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## An Accurate Crystal Structure Determination of 2,2'-Diaminodiphenyl Disulphide

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The crystal structure of 2,2'-diaminodiphenyl disulphide has been determined accurately from three-dimensional X-ray diffraction data. Crystals are orthorhombic, and belong to the space group *Pbca*. The unit cell has dimensions  $a = 8.21$ ,  $b = 13.14$ ,  $c = 22.77$  Å, and contains eight molecules. The positional and anisotropic thermal parameters for the sulphur, carbon and nitrogen atoms have been refined by Fourier and full-matrix least-squares methods on 1313 independent observed reflexions. In the later stages hydrogen atoms were included in fixed positions, and the final agreement factor  $R = 8.6\%$ . The central part of the molecule C-S-S-C has a skewed non-planar conformation similar to H<sub>2</sub>O<sub>2</sub>, with a dihedral angle of 90.5°. The S-S bond length is 2.06 Å, which is longer than in diphenyl and dibenzyl disulphides. The C-S bond lengths of 1.77 and 1.75 Å are significantly short. This indicates some double bond character, which may be explained by  $p\pi-d\pi$  bonding. The benzene rings are inclined at an angle of 32.5° to each other.

### Experimental

A sample of 2,2'-diaminodiphenyl disulphide, H<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-S-S-C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub>, kindly provided by the Clayton Aniline Co. Ltd, was recrystallized from ethanol and gave pale yellow-green platelets elongated along **a**. These showed straight extinction parallel and perpendicular to **a** when viewed under the polarizing microscope. The density of the crystals was measured by flotation in aqueous potassium iodide solution, and was found to be 1.33 (5) g.cm<sup>-3</sup>.

Considerable difficulty was experienced in selecting a single crystal for X-ray examination. Many crystals consisted of several parallel platelets, indistinguishable from a single crystal under the polarizing microscope but detectable on higher layer line Weissenberg photographs. Eventually a suitable single crystal of dimensions 0.4 × 0.3 × 0.15 mm was used to obtain oscillation photographs about the *a* and *b* axes, and equi-inclination Weissenberg photographs for the *Ok*l-*6kl* and *h*0*l* zones. The relative intensities of 1313 independent reflexions were measured visually and corrected for Lorentz and polarization factors. Absorption corrections

were considered unnecessary, in view of the small crystal size compared with the optimum size of 0.50 mm (Buerger, 1958). Reflexions too weak to be observed were omitted.

### Crystal data

C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>, M.W. 248.36,

Orthorhombic;  $a = 8.21 \pm 0.02$ ,  $b = 13.14 \pm 0.02$ ,  
 $c = 22.77 \pm 0.03$  Å

$U = 2456.4$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.33$  (5) g.cm<sup>-3</sup>,  
 $D_c = 1.343$  g.cm<sup>-3</sup>

$F(000) = 1040$ , Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 39.7$  cm<sup>-1</sup>.

Absent reflexions *hk*0 when *h* odd, 0*kl* when *k* odd, *h*0*l* when *l* odd. The space group is thus uniquely determined as *Pbca* ( $D_{2h}^{15}$ ), no. 61.

### Structure analysis

The determination of the crystal structure of 2,2'-diaminodiphenyl disulphide was undertaken as part of a series of accurate structure determinations on disul-

Table 1. *Final coordinates and standard deviations*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$\sigma x/a$	$\sigma y/b$	$\sigma z/c$
S(1)	0.3196	0.5110	0.1644	0.0002	0.0001	0.0001
S(2)	0.5257	0.5611	0.2072	0.0003	0.0002	0.0001
C(1)	0.2927	0.6023	0.1083	0.0007	0.0005	0.0003
C(2)	0.2072	0.6922	0.1205	0.0008	0.0005	0.0003
C(3)	0.1772	0.7582	0.0739	0.0010	0.0006	0.0004
C(4)	0.2351	0.7359	0.0184	0.0013	0.0007	0.0004
C(5)	0.3174	0.6450	0.0068	0.0010	0.0008	0.0003
C(6)	0.3470	0.5810	0.0524	0.0009	0.0006	0.0003
C(7)	0.6839	0.5010	0.1695	0.0008	0.0005	0.0003
C(8)	0.7328	0.4021	0.1839	0.0010	0.0005	0.0003
C(9)	0.8612	0.3602	0.1542	0.0012	0.0006	0.0004
C(10)	0.9434	0.4142	0.1121	0.0011	0.0010	0.0005
C(11)	0.8942	0.5119	0.0973	0.0012	0.0009	0.0004
C(12)	0.7682	0.5538	0.1266	0.0010	0.0006	0.0003
N(1)	0.1497	0.7145	0.1768	0.0007	0.0004	0.0002
N(2)	0.6443	0.3469	0.2271	0.0009	0.0005	0.0003

phides in this laboratory. Whilst the collection of data was in progress, a short communication appeared (Gomes de Mesquita, 1967), giving the molecular conformation on a limited amount of data, without emphasis on high accuracy or bond lengths and angles. Some of the standard deviations were excessively high and after consultation it was decided to proceed with an accurate structure determination.

The essential features of the structure were confirmed by a three-dimensional Patterson synthesis, and the reported atomic positions were used as starting parameters. All calculations were carried out using the X-ray 63 system of programs by Professor J. M. Stewart as adapted for the SRC Atlas computer by Dr J. C. Baldwin. The atomic scattering factors used were those due to Hanson, Herman, Lea & Skillman (1964), and that for sulphur was corrected for both the real and imaginary parts of anomalous dispersion (Dauben & Templeton, 1955). Initially reflexions were put on to a common scale by means of spots present on more than one layer.

Positional and isotropic temperature factors for the S, C and N atoms were refined by full-matrix least-squares methods using unit weights, and layers were rescaled using the sums of observed and calculated structure factors. Anisotropic temperature factors were introduced for the S atoms, various weighting schemes were used and at  $R=13.8\%$  positions for the aromatic hydrogen atoms were calculated assuming a C-H bond length of 1.075 Å. These hydrogen atoms were included in the structure factor calculations, with isotropic temperature factors of  $B=7.0 \text{ \AA}^2$ . The hydrogen parameters were not refined, but after each cycle of refinement of the S, C and N atoms, new H positions were calculated. Anisotropic temperature factors were then introduced for the C atoms. The amino hydrogen atoms were located on a difference Fourier map, at approximately the right distance. These H atoms were included in the calculations with  $B=7.0 \text{ \AA}^2$ , but were not refined and finally the N atoms allowed to refine anisotropically. The weighting scheme used was

$$w = \{A + B|F_o| + C|F_o|^2\}^{-1}$$

with final values of  $A=1.0$ ,  $B=0.305$  and  $C=0.0$ . A difference map showed no unexplained features. The final value of  $R$  was 8.6% based on 1313 independent observed reflexions.

The final coordinates and their estimated standard deviations are given in Table 1, and the calculated hydrogen positions are given in Table 2. Anisotropic temperature factors given by the equation

$$TF = \exp \left[ -\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23}) \right]$$

are shown 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. *Calculated positions of hydrogen atoms*

	Bonded to	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(3)	C(3)	0.1087	0.8268	0.0811
H(4)	C(4)	0.2165	0.7895	-0.0166
H(5)	C(5)	0.3561	0.6263	-0.0370
H(6)	C(6)	0.4143	0.5121	0.0446
H(9)	C(9)	0.8982	0.2836	0.1640
H(10)	C(10)	1.0465	0.3807	0.0904
H(11)	C(11)	0.9554	0.5534	0.0631
H(12)	C(12)	0.7321	0.6303	0.1163
H(1)	N(1)	0.0342	0.7531	0.1762
H(1*)	N(1)	0.1400	0.6360	0.1912
H(2)	N(2)	0.7077	0.3572	0.2679
H(2*)	N(2)	0.5200	0.3636	0.2353

All hydrogen atoms were assumed to have an isotropic temperature factor  $B=7.00 \text{ \AA}^2$ .

Hydrogen atoms bonded to carbon were assumed to have a C-H bond length of 1.075 Å, whilst those bonded to nitrogen are in positions suggested by difference maps.

## Discussion

The atoms C(1), S(1), S(2), C(7) in the centre of the molecule adopt a skewed non-planar configuration like that found in  $\text{H}_2\text{O}_2$  (Abrahams, Collin & Lipscomb, 1951),  $\text{H}_2\text{S}_2$  (Wilson & Badger, 1949),  $(\text{CH}_3)_2\text{S}_2$  (Stevenson & Beach, 1938),  $(\text{C}_6\text{H}_5)_2\text{S}_2$  (Lee & Bryant, 1969a) and  $(\text{C}_6\text{H}_5, \text{CH}_2)_2\text{S}_2$  (Lee & Bryant, 1969b). A view of the structure is shown in Fig. 1. The bond lengths and angles together with their estimated standard deviations

are listed in Tables 6 and 7. Equations of the best least-squares planes through the benzene rings, and equations to the planes through the atoms C(1), S(1), S(2) and through S(1), S(2), C(7) have been calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) and are shown in Table 8. The benzene rings are inclined at an angle of 32.5 Å to each other.

The observed S-S bond length is 2.06 Å with a standard deviation of 0.003 Å. If the Pauling (1960) pure

single bond value for divalent sulphur of 2.08 Å and the double bond length of 1.88 Å are accepted, then this bond possesses 6% of double bond character. The observed value is 10 standard deviations longer than the value of 2.03 Å found in diphenyl disulphide (Lee & Bryant 1969a), and differs even more from the length 2.02 Å in dibenzyl disulphide (Lee & Bryant, 1969b). Hordvik (1966) suggests a relationship between the dihedral angle between the planes C(1), S(1), S(2) and

Table 3. Final temperature factor parameters

Table with 7 columns: Labels (S(1) to N(2)), B11, B22, B33, B12, B13, B23. Values range from 5.08 to 6.75 and -0.11 to -1.22.

Table 4. Observed and calculated structure factors

Large multi-column table of structure factors. Headers include h k l, Fo, Fc for multiple reflections. Data points are numerical values for observed and calculated intensities.

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>		
4 5 4	21.9	-22.3	4 10 14	8.8	-7.4	5 5 5	17.7	17.9	6 2 12	10.2	8.9	6 1 0	5.7	7.0	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 5	24.0	-24.4	4 10 16	5.5	3.8	5 5 6	13.5	-13.9	6 2 16	21.1	-15.4	6 2 0	20.9	20.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 6	11.4	15.6	4 11 4	9.1	24.6	5 5 7	13.4	-14.0	6 3 18	18.7	13.3	6 2 0	20.9	20.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 7	21.8	20.9	4 11 4	11.9	-10.0	5 5 8	11.4	9.6	6 2 22	9.5	-9.9	6 2 0	20.9	20.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 8	11.3	-13.5	4 11 5	7.4	-6.3	5 5 9	24.2	-24.6	6 2 26	7.8	-6.9	6 2 0	20.9	20.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 9	10.2	10.8	4 11 6	9.5	8.8	5 5 10	1.5	0.9	6 3 3	11.8	-11.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 10	17.7	-9.9	4 11 7	11.0	9.0	5 5 11	14.0	13.4	6 3 7	17.4	17.6	2 0 0	210.1	-212.7	2 0 0	210.1	-212.7	2 0 0	210.1	-212.7	
4 5 11	21.0	-23.8	4 11 8	11.7	-11.5	5 5 12	6.4	5.5	6 3 11	21.4	22.0	2 0 0	210.1	-212.7	2 0 0	210.1	-212.7	2 0 0	210.1	-212.7	
4 5 12	15.4	-16.2	4 11 11	13.5	-11.2	5 5 13	24.4	27.2	6 3 15	3.0	-3.2	6 2 0	20.9	20.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 13	10.5	13.1	4 11 12	13.7	17.0	5 5 14	17.2	-21.8	6 3 19	6.2	-6.9	6 2 0	20.9	20.8	6 2 0	20.9	20.8	6 2 0	20.9	20.8	
4 5 14	8.3	-6.4	4 11 13	6.7	6.3	5 5 15	8.3	5.1	6 3 23	14.8	-17.6	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	
4 5 15	12.9	13.1	4 11 14	7.9	-7.3	5 5 16	2.2	22.9	6 3 27	13.1	-15.1	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	
4 5 16	5.8	-5.2	4 11 17	9.0	-6.2	5 5 17	28.5	-21.4	6 3 31	12.7	-9.1	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	
4 5 17	7.4	-7.2	4 11 18	5.3	5.1	5 5 18	8.1	6.1	6 3 35	12.8	11.8	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	1 0 4	80.4	-81.4	
4 6 1	8.7	-6.2	4 12 1	18.3	14.1	5 5 19	3.9	5.3	6 4 3	19.2	-22.3	2 0 18	19.7	21.4	2 0 18	19.7	21.4	2 0 18	19.7	21.4	
4 6 2	29.2	20.3	4 12 3	10.9	-9.7	5 5 20	18.2	-18.3	6 4 7	13.4	13.4	1 0 14	22.5	-23.1	1 0 14	22.5	-23.1	1 0 14	22.5	-23.1	
4 6 3	10.8	10.4	4 12 6	8.7	8.0	5 5 21	8.2	-5.9	6 4 11	5.8	-4.9	1 0 14	19.3	18.2	1 0 14	19.3	18.2	1 0 14	19.3	18.2	
4 6 4	15.8	-7.7	4 12 7	7.4	7.8	5 5 22	8.8	8.1	6 4 15	19.7	-21.4	1 0 26	7.0	-6.8	1 0 26	7.0	-6.8	1 0 26	7.0	-6.8	
4 6 5	9.2	-9.8	4 12 11	9.2	8.6	5 5 23	11.0	-9.8	6 4 19	2.3	-1.4	1 0 20	21.7	-23.4	1 0 20	21.7	-23.4	1 0 20	21.7	-23.4	
4 6 6	10.7	-11.4	4 12 12	8.2	-5.2	5 5 24	8.5	-6.5	6 4 23	1.7	-1.4	1 0 26	7.0	-6.8	1 0 26	7.0	-6.8	1 0 26	7.0	-6.8	
4 6 7	2.5	1.4	4 12 4	11.0	-10.3	5 5 25	13.3	-14.2	6 4 27	22.8	-26.0	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	
4 6 8	9.2	6.5	4 12 5	6.6	5.3	5 5 26	16.1	-19.1	6 4 31	8.3	8.8	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	
4 6 9	16.8	-18.9	4 12 6	11.8	10.7	5 5 27	11.1	20.1	6 4 35	9.5	-9.7	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	
4 6 10	27.2	-29.6	4 12 7	6.4	4.8	5 5 28	2.2	-7.1	6 4 39	9.5	-9.7	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	2 0 2	77.6	-66.5	
4 6 11	5.2	3.8	4 12 10	14.0	-15.0	5 5 29	20.2	-19.3	6 4 43	24.4	24.6	2 0 12	68.5	71.5	2 0 12	68.5	71.5	2 0 12	68.5	71.5	
4 6 12	19.6	21.2	4 12 12	8.1	8.9	5 5 30	17.8	17.5	6 4 47	9.6	-8.9	2 0 12	68.5	71.5	2 0 12	68.5	71.5	2 0 12	68.5	71.5	
4 6 13	1.4	-3.0	4 12 14	8.9	-9.3	5 5 31	6.1	-1.6	6 4 51	10.4	9.8	2 0 14	21.1	25.0	2 0 14	21.1	25.0	2 0 14	21.1	25.0	
4 6 14	9.7	-9.1	4 14 1	10.7	8.9	5 5 32	24.5	-26.0	6 4 55	10.4	9.8	2 0 14	21.1	25.0	2 0 14	21.1	25.0	2 0 14	21.1	25.0	
4 6 15	8.1	9.0	4 15 1	4.4	3.4	5 5 33	31.5	34.0	6 4 59	13.7	-11.3	2 0 18	30.9	-27.7	2 0 18	30.9	-27.7	2 0 18	30.9	-27.7	
4 6 16	3.2	-8.0	4 15 3	14.4	-16.4	5 5 34	19.9	-20.9	6 4 63	3.2	-3.6	2 0 20	23.9	32.0	2 0 20	23.9	32.0	2 0 20	23.9	32.0	
4 6 17	9.2	6.3	4 15 4	4.3	-3.4	5 5 35	13.2	13.7	6 4 67	17.5	18.6	2 0 24	8.1	-7.5	2 0 24	8.1	-7.5	2 0 24	8.1	-7.5	
4 6 18	3.8	6.8	4 15 6	13.2	-14.8	5 5 36	11.8	11.3	6 4 71	11.4	-10.7	3 0 6	8.4	-6.6	3 0 6	8.4	-6.6	3 0 6	8.4	-6.6	
4 6 19	5.6	-0.6	4 15 7	6.1	6.8	5 5 37	11.1	11.3	6 4 75	9.4	-6.2	3 0 6	8.4	-6.6	3 0 6	8.4	-6.6	3 0 6	8.4	-6.6	
4 7 1	9.4	7.4	5 0 4	37.6	-34.9	5 5 38	9.2	-9.4	6 4 79	11.6	12.6	3 0 6	8.4	-6.6	3 0 6	8.4	-6.6	3 0 6	8.4	-6.6	
4 7 2	10.6	-9.9	5 0 5	96.2	-87.7	5 5 39	3.2	3.8	6 4 83	18.0	17.7	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	
4 7 3	37.3	37.6	5 0 6	12.2	-10.3	5 5 40	14.1	-12.8	6 4 87	11.6	12.6	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	
4 7 4	13.6	15.1	5 0 7	24.1	23.3	5 5 41	9.0	5.8	6 4 91	5.7	-5.7	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	
4 7 5	13.6	14.1	5 0 8	14.3	15.2	5 5 42	14.0	-13.4	6 4 95	2.3	3.2	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	3 0 8	28.3	-26.2	
4 7 6	16.1	-16.3	5 0 9	11.4	7.3	-6.2	5 5 43	18.1	18.1	6 4 99	7.5	8.1	4 0 4	11.4	13.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2
4 7 7	18.8	19.7	5 0 10	17.9	20.8	5 5 44	8.2	8.1	6 4 103	2.7	2.7	4 0 4	11.4	13.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	
4 7 8	9.7	-10.7	5 0 11	17.9	20.8	5 5 45	8.2	8.1	6 4 107	9.7	10.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	
4 7 9	11.2	-23.7	5 0 12	16.7	-18.4	5 5 46	10.1	-10.4	6 4 111	9.7	10.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	
4 7 10	12.2	16.4	5 0 13	16.7	-18.4	5 5 47	10.1	-10.4	6 4 115	9.7	10.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	
4 7 11	23.0	26.4	5 0 14	20.8	-21.7	5 5 48	10.1	-10.4	6 4 119	9.7	10.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	
4 7 12	8.4	8.2	5 0 15	21.7	36.8	5 5 49	13.0	12.1	6 4 123	9.7	10.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	4 0 4	11.4	13.2	
4 7 13	12.2	12.3	5 0 16	16.4	-14.8	5 5 50	13.7	-12.7	6 4 127	14.7	14.9	4 0 22	18.6	-18.6	4 0 22	18.6	-18.6	4 0 22	18.6	-18.6	
4 7 14	4.8	-5.8	5 0 17	3.6	-4.1	5 5 51	14.1	-16.5	6 4 131	13.1	11.1	5 0 4	33.8	-24.9	5 0 4	33.8	-24.9	5 0 4	33.8	-24.9	
4 7 15	20.7	-22.0	5 0 18	20.7	-22.0	5 5 52	14.1	-16.5	6 4 135	13.1	11.1	5 0 4	33.8	-24.9	5 0 4	33.8	-24.9	5 0 4	33.8	-24.9	
4 7 16	22.9	23.0	5 0 19	16.9	-16.0	5 5 53	29.9	-32.0	6 4 139	6.2	-6.5	5 0 8	4.0	3.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	
4 7 17	13.1	14.2	5 0 20	11.1	9.7	5 5 54	30.5	-33.9	6 4 143	3.4	5.3	5 0 8	4.0	3.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	
4 7 18	11.4	-11.9	5 0 21	22.8	22.9	5 5 55	34.2	-34.9	6 4 147	6.2	-6.5	5 0 8	4.0	3.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	
4 7 19	15.5	-16.2	5 0 22	28.7	-29.2	5 5 56	15.3	-14.8	6 4 151	17.9	18.3	5 0 8	4.0	3.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	
4 7 20	6.0	5.1	5 0 23	32.1	-37.0	5 5 57	18.8	18.9	6 4 155	14.7	16.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	
4 7 21	11.3	12.3	5 0 24	3.4	4.0	5 5 58	7.8	8.6	6 4 159	14.7	16.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	
4 7 22	10.6	8.6	5 0 25	11.5	10.8	5 5 59	22.5	-16.8	6 4 163	11.7	-11.6	5 0 8	4.0	3.0	5 0 8	4.0	3.0	5 0 8	4.0	3.0	
4 7 23	12.6	-12.6	5 0 26	17.2	-17.8	5 5 60	24.7	21.5	6 4 167	7.4	5.8	6 0 4	8.8	9.1	6 0 4	8.8	9.1	6 0 4	8.8	9.1	
4 7 24	6.5	5.9	5 0 27	18.7	18.6	5 5 61	6.7	-6.2	6 4 171	11.7	11.6	6 0 4	8.8	9.1	6 0 4	8.8	9.1	6 0 4	8.8	9.1	
4 7 25	12.9	-7.6	5 0 28	21.7	-21.7	5 5 62	9.3	11.5	6 4 175	14.0	-12.3	6 0 8	33.2	-24.8	6 0 8	33.2	-24.8	6 0 8	33.2	-24.8	
4 7 26	3.4	3.4	5 0 29	11.3	-8.1	5 5 63	1.1	5.4	6 4 179	9.0	7.9	6 0 8	33.2	-24.8	6 0 8	33.2	-24.8	6 0 8	33.2	-24.8	
4 7 27	9.6	-6.8	5 0 30	8.3	3.4	5 5 64	15.2	-18.5	6 4 183	9.8	-9.7	6 0 8	33.2	-24.8	6 0 8	33.2	-24.8	6 0 8	33.2	-24.8	

Table 6. Bond lengths and their standard deviations

	Distance	$\sigma$
S(1)—S(2)	2.06 Å	0.003 Å
S(1)—C(1)	1.77	0.006
S(2)—C(7)	1.75	0.007
C(1)—C(2)	1.40	0.009
C(2)—C(3)	1.39	0.010
C(3)—C(4)	1.38	0.012
C(4)—C(5)	1.40	0.014
C(5)—C(6)	1.36	0.011
C(6)—C(1)	1.38	0.009
C(7)—C(8)	1.40	0.010
C(8)—C(9)	1.37	0.012
C(9)—C(10)	1.37	0.015
C(10)—C(11)	1.39	0.018
C(11)—C(12)	1.35	0.013
C(12)—C(7)	1.38	0.010
C(2)—N(1)	1.40	0.008
C(8)—N(2)	1.42	0.010

Table 7. Bond angles and their standard deviations

	Angle	$\sigma$
C(1)—S(1)—S(2)	103.2°	0.2°
C(7)—S(2)—S(1)	103.5	0.2
S(1)—C(1)—C(2)	119.5	0.5
S(1)—C(1)—C(6)	119.3	0.5
C(2)—C(1)—C(6)	121.1	0.6
S(2)—C(7)—C(8)	121.2	0.5
S(2)—C(7)—C(12)	119.5	0.6
C(8)—C(7)—C(12)	119.2	0.7
C(1)—C(2)—C(3)	117.5	0.6
C(1)—C(2)—N(1)	121.9	0.6
C(3)—C(2)—N(1)	120.6	0.6
C(7)—C(8)—C(9)	118.6	0.7
C(7)—C(8)—N(2)	119.3	0.7
C(9)—C(8)—N(2)	122.0	0.7
C(2)—C(3)—C(4)	120.2	0.7
C(3)—C(4)—C(5)	121.4	0.8
C(4)—C(5)—C(6)	118.2	0.7
C(1)—C(6)—C(5)	121.5	0.7
C(8)—C(9)—C(10)	121.1	0.9
C(9)—C(10)—C(11)	120.4	0.9
C(10)—C(11)—C(12)	118.8	0.9
C(7)—C(12)—C(11)	121.9	0.8

The observed C—S distances of 1.77 and 1.75 Å (standard deviations 0.006 and 0.007 Å respectively) are significantly shorter than the values of 1.81 and 1.79 Å in diphenyl disulphide (Lee & Bryant 1969a), the average value of 1.812 Å obtained by Cox & Jeffrey (1951) as the mean of 11 molecules containing a single bond, 1.81 (5) Å (Sutton 1958) and 1.85 and 1.84 Å in dibenzyl disulphide (Lee & Bryant 1969b).

The shorter C—S bonds and longer S—S bond length in 2,2'-diaminodiphenyl disulphide compared with diphenyl disulphide may be explained by the amino groups releasing electrons into the aromatic rings. This would favour the donation of electrons from the ring to the sulphur atom, a  $p\pi-d\pi$  interaction between the full  $p_z$  orbital on the carbon atom (part of the aromatic  $\pi$  cloud) with an empty  $d$  orbital on the sulphur atom. The consequent build up of negative charge on the sulphur atoms would result in a lengthening of the S—S bond. One of three favourable positions for  $p\pi-d\pi$  overlap occurs when the carbon  $p_z$  orbital lies in the same plane as the carbon and two sulphur atoms, that is the planes through C(1), S(1), S(2) and the ring C(1)—C(6) should be perpendicular to one another, and similarly for C(7), S(1), S(2) and the ring C(7)—C(12). These angles are 83.6° and 83.4° respectively in the diamino compound compared with 0.2° and 17.7° in the diphenyl disulphide, showing the possibility of such overlap in the diamino compound. It is interesting that whilst  $p\pi-d\pi$  bonding has been reported (Cruickshank, 1961) for sulphur and phosphorus in their highest oxidation states S(VI) and P(V), the above explanation involves S(II).

The bond angles C(1)—S(1)—S(2) and C(7)—S(2)—S(1) are 103.2° and 103.5° respectively. The outer orbitals on S(1) and S(2) are roughly  $sp^3$  hybridized, the distortion arising because repulsion between the lone pairs of electrons exceeds that between the bonding pairs of electrons. The corresponding angles in diphenyl disul-

Table 8. Equations to planes

Atoms in plane	Equation
C(1), S(1), S(2)	$-4.66X + 7.22Y + 13.98Z = 4.50$
C(7), S(1), S(2)	$-0.48X - 10.22Y + 14.26Z = -3.03$

Angle between above two planes = 90.5°

Atoms in plane	Equation
C(1), C(2), C(3), C(4), C(5), C(6)	$7.08X + 6.15Y + 4.43Z = 6.26$
C(7), C(8), C(9), C(10), C(11), C(12)	$5.13X + 4.77Y + 15.74Z = 8.57$

Angle between above two planes = 32.5°

Distance of atoms from planes			
	Distance from plane		Distance from plane
C(1)	-0.000 Å	C(7)	0.002 Å
C(2)	-0.003	C(8)	-0.003
C(3)	0.011	C(9)	0.007
C(4)	-0.016	C(10)	-0.010
C(5)	0.013	C(11)	0.009
C(6)	-0.005	C(12)	-0.005

$X, Y, Z$  refer to the real unit-cell axes.

Table 9. *Intramolecular contacts of less than 3.0 Å between atoms which are not directly bonded.*

(H atoms excluded)	
S(1)····C(2)	2.74 Å
S(1)····C(6)	2.72
S(2)····C(8)	2.75
S(2)····C(12)	2.71
C(1)····C(3)	2.39
C(1)····C(4)	2.74
C(1)····C(5)	2.39
C(1)····N(1)	2.45
C(2)····C(4)	2.41
C(2)····C(5)	2.81
C(2)····C(6)	2.42
C(3)····C(5)	2.42
C(3)····C(6)	2.76
C(3)····N(1)	2.42
C(4)····C(6)	2.36
C(7)····C(9)	2.38
C(7)····C(10)	2.75
C(7)····C(11)	2.39
C(7)····N(2)	2.44
C(8)····C(10)	2.39
C(8)····C(11)	2.78
C(8)····C(12)	2.40
C(9)····C(11)	2.39
C(9)····C(12)	2.73
C(9)····N(2)	2.44
C(10)····C(12)	2.36

phide are 105.8° and 106.5°. The smaller bond angles in the diamino compound are associated with an angle of 32.5° between the planes of the benzene rings compared with 77.3° in diphenyl disulphide. The smaller interplanar angle allows the rings to pack more easily without causing close approaches, and minimizes repulsions between the atoms S(1)···C(2) and S(2)···C(12). Repulsions of this sort were significant in diphenyl disulphide, but are not in the diamino compound. These factors give rise to the more distorted, that is smaller, bond angles at S(1) and S(2) in the diamino compound.

The sums of the three angles round C(1) and C(7) are both 359.9°, in accord with a planar structure and *sp*<sup>2</sup> hybridization. The range of bond lengths in the benzene rings is 1.35 to 1.40 Å, and the rings are planar to within 0.016 Å. (Table 8). The nitrogen atoms are coplanar with their respective rings, and the sums of the three angles round C(2) and C(8) are 360.0 and 359.9° respectively. The C–N bond lengths of 1.40 and 1.42 Å may be compared with the value of 1.43 Å in acetanilide (Brown & Corbridge, 1954).

Intramolecular contacts of less than 3Å between atoms which are not directly bonded are given in Table 9. (Hydrogen contacts are excluded.) These are unavoidable

Table 10. *Intermolecular contacts less than 3.0 Å*

	Distance	Symmetry operation applied to second atom		Distance	Symmetry operation applied to second atom
S(2)····H(1*)	2.68 Å	(1)	H(9)····H(2*)	2.73 Å	(1)
C(9)····H(2*)	2.83	(1)	H(2)····H(2*)	2.57	(1)
H(1)····N(2)	2.24	(7)	H(5)····H(3)	2.40	(9)
C(3)····H(10)	2.81	(3)	H(12)····H(4)	2.50	(9)
N(2)····H(1)	2.24	(8)	H(12)····H(9)	2.52	(3)
H(10)····C(3)	2.81	(5)	H(1)····H(2*)	2.03	(7)
H(1*)····S(2)	2.68	(6)	H(3)····H(10)	2.92	(3)
H(2*)····C(9)	2.83	(6)	H(10)····H(3)	2.92	(5)
N(1)····H(2*)	2.75	(7)	H(9)····H(12)	2.52	(5)
H(2*)····N(1)	2.75	(8)	H(2*)····H(1)	2.03	(8)
H(2)····S(1)	2.70	(1)	H(2*)····H(9)	2.73	(6)
N(1)····H(2)	2.55	(2)	H(2*)····H(2)	2.57	(6)
H(2)····N(1)	2.55	(4)	H(3)····H(5)	2.40	(10)
S(1)····H(2)	2.70	(6)	H(4)····H(12)	2.50	(10)
H(1)····C(8)	2.95	(7)	H(6)····H(5)	2.63	(11)
C(8)····H(1)	2.95	(8)	H(5)····H(6)	2.63	(11)
H(1)····H(2)	2.83	(2)	H(6)····H(6)	2.50	(11)
H(2)····H(1)	2.83	(4)	H(3)····H(6)	2.57	(7)
			H(6)····H(3)	2.57	(8)

Intermolecular contacts between 3.0–3.5 Å (excluding H atoms)

C(11)····C(1)	3.49 Å	(12)	N(1)····S(2)	3.48 Å	(6)
S(2)····N(1)	3.48	(1)	N(2)····N(1)	3.19	(8)
N(1)····N(2)	3.27	(2)	N(1)····N(2)	3.19	(7)
N(2)····N(1)	3.27	(4)	C(1)····C(11)	3.49	(13)

## Key to symmetry operations

(1)	$x + \frac{1}{2}$	$y$	$\frac{1}{2} - z$	(9)	$x + \frac{1}{2}$	$1\frac{1}{2} - y$	$-z$
(2)	$1 - x$	$y + \frac{1}{2}$	$\frac{1}{2} - z$	(10)	$x - \frac{1}{2}$	$1\frac{1}{2} - y$	$-z$
(3)	$1\frac{1}{2} - x$	$y + \frac{1}{2}$	$z$	(11)	$1 - x$	$1 - y$	$-z$
(4)	$1 - x$	$y - \frac{1}{2}$	$\frac{1}{2} - z$	(12)	$1 + x$	$y$	$z$
(5)	$1\frac{1}{2} - x$	$y - \frac{1}{2}$	$z$	(13)	$x - 1$	$y$	$z$
(6)	$x - \frac{1}{2}$	$y$	$\frac{1}{2} - z$				
(7)	$\frac{1}{2} - x$	$y + \frac{1}{2}$	$z$				
(8)	$\frac{1}{2} - x$	$y - \frac{1}{2}$	$z$				

able contacts such as distances across benzene rings, and show no special features.

Two intramolecular contacts with hydrogen atoms are of interest. The distance between S(1)···H(1\*) of 2.29 Å is very short and indicates a strong intramolecular hydrogen bond. The N–H···S bond angle is 124°. Hydrogen bonding of this sort would remove some negative charge from the sulphur atom. By analogy with the shortening of the O–O bond in F<sub>2</sub>O<sub>2</sub> compared with H<sub>2</sub>O<sub>2</sub> arising because the fluorine atoms tend to withdraw electrons from the filled *anti*-bonding  $\pi$  orbitals, the hydrogen bond in this case would be expected to result in a slight shortening of the S–S bond. The contact between S(2)···H(2\*) is 2.67 Å, which is slightly short and may indicate a weak hydrogen bond. Neutron diffraction data are really needed to obtain the hydrogen positions more accurately.

All the intermolecular distances less than 3.0 Å are listed in Table 10. These all involve hydrogen atoms. There are only two H···H contacts less than 2.40 Å, the value suggested by Pauling's (1960) van der Waals radius of 1.20 Å for hydrogen. The closest C···H contacts are 2.81 Å, close to the sum of Pauling's van der Waals radii for C and H (1.70 + 1.20 Å). The H(1)···N(2) approach of 2.24 Å is appreciably shorter than the sum of Pauling's van der Waals radii for N and H (1.50 + 1.20 Å). This suggests that hydrogen bonding occurs between amino groups in adjacent molecules, to give an infinite chain of molecules hydrogen bonded together. This gives an N···H···N angle of 146° and a N···N intermolecular approach of 3.19 Å. The contact between S(2)···H(1\*) (an amino hydrogen atom) is 2.68 Å. Taking the Pauling (1960) van der Waals radius for S of 1.85 Å, this contact is very short. It has recently been suggested that the van der Waals radius for S should be 1.72 to 1.73 Å (Lee & Bryant, 1969*b*), but even with this value, the contact is slightly short. Since hydrogen bonding would involve N···H···S bonds bent to 111°, and the H···S distance is 2.68 Å, this possibility is precluded.

Intermolecular contacts between 3.0 and 3.5 Å are also given in Table 10 for the S, C and N atoms. These distances are all normal.

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