carbamate	2.00 ± 0.01	99.6	Karle, Estlin & Britts (1967)
			Mitchell (1969)

Table 10. *Distances less than 3.5 Å within the same molecule which are not directly bonded*

Contacts with hydrogen atoms are excluded.

S(1)–C(2)	2.82 Å
S(1)–C(6)	2.68
S(1)–C(7)	3.06
S(1)–C(12)	3.25
S(2)–C(1)	3.06
S(2)–C(2)	3.25
S(2)–C(8)	2.72
S(2)–C(12)	2.81
C(1)–C(3)	2.40
C(1)–C(4)	2.76
C(1)–C(5)	2.39
C(2)–C(4)	2.40
C(2)–C(5)	2.77
C(2)–C(6)	2.42
C(3)–C(5)	2.40
C(3)–C(6)	2.79
C(4)–C(6)	2.40
C(7)–C(9)	2.38
C(7)–C(10)	2.78
C(7)–C(11)	2.41
C(8)–C(10)	2.40
C(8)–C(11)	2.79
C(8)–C(12)	2.39
C(9)–C(11)	2.41
C(9)–C(12)	2.76
C(10)–C(12)	2.42

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## Crystal and Molecular Structure of 2-Diazonium-4-phenolsulfonate Monohydrate, $C_6H_3.N_2^+.SO_3^-.OH.H_2O$

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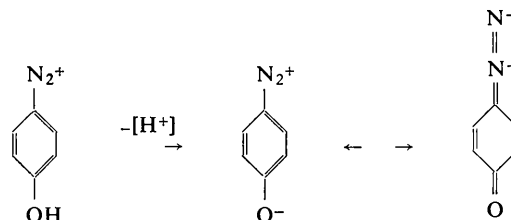
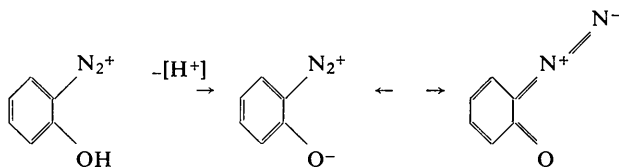
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The absorption spectra of a stable product of diazotization of 2-amino-4-phenolsulfonic acid exhibit characteristics of a diazonium salt; this is an exception to the generally established rule that a diazo-oxide structure is more stable than the corresponding diazonium salt. The monohydrate of the compound was therefore studied by the X-ray diffraction method. The crystal belongs to the monoclinic system with  $a = 8.97 \pm 0.02$ ,  $b = 11.63 \pm 0.02$ ,  $c = 8.62 \pm 0.02$  Å,  $\beta = 102.5^\circ$ ; the space group is  $P2_1/n$ . The structure was determined from three-dimensional intensity data obtained with Cu  $K\alpha$  radiation. The observed bond distances and angles in the molecule established that the molecule possesses a zwitterion configuration, 2-diazonium-4-phenolsulfonate monohydrate,  $C_6H_3N_2^+SO_3^- \cdot OH \cdot H_2O$ . The crystal structure is essentially ionic with short intermolecular N—O electrostatic attraction (2.88 Å) between the diazonium groups and the sulfonate groups. The water molecules connect the zwitterions by forming a three-dimensional network of O—H $\cdots$ O hydrogen bonds. The unusual stability of the diazonium structure is explained in terms of the zwitterion configuration and the crystal structure of the compound.

### Introduction

The diazo-oxides are stable compounds derived from *ortho*- and *para*-hydroxy substituted aromatic diazonium salts, sometimes through the action of alkali.



The structure of these compounds, once thought to be cyclic, is now generally accepted to be resonance hybrid of the type shown above, and the resultant reson-