The Crystal and Molecular Structure of Dibenzyl Disulphide. The Refinement of a Structure with High Correlation Coefficients

BY J. D. LEE AND M. W. R. BRYANT

Department of Chemistry, University of Technology, Loughborough, Leicestershire, England

The crystal structure of dibenzyl disulphide, $C_6H_5-CH_2-S-S-CH_2-C_6H_5$, has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic and belong to the space group Cc. The unit cell has dimensions $a=13\cdot46$, $b=8\cdot23$, $c=11\cdot29$ Å, $\alpha=\gamma=90°$, $\beta=99°30'$, and contains four molecules. Difficulty was experienced because of a very strong tendency to twinning of the crystals, often only detected on high-layer line photographs. Positional and temperature factor parameters for sulphur and carbon atoms have been refined by Fourier, block-diagonal least squares and finally by full-matrix least squares. Refinement was unusually difficult because of large correlation coefficients between parameters, associated with a pseudo twofold axis of symmetry in the molecule. In the final stages, hydrogen atoms were included in fixed positions. The final R value based on 867 independent observed reflexions was $7\cdot9\%$. The precise chemical nature of the S–S bond is examined.

Experimental

A sample of dibenzyl disulphide was recrystallized from ethanol and gave colourless plate-like crystals, which showed straight extinction parallel to the plate edges when viewed under the polarizing microscope. The density of the crystals was measured by the method of flotation in aqueous solutions of potassium iodide and found to be $1\cdot28$ g.cm^{-3}.

Considerable difficulty was experienced in selecting a suitable crystal for X-ray analysis since many crystals which appeared suitable after optical and preliminary X-ray examination proved to be twinned when high layer line Weissenberg photographs were taken. A single crystal of dimensions $0\cdot025 \times 0\cdot025 \times 0\cdot015$ cm was eventually used for X-ray analysis, and three-dimensional equi-inclination Weissenberg data were collected for the $hk0$, $hk1\ldots hk8$, $h0l$ and $h1l$ zones. The intensities of 867 independent reflexions were collected photographically, measured visually and converted to $|F|^2$ and $|F|$ by applying Lorentz and polarization corrections. In view of the small crystal size and the low absorption coefficient, corrections for absorption were considered unnecessary. No correction was made for extinction. Reflexions too weak to be observed were ignored.

Crystal data

$(C_6H_5 \cdot CH_2)_2S_2$, $M = 246\cdot3$.
Monoclinic, $a = 13\cdot46$, $b = 8\cdot23$, $c = 11\cdot29$ Å, all $\pm 0\cdot02$ Å
$\qquad \alpha = \gamma = 90°$, $\beta = 99°30' \pm 30'$.
$U = 1233\cdot5$ Å^3, $Z = 4$, $D_m = 1\cdot28$ g.cm^{-3}, $D_c = 1\cdot32$ g.cm^{-3}
$F_{000} = 520$, Cu $K\alpha$, $\lambda = 1\cdot542$ Å, $\mu = 36$ cm^{-1} .
Absent reflexions: hkl when $h+k$ is odd, $h0l$ when l is odd (and when h is odd), $0k0$ when k is odd.
These absences restrict the space group to Cc or $C2/c$, but the former was confirmed by the pyroelectric test, the statistical test and by the structure refinement.

Structure analysis

There are four molecules in the unit cell, and for the space group Cc these must occupy the general positions (x,y,z); $(x, -y, \frac{1}{2}+z)$; $(\frac{1}{2}+x, \frac{1}{2}+y, z)$ and $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$. Patterson summations were performed with $hk0$ and $h0l$ data, but these were not interpreted in terms of a satisfactory trial structure because of the diffuse nature of the peaks. The corresponding sharpened $hk0$ Patterson projection (corrected for point sulphur atoms at rest) indicated the orientation and position of the sulphur atoms and the benzene rings. An $h0l$ Fourier synthesis based on phases obtained for the sulphur atoms only indicated the positions of the fourteen carbon atoms. Structure factor calculations were performed with the scattering factors due to Hanson, Herman, Lea & Skillman (1964), and by Fourier techniques the agreement values R were reduced to 19% for 71 $hk0$ reflexions and 20% for 93 $h0l$ reflexions.

Least-squares refinement of positional and isotropic temperature factors was commenced with three-dimensional data and a block-diagonal least-squares program written by G. S. D. King (Union Carbide, European Research Associates, Brussels) for the IBM 1620 computer. Reflexions were put on a common scale by means of spots common to more than one layer, and with unit weights the R value reduced to 20% after 6 cycles. Rescaling of layers from the sums of observed and calculated structure factors, the introduction of various weighting schemes and 6 further cycles of refinement reduced R to 14%.

Subsequent refinement was performed on the S. R. C. Chilton Atlas computer, using the X-ray 63 system of Professor J. M. Stewart as adapted by Dr J. C. Baldwin. On attempting full-matrix least-squares refinement of the atomic parameters, a singular matrix was obtained without any zero diagonal elements. The origin for the space group Cc is defined as anywhere in the xz plane.

Refinement of all the atomic positions would allow the whole molecule to move throughout the cell. This was overcome by fixing the x and z coordinates of one atom, S(1), thus defining the origin. The scattering factors for sulphur were corrected for both the real and imaginary parts of anomalous dispersion (Dauben & Templeton, 1955). Inter-layer scale factors were refined initially while all the atoms were isotropic, but when anisotropic temperature factors were introduced for sulphur this was discontinued. Weighting schemes were chosen from a careful analysis of the structure factors. Refinement stopped at $R=12.9\%$, after 12 cycles of full-matrix least-squares refinement.

It was observed that though the R value did not change, there were severe oscillations in parameters from one cycle to the next, particularly the temperature factors. In addition there were several improbable bond lengths, the most extreme being a distance of 1·1 Å in one benzene ring and 1·7 Å in the other ring. The correlation matrix, which gives a good indication of the interdependence of parameters during the course of refinement was examined. Taking an arbitrary value of 0·3 as indicating a strong degree of correlation it was found that the x, y and z parameters and the temperature factors for S(1) were strongly correlated

to the corresponding x, y, z and temperature factor terms for S(2). A similar correlation was found between the parameters in pairs of atoms C(1)–C(8), C(2)–C(9), C(3)–C(10), C(4)–C(11), C(5)–C(12), C(6)–C(13), C(7)–C(14). Very few of the other correlations were above 0·1.

Examination of the atomic coordinates showed that the atoms S(1), C(1)–C(7) were very nearly related to the atoms S(2), C(8)–C(14) by a twofold axis of symmetry. If this symmetry element is really present then the space group should be $C2/c$. Average value of the coordinates and temperature factors for the atoms in the two halves of the molecule were used in a structure factor calculation for space group $C2/c$. The R value was 17%, but attempts to refine the parameters by least-squares resulted in divergence. It was concluded that there was nearly, but not quite, a twofold axis, and attempts to use the space group $C2/c$ were abandoned.

Refinement was continued with the original space group Cc. Next an attempt was made to refine a disordered model by calculations based on half an atom at each of the positions, and half an atom at positions related to these by a twofold axis. The agreement factor was worse, and the structure still would not refine, so

Table 1. *Final coordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
S(1)	0·0032	0·0112	0·0890	0·0003	0·0005	0·0003
S(2)	−0·0047	0·0106	−0·0912	0·0003	0·0005	0·0003
C(1)	0·1030	0·1605	0·1398	0·0009	0·0018	0·0010
C(2)	0·2065	0·1026	0·1330	0·0009	0·0016	0·0011
C(3)	0·2545	−0·0157	0·2388	0·0012	0·0015	0·0011
C(4)	0·3491	−0·0662	0·2040	0·0010	0·0017	0·0013
C(5)	0·3994	0·0029	0·1230	0·0012	0·0020	0·0015
C(6)	0·3563	0·1219	0·0480	0·0010	0·0017	0·0012
C(7)	0·2577	0·1720	0·0522	0·0008	0·0014	0·0010
C(8)	−0·1029	0·1645	−0·1414	0·0011	0·0019	0·0014
C(9)	−0·2068	0·1048	−0·1313	0·0011	0·0018	0·0014
C(10)	−0·2537	−0·0155	−0·2131	0·0011	0·0015	0·0011
C(11)	−0·3508	−0·0617	−0·2040	0·0011	0·0021	0·0012
C(12)	−0·4064	0·0079	−0·1225	0·0010	0·0014	0·0011
C(13)	−0·3589	0·1226	−0·0461	0·0012	0·0023	0·0014
C(14)	−0·2620	0·1722	−0·0548	0·0012	0·0019	0·0012

Table 2. *Final temperature factor parameters*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	3·57	5·77	4·22	−1·66	0·84	0·84
S(2)	3·92	4·68	3·80	−0·67	1·11	−0·21
C(1)	3·15	4·09	4·16	0·45	0·96	−0·28
C(2)	3·38	3·83	4·45	0·08	0·63	−0·07
C(3)	4·45	3·36	4·01	−0·44	0·09	0·18
C(4)	4·15	3·30	4·66	0·10	−0·17	−0·07
C(5)	4·68	5·62	5·05	−0·08	−0·21	−0·53
C(6)	3·91	4·21	4·13	−0·57	0·91	−0·16
C(7)	2·82	3·35	3·14	−0·21	0·50	0·27
C(8)	4·94	4·84	4·81	0·02	0·60	0·02
C(9)	3·20	2·91	2·29	−0·14	0·10	0·34
C(10)	3·97	3·63	3·52	−0·08	0·56	−0·30
C(11)	4·04	4·45	4·61	−0·26	0·04	−0·09
C(12)	3·37	3·49	3·94	−0·17	0·22	0·51
C(13)	5·12	6·10	5·46	0·24	0·84	−0·21
C(14)	4·87	4·59	4·57	−0·11	0·61	−0·44

work on the original ordered structure was continued. To prevent an increase in a parameter in one half of the molecule being compensated by a decrease in the corresponding parameter in the other half of the molecule, it was decided to refine the atoms S(1), C(1)–C(7) in one cycle keeping S(2), C(8)–C(14) fixed, and to refine S(2), C(8)–C(14) in the next cycle keeping S(1), C(1)–C(7) fixed. The weighting scheme was re-examined every second cycle. It was thought that a small number of reflexions with unusually large $w\Delta F$ values might dominate the matrix, and these were excluded from the matrix, but not from the calculation of R. It was found that the predicted shifts were in fact over correcting, so half shifts were applied. By these means the R value gradually fell, and the shape of the molecule became much more reasonable. Hydrogen atoms were included in fixed positions at a distance of 1·075 Å from the carbon atoms to which they are bonded. The carbon atoms were then allowed to refine, and new hydrogen positions calculated. In the last stages the
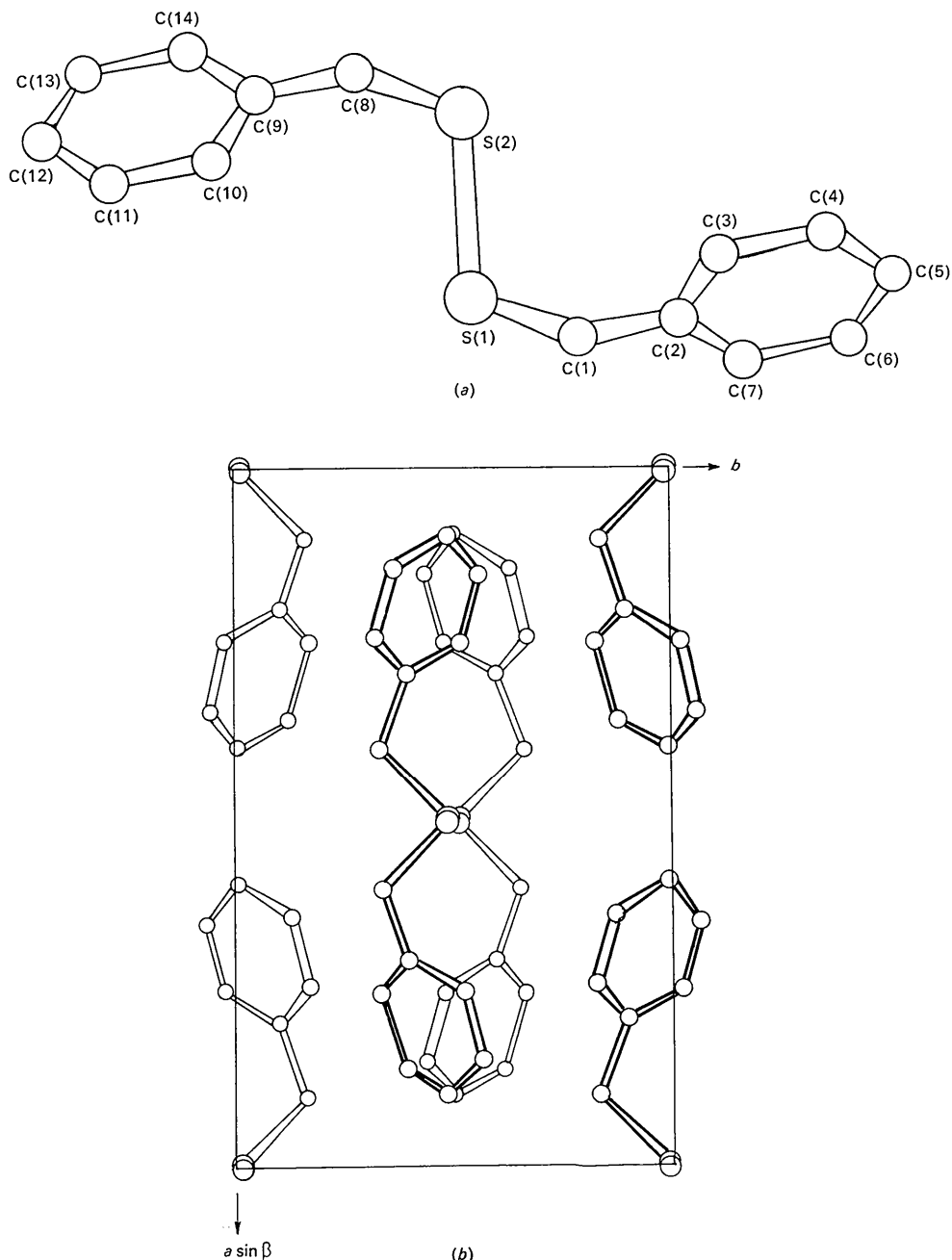

Fig. 1. (a) A view of the molecule, (b) the contents of the unit cell as seen down the c axis.

Table 3. *Calculated positions of hydrogen atoms*

	Bonded to	x/a	y/b	z/c
H(1)	C(1)	0·0886	0·2672	0·0848
H(1*)	C(1)	0·0997	0·1911	0·2316
H(3)	C(3)	0·2148	−0·0695	0·2742
H(4)	C(4)	0·3838	−0·1596	0·2635
H(5)	C(5)	0·4747	−0·0367	0·1177
H(6)	C(6)	0·3981	0·1775	−0·0145
H(7)	C(7)	0·2228	0·2644	−0·0080
H(8)	C(8)	−0·0871	0·2714	−0·0868
H(8*)	C(8)	−0·1008	0·1944	−0·2336
H(10)	C(10)	−0·2148	−0·0682	−0·2795
H(11)	C(11)	−0·3855	−0·1560	−0·2625
H(12)	C(12)	−0·4830	−0·0274	−0·1203

Table 3 (*cont.*)

	Bonded to	x/a	y/b	z/c
H(13)	C(13)	−0·3969	0·1748	0·0214
H(14)	C(14)	−0·2292	0·2693	0·0024

All hydrogen atoms were assumed to have an isotropic temperature factor $B = 5·00$ Å^2, and to have a C–H bond length of 1·075 Å.

carbon atoms were refined anisotropically but this only reduced R by 1%.

The weighting scheme used was of the Cruickshank (1961) type,

Table 4. *Observed and calculated structure amplitudes*

h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc
4	0	0	62.6	61.0		10	0	-8	14.7	15.3		5	7	0	18.7	18.1		2	6	2	8.6	9.2		14	4	4	7.6	8.3
6	0	0	17.1	17.5		12	0	-8	12.4	12.7		7	7	0	23.5	20.8		6	6	2	21.9	21.1		1	5	4	6.9	8.1
8	0	0	77.4	93.7		14	0	-8	8.8	8.5		9	7	0	8.7	9.1		8	6	2	5.7	5.5		3	5	4	25.9	29.4
10	0	0	36.3	33.6		0	0	-10	15.2	13.7		11	7	0	8.4	9.4		3	7	2	8.1	8.0		5	5	4	16.6	17.6
12	0	0	38.0	34.6		2	0	-10	25.2	24.0		0	8	0	20.5	19.4		7	7	2	8.6	7.6		7	5	4	27.1	25.8
14	0	0	15.8	15.8		4	0	-10	16.6	17.0		2	8	0	13.2	13.1		9	7	2	6.5	6.0		9	5	4	7.3	7.1
16	0	0	7.5	7.6		6	0	-10	31.8	29.7		4	8	0	15.1	13.9		2	8	2	12.5	12.7		11	5	4	9.5	9.5
2	0	2	63.8	64.2		8	0	-10	8.7	8.5		6	8	0	8.0	7.3		6	8	2	7.0	6.4		13	5	4	7.5	8.4
4	0	2	32.5	33.4		10	0	-10	12.9	11.8		8	8	0	9.5	9.1		3	9	2	8.0	8.2		0	6	4	18.9	19.9
6	0	2	4.1	4.3		12	0	-10	13.1	13.6		10	8	0	10.8	11.3		2	10	2	5.2	5.2		2	6	4	19.9	22.3
8	0	2	31.6	29.3		0	0	-12	9.1	8.1		1	9	0	7.4	6.2		0	2	2	28.7	24.4		6	6	4	12.4	13.7
10	0	2	6.7	6.7		2	0	-12	24.2	22.9		3	9	0	6.4	6.0		2	6	2	17.8	17.0		8	6	4	13.3	12.8
12	0	2	9.9	10.0		4	0	-12	19.5	15.8		5	9	0	17.6	18.4		0	8	2	9.0	8.4		10	6	4	12.9	12.9
14	0	2	11.6	11.5		6	0	-12	27.4	22.8		7	9	0	6.0	5.7		1	1	3	95.1	107.6		12	6	4	10.4	11.3
16	0	2	1.6	1.7		8	0	-12	12.9	12.6		0	10	0	9.3	9.6		3	1	3	44.5	41.5		1	7	4	11.4	12.5
2	0	4	53.6	62.3		10	0	-12	15.7	16.3		4	10	0	8.1	8.7		5	1	3	3.7	3.2		3	7	4	15.9	16.5
4	0	4	25.3	23.3		12	0	-12	4.7	5.2		5	1	1	9.2	8.4		7	1	3	15.1	13.5		5	7	4	2.9	2.9
6	0	4	23.4	22.4		0	0	-14	5.9	5.6		9	1	1	15.8	14.9		9	1	3	18.0	17.2		7	7	4	13.8	13.6
8	0	4	16.9	26.7		2	0	-14	3.6	3.9		11	1	1	6.3	6.2		11	1	3	4.9	4.6		9	7	4	9.5	10.3
10	0	4	58.6	45.5		6	0	-14	5.8	6.6		2	2	1	64.9	77.8		0	2	3	1.5	1.6		11	7	4	6.4	3.2
12	0	4	7.4	9.5		1	1	-9	21.8	19.5		4	2	1	11.4	11.7		2	2	3	8.2	7.9		0	8	4	12.1	12.0
14	0	4	11.6	10.4		3	1	-9	4.1	4.2		6	2	1	6.1	5.8		4	2	3	11.8	10.7		4	8	4	8.2	8.9
2	0	6	13.4	11.8		1	1	-10	34.0	32.2		8	2	1	28.1	25.8		6	2	3	6.5	5.9		6	8	4	10.1	10.6
4	0	6	71.4	81.7		3	1	-10	26.4	25.3		1	3	1	19.9	17.6		8	2	3	24.3	25.9		3	9	4	11.1	12.0
6	0	6	27.9	26.8		5	1	-10	24.1	23.0		3	3	1	18.0	16.5		10	2	3	19.5	20.2		5	9	4	3.7	3.9
8	0	6	31.4	25.7		7	1	-10	12.0	13.2		5	3	1	20.1	17.9		12	2	3	4.6	4.4		1	1	5	12.6	13.8
10	0	6	1.5	1.9		9	1	-10	9.3	10.1		7	3	1	7.7	7.7		14	2	3	4.7	5.7		3	1	5	12.0	10.4
12	0	6	25.7	25.2		11	1	-10	9.7	10.7		9	3	1	23.8	22.7		1	3	3	52.5	59.6		5	1	5	6.1	5.7
14	0	6	6.9	6.7		1	1	-10	9.2	10.6		13	3	1	6.2	5.7		3	3	3	31.7	29.3		7	1	5	6.4	5.3
2	0	8	1.2	1.5		1	1	-12	16.1	14.9		2	4	1	16.9	16.6		7	3	3	6.0	5.5		9	1	5	23.7	20.2
4	0	8	9.2	9.8		3	1	-12	16.2	13.7		4	4	1	30.3	28.9		9	3	3	6.9	6.2		11	1	5	8.3	7.4
6	0	8	7.5	7.8		5	1	-12	8.4	9.2		6	4	1	14.4	14.6		11	3	3	12.4	5.8		0	2	5	33.9	36.1
8	0	8	6.0	6.0		7	1	-12	22.7	23.1		8	4	1	15.1	14.7		0	4	3	8.6	9.1		2	2	5	38.3	40.2
10	0	8	22.8	20.4		9	1	-12	11.4	12.7		10	4	1	12.9	11.6		2	4	3	17.4	15.4		4	2	5	17.4	17.1
12	0	8	5.1	5.3		11	1	-12	9.0	9.6		12	4	1	9.3	8.0		4	4	3	18.2	18.5		6	2	5	5.6	5.5
2	0	10	27.7	23.3		1	1	-13	4.7	5.1		14	4	1	7.1	6.3		6	4	3	11.6	11.3		8	2	5	15.5	14.7
4	0	10	25.2	24.2		5	1	-13	4.6	4.2		1	5	1	35.1	41.6		8	4	3	9.5	10.4		10	2	5	6.2	5.6
6	0	10	12.7	11.8		7	1	-13	4.1	4.2		3	5	1	5.1	5.1		10	4	3	6.7	6.7		12	2	5	3.6	3.8
8	0	10	14.7	12.9		1	1	-14	6.2	6.6		5	5	1	15.6	14.4		1	5	3	7.8	7.5		1	3	5	7.9	6.8
10	0	10	3.7	3.4		3	1	0	112.3	135.3		7	5	1	7.7	7.0		3	5	3	5.9	5.2		3	3	5	23.4	27.1
2	0	12	31.6	27.0		5	1	0	126.1	109.1		9	5	1	12.9	12.5		5	5	3	6.3	5.8		5	3	5	6.3	6.5
4	0	12	10.8	11.0		7	1	0	25.7	27.1		11	5	1	6.1	6.2		7	5	3	11.2	11.6		7	3	5	5.2	4.9
6	0	12	11.5	11.6		9	1	0	54.4	48.3		11	5	1	10.6	11.1		9	5	3	5.8	5.9		9	3	5	19.2	16.5
2	0	14	8.0	8.1		11	1	0	40.4	38.6		2	6	1	13.5	13.0		0	6	3	7.7	7.3		0	4	5	25.0	29.0
1	1	9	8.6	7.7		13	1	0	8.6	8.7		4	6	1	16.6	15.9		2	6	3	8.6	8.2		2	4	5	7.3	8.0
3	1	9	7.1	7.6		15	1	0	21.3	20.0		6	6	1	9.7	9.9		4	6	3	6.9	6.4		4	4	5	8.5	9.1
5	1	9	7.0	6.8		17	1	0	8.5	9.5		8	6	1	7.2	7.4		1	7	3	8.4	8.1		6	4	5	8.8	7.5
3	1	10	22.3	21.7		2	2	0	70.9	73.3		12	6	1	11.2	11.5		7	7	3	4.6	4.9		8	4	5	5.2	5.0
5	1	10	14.4	13.4		4	2	0	77.7	74.8		1	7	1	19.9	19.8		9	7	3	6.6	6.3		12	4	5	4.6	4.0
7	1	10	19.4	18.4		6	2	0	63.7	59.1		7	7	1	19.9	19.2		2	8	3	11.4	10.5		1	5	5	5.7	5.7
9	1	10	10.2	11.3		8	2	0	56.5	50.8		9	7	1	4.7	4.6		2	0	4	66.2	62.3		3	5	5	30.3	31.5
1	1	12	22.0	22.7		10	2	0	34.5	29.7		2	8	1	7.9	7.9		4	0	4	21.5	23.3		5	5	5	6.3	6.3
3	1	12	6.5	6.3		12	2	0	30.9	28.7		6	8	1	5.6	5.8		6	0	4	23.5	22.4		11	5	5	12.6	11.5
5	1	12	6.6	6.0		14	2	0	18.6	17.8		8	8	1	7.5	8.1		8	0	4	30.7	26.7		0	6	5	17.5	17.7
7	1	12	7.5	8.5		16	2	0	8.7	8.8		5	9	1	9.1	9.8		10	0	4	46.4	45.5		2	6	5	15.4	15.7
1	1	13	7.5	7.3		1	3	0	38.2	38.9		2	10	1	10.0	9.6		4	4	4	13.1	9.5		6	6	5	5.9	4.9
3	1	13	2.1	2.5		3	3	0	68.0	76.1		4	0	2	33.4	33.4		14	0	4	10.2	10.4		8	6	5	11.0	10.4
1	1	14	7.0	7.7		5	3	0	85.2	83.0		6	0	2	4.3	4.3		1	1	4	34.4	34.6		7	7	5	11.7	10.3
2	0	-2	42.8	41.0		7	3	0	52.7	57.0		8	0	2	29.3	29.3		3	1	4	26.3	26.1		5	7	5	9.8	10.6
4	0	-2	44.2	43.1		9	3	0	23.6	21.3		10	0	2	7.1	6.7		5	1	4	54.3	56.1		7	7	5	8.8	9.2
6	0	-2	62.0	62.9		11	3	0	10.4	11.6		12	0	2	10.9	10.0		7	1	4	33.3	34.3		0	8	5	9.7	9.5
8	0	-2	12.7	12.7		13	3	0	24.4	23.5		14	0	2	12.1	11.5		9	1	4	22.8	22.9		2	8	5	4.6	5.4
10	0	-2	25.1	24.7		15	3	0	18.1	16.0		3	1	2	13.0	14.0		11	1	4	15.6	14.1		6	8	5	4.0	4.0
12	0	-2	33.5	29.5		0	4	0	36.5	43.5		5	1	2	20.9	20.9		13	1	4	11.4	11.9		8	8	5	6.9	7.4
14	0	-2	7.3	7.3		2	4	0	65.8	67.0		7	1	2	45.9	43.3		15	1	4	12.9	12.4		2	0	6	12.0	11.8
16	0	-2	13.5	13.1		4	4	0	58.2	63.2		2	2	2	112.3	130.6		0	2	4	52.8	53.6		4	0	6	97.8	81.7
0	0	-4	71.4	79.7		6	4	0	19.9	20.3		4	2	2	23.4	21.7		2	2	4	73.3	69.7		6	0	6	27.3	26.8
2	0	-4	85.4	92.1		8	4	0	37.3	36.5		6	2	2	7.7	6.8		4	2	4	20.2	21.0		8	0	6	23.9	25.7
4	0	-4	18.8	20.2		10	4	0	23.0	22.6		8	2	2	14.3	13.2		6	2	4	24.6	25.6		10	0	6	2.3	1.9
6	0	-4	13.2	13.3		12	4	0	31.0	28.5		10	2	2	18.7	18.1		8	2	4	28.2	21.5		12	0	6	24.0	25.2
10	0	-4	34.7	60.8		14	4	0	5.7	5.5		12	2	2	1.1	1.6		10	2	4	34.3	34.2		14	0	6	6.7	6.7
14	0	-4	3.4	5.6		1	5	0	36.8	38.8		14	2	2	9.0	7.9		12	2	4	8.0	8.4		1	1	6	76.3	61.6
16	0	-4	3.4	3.2		3	5	0	39.0	39.8		2	2	2	2.4	2.5		14	2	4	13.9	14.5		3	1	6	26.6	25.9
0	0	-6	59.8	56.8		5	5	0	22.2	23.7		1	3	2	65.5	62.7		1	3	4	36.2	33.9		5	1	6	34.0	33.4
2	0	-6	86.0	91.8		7	5	0	47.8	53.2		3	3	2	8.8	9.4		3	3	4	78.5	76.8		7	1	6	29.1	30.0
4	0	-6	27.5	25.9		9	5	0	11.1	10.3		5	3	2	14.2	13.2		5	3	4	35.6	37.7		9	1	6	45.9	43.1
6	0	-6	48.4	49.1		11	5	0	14.8	14.0		7	3	2	13.3	11.5		7	3	4	41.2	44.0		11	1	6	9.4	10.5
8	0	-6	45.5	47.2		13	5	0	14.1	13.3		9	3	2	11.6	12.4		9	3	4	10.2	10.8		0	2	6	54.8	48.9
10	0	-6	37.1	38.5		15	5	0	9.2	10.1		2	4	2	52.4	62.0		11	3	4	21.9	20.8		2	2	6	59.8	52.4
12	0	-6	15.5	16.6		0	6	0	48.8	52.2		4	4	2	12.6	12.2		13	3	4	11.2	11.4		4	2	6	32.0	51.1
14	0	-6	19.8	19.6		2	6	0	25.7	27.3		6	4	2	20.0	21.6		0	4	4	19.8	22.5		6	2	6	22.8	23.7
16	0	-6	16.2	16.9		4	6	0	30.4	32.0		8	4	2	30.0	27.0		2	4	4	56.1	62.8		8	2	6	10.5	11.2
0	0	-8	4.9	5.3		6	6	0	37.7	34.1		10	4	2	16.8	15.8		4	4	4	2.8	3.5		10	2	6	17.1	17.1
2	0	-8	14.4	13.2		8	6	0	18.5	15.6		6	4	2	6.9	7.0		6	4	4	18.2	20.9		12	2	6	18.3	17.6
4	0	-8	24.6	21.8		12	6	0	21.8	21.0		1	5	2	16.8	14.8		8	4	4	23.8	20.3		14	2	6	7.4	8.6
6	0	-8	19.6	19.0		1	7	0	20.7	20.4		7	5	2	28.2	26.5		10	4	4	23.1	18.0		1	3	6	46.6	48.6
8	0	-8	36.3	31.9		3	7	0	17.6	18.8		13	5	2	9.8	10.5		12	4	4	13.1	11.6		3	3	6	20.1	22.7

Table 4 (cont.)

h	k	l	Fo	Fc
5	3	6	27.1	28.4
7	3	6	24.9	23.3
9	3	6	22.5	20.0
11	3	6	11.0	12.9
13	3	6	6.5	7.1
0	4	6	35.9	38.6
2	4	6	58.6	56.8
4	4	6	20.4	22.8
6	4	6	14.6	16.1
8	4	6	7.4	7.8
10	4	6	16.7	17.3
12	4	6	9.1	10.1
1	5	6	33.7	33.5
3	5	6	4.2	6.1
5	5	6	30.1	37.7
7	5	6	13.0	14.8
9	5	6	12.0	12.3
11	5	6	6.4	7.5
0	6	6	20.8	23.1
2	6	6	16.2	20.4
4	6	6	14.9	17.4
6	6	6	10.9	12.2
8	6	6	10.9	11.7
10	6	6	2.8	3.6
1	7	6	12.0	12.4
5	7	6	17.4	18.4
7	7	6	6.8	7.5
9	7	6	8.5	9.5
0	8	6	9.8	10.6
2	8	6	12.1	13.7
4	8	6	7.4	8.2
6	8	6	4.2	4.2
3	1	7	5.1	5.2
5	1	7	1.9	2.2
7	1	7	3.7	3.7
11	1	7	3.5	3.2
13	1	7	2.5	2.7
0	2	7	14.7	14.7
2	2	7	4.1	4.1
6	2	7	1.7	1.8
8	2	7	8.5	7.6
10	2	7	10.7	9.9
12	2	7	5.5	5.6
1	3	7	2.3	2.0
3	3	7	8.9	8.3
5	3	7	4.3	4.5
7	3	7	9.3	8.9
9	3	7	1.9	1.7
0	4	7	9.2	10.1
2	4	7	24.1	23.9
4	4	7	5.9	5.4
10	4	7	9.4	9.3
12	4	7	1.5	2.1
1	5	7	4.7	4.2
3	5	7	4.7	4.8
7	5	7	7.7	7.3
11	5	7	2.6	2.9
0	6	7	1.6	1.6
2	6	7	11.5	10.9
10	6	7	6.0	7.7
1	7	7	5.5	5.3
3	7	7	7.4	7.4
5	7	7	10.2	11.4
4	8	7	3.8	4.0
2	0	8	1.5	1.5
4	0	8	10.8	9.8
6	0	8	7.8	7.8
8	0	8	6.3	6.3
10	0	8	19.0	20.4
12	0	8	5.0	5.3
3	1	8	25.1	23.4
5	1	8	13.2	12.7
7	1	8	0.8	0.9
9	1	8	5.9	6.0
11	1	8	9.5	10.9
0	2	8	2.4	2.6
2	2	8	9.3	8.0
4	2	8	3.8	3.6
6	2	8	8.3	8.6
10	2	8	5.3	4.9
12	2	8	4.2	4.3
1	3	8	2.6	2.7
3	3	8	7.9	8.9
7	3	8	4.3	4.1
9	3	8	1.9	1.7
11	3	8	3.8	4.1
0	4	8	4.1	4.0
4	4	8	9.5	8.6
1	5	8	5.6	5.0
3	5	8	1.5	1.1
0	6	8	4.8	4.8
2	6	8	8.0	7.6
4	6	8	17.7	18.7
6	6	8	2.0	2.6
1	7	8	5.9	5.5
3	7	8	4.8	4.9
5	7	8	5.0	5.5
7	7	8	0.8	1.6
-3	1	1	22.3	18.7
-5	1	1	15.9	13.4
-7	1	1	27.8	25.9
-11	1	1	18.4	20.0
-2	2	1	20.7	18.9
-4	2	1	9.9	9.4
-6	2	1	11.9	10.4
-8	2	1	11.5	12.4
-10	2	1	8.2	8.1
-3	3	1	4.5	5.2
-11	3	1	31.2	35.0
-13	3	1	15.9	18.3
-2	4	1	30.6	28.3
-4	4	1	14.1	13.9
-6	4	1	19.0	15.9
-8	4	1	15.0	16.0
-10	4	1	15.7	14.1
-1	5	1	15.7	14.1
-5	5	1	21.7	22.1
-7	5	1	20.5	22.1
-13	5	1	9.6	10.3
-2	6	1	19.4	20.7
-4	6	1	14.7	14.6
-6	6	1	6.3	6.2
-8	6	1	14.8	15.2
-10	6	1	9.3	9.1
-3	7	1	17.1	18.1
-7	7	1	12.8	13.6
-11	7	1	6.7	6.8
-13	7	1	6.9	6.9
-2	8	1	9.7	9.3
-3	1	2	70.1	62.9
-7	1	2	44.5	47.8
-7	1	2	15.6	13.9
-11	1	2	31.4	26.1
-13	1	2	21.8	23.1
-2	2	2	42.5	40.5
-4	2	2	62.9	72.3
-6	2	2	22.1	21.3
-10	2	2	35.6	40.8
-12	2	2	5.4	4.7
-14	2	2	11.5	10.8
-1	3	2	36.0	36.5
-3	3	2	22.2	20.2
-5	3	2	29.3	33.0
-7	3	2	29.1	32.0
-9	3	2	24.7	25.9
-11	3	2	6.6	6.5
-13	3	2	22.8	23.5
-2	4	2	24.9	23.8
-4	4	2	12.7	12.7
-6	4	2	24.7	23.5
-8	4	2	32.0	30.1
-10	4	2	27.1	29.7
-14	4	2	9.8	10.6
-3	5	2	19.3	19.7
-5	5	2	32.1	33.3
-7	5	2	15.5	18.1
-9	5	2	7.7	7.0
-11	5	2	20.7	21.3
-2	6	2	11.9	11.4
-4	6	2	16.0	17.0
-6	6	2	8.6	8.3
-8	6	2	17.7	20.7
-10	6	2	9.6	7.6
-12	6	2	18.1	10.6
-14	6	2	7.6	8.6
-1	7	2	12.0	11.8
-3	7	2	25.7	24.1
-5	7	2	15.6	17.2
-7	7	2	7.3	7.1
-9	7	2	9.3	9.9
-11	7	2	10.0	10.9
-13	7	2	8.2	8.7
-2	8	2	8.7	8.2
-4	8	2	11.0	11.6
-6	8	2	21.9	22.2
-8	8	2	7.0	7.0
-10	8	2	16.8	16.8
-14	8	2	7.2	6.9
-1	9	2	5.1	4.6
-3	9	2	7.9	6.8
-5	9	2	8.0	6.8
-11	3	3	20.8	25.6
-6	4	3	27.4	28.3
-8	4	3	8.4	8.3
-7	1	3	15.2	15.8
-2	2	3	32.6	31.4
-6	2	3	30.2	29.9
-8	2	3	5.0	4.7
-10	2	3	26.1	31.5
-12	2	3	16.7	18.8
-1	3	3	14.0	13.5
-3	3	3	27.3	27.6
-5	3	3	30.7	30.4
-11	3	3	5.2	4.7
-13	3	3	9.9	8.6
-2	4	3	6.2	5.7
-6	4	3	19.0	15.9
-5	5	3	13.5	14.2
-2	6	3	14.0	14.1
-4	8	3	5.1	4.2
-6	6	3	11.3	10.3
-8	6	3	3.6	3.6
-3	7	3	9.6	8.8
-5	7	3	12.9	12.1
-7	7	3	14.5	12.7
-1	1	3	23.9	33.3
-11	7	3	6.5	6.6
-5	1	3	51.0	57.7
-7	1	3	48.7	49.9
-11	1	3	49.6	50.7
-13	1	3	21.9	21.7
-2	8	3	13.0	11.6
-7	1	3	7.7	7.3
-9	1	3	12.8	12.1
-2	2	4	57.0	71.5
-4	2	4	66.2	60.2
-6	2	4	27.4	27.5
-8	2	4	46.8	47.4
-2	2	4	22.7	23.6
-10	2	4	12.7	12.1
-12	2	4	57.1	53.6
-14	2	4	37.1	39.3
-1	3	4	36.1	38.4
-3	3	4	23.5	24.9
-5	3	4	12.3	12.8
-7	3	4	24.2	21.8
-9	3	4	15.7	13.8
-11	3	4	42.3	41.8
-4	3	4	16.8	17.2
-2	4	4	58.5	59.4
-4	4	4	15.9	16.6
-6	4	4	21.2	22.5
-8	4	4	11.8	11.7
-10	4	4	12.1	12.1
0	4	4	23.6	22.5
-2	4	4	29.4	30.4
-4	4	4	11.0	10.5
-6	4	4	25.4	25.4
-8	4	4	17.7	16.7
-12	4	4	15.1	15.7
-1	5	4	13.1	12.1
-3	5	4	33.4	34.1
-5	5	4	10.7	11.9
-7	5	4	15.3	14.9
-9	5	4	11.2	9.4
0	6	4	21.2	19.9
-2	6	4	36.3	36.9
-4	6	4	8.9	8.2
-6	6	4	4.8	4.8
-8	6	4	10.9	10.1
-10	6	4	13.2	12.1
-1	7	4	5.8	5.2
-3	7	4	7.4	7.0
-5	7	4	18.8	17.8
0	8	4	15.1	12.0
-2	8	4	15.8	13.4
-4	8	4	4.2	4.9
-6	8	4	6.0	6.8
-8	8	4	4.4	5.4
-10	8	4	9.5	10.0
-5	9	4	19.5	20.0
-10	8	4	8.6	9.0
-1	9	4	19.3	23.4
-5	9	4	11.2	11.4
-3	9	6	13.0	11.9
-5	9	4	6.4	6.5
-11	1	5	19.9	19.9
-7	9	6	6.3	7.1
-2	2	5	24.2	29.9
-4	2	5	11.5	9.6
-6	2	5	10.5	10.0
-8	2	5	4.8	5.0
-10	2	5	16.8	16.8
-14	2	5	6.4	5.7
-1	5	5	14.9	15.0
-3	3	5	4.8	5.5
3	3	5	26.0	29.7
-11	3	5	14.5	13.6
-6	4	5	19.3	21.0
-8	4	5	16.3	16.4
-12	4	5	9.4	9.4
-1	5	5	12.5	11.3
-3	5	5	10.8	10.8
-5	5	5	15.1	16.1
-7	3	5	6.5	7.5
-9	5	5	19.2	18.3
-11	3	5	14.1	14.2
-4	6	5	12.1	11.2
-6	6	5	17.3	15.0
-8	6	5	12.9	11.3
-12	6	5	29.4	26.9
-3	7	5	4.5	4.5
-5	7	5	9.5	8.7
-7	7	5	7.6	8.3
-9	5	5	8.0	7.6
-11	7	5	8.7	7.2
-2	8	5	13.2	11.6
-13	5	5	5.1	4.2
-4	8	5	5.4	5.6
-6	8	5	4.2	4.7
-10	8	5	8.2	7.8
-1	1	6	23.9	33.3
-3	1	6	71.3	85.7
-5	1	6	51.0	57.7
-7	1	6	48.7	49.9
-9	1	6	6.0	2.4
-11	1	6	49.6	50.7
-13	1	6	21.9	21.7
-2	2	6	46.0	48.5
-4	2	6	27.4	27.5
-6	2	6	46.8	47.4
-8	2	6	48.2	50.5
-2	2	6	32.8	34.0
-12	2	6	19.8	15.6
-14	2	6	13.9	13.1
-1	3	6	49.6	47.1
-3	3	6	45.1	44.6
-5	3	6	36.7	35.2
-7	3	6	33.3	34.8
-9	3	6	38.9	36.1
-11	3	6	23.9	19.5
-13	3	6	21.6	18.4
-2	4	6	12.4	11.2
-4	4	6	40.1	37.0
-6	4	6	31.9	32.0
-8	4	6	34.4	35.2
-10	4	6	25.6	24.0
-12	4	6	17.0	16.0
-14	4	6	10.9	11.3
-1	5	6	21.7	18.5
-3	5	6	56.7	57.0
-5	5	6	9.2	10.1
-7	5	6	26.1	24.7
-9	5	6	21.9	18.2
-11	5	6	19.2	17.0
-13	5	6	13.2	12.9
-2	6	6	7.9	7.8
-4	6	6	33.3	30.6
-6	6	6	20.2	18.8
-8	6	6	17.6	16.0
-10	6	6	13.7	13.8
-12	6	6	10.7	11.9
-1	7	6	12.4	11.7
-3	7	6	33.7	29.5
-5	7	6	9.8	10.6
-7	7	6	12.2	13.1
-11	7	6	11.0	12.2
-2	8	6	8.3	8.1
-4	8	6	4.2	4.9
-6	8	6	13.1	14.1
-8	8	6	9.5	10.0
-10	8	6	8.6	9.0
-1	9	6	11.2	11.4
-3	9	6	6.7	5.2
-5	9	6	6.4	6.5
-7	9	6	6.3	7.1
-1	1	7	14.3	14.8
-3	1	7	17.3	16.9
-7	1	7	15.7	14.3
-9	1	7	20.9	19.9
-11	1	7	7.8	7.8
-2	2	7	17.6	16.4
-4	2	7	4.5	4.1
-6	2	7	4.7	4.6
-8	2	7	5.6	5.5
-10	2	7	5.6	6.0
-12	2	7	3.2	3.0
-1	3	7	6.5	6.8
-3	3	7	3.2	2.7
-5	3	7	3.7	3.4
-7	3	7	12.2	13.3
-9	3	7	6.4	6.6
-11	3	7	4.5	4.6
-13	3	7	7.1	7.5
-1	4	7	16.1	16.6
-4	4	7	5.8	7.2
-6	4	7	5.4	5.7
-8	4	7	5.4	5.6
-10	4	7	10.5	11.2
-12	4	7	5.0	5.2
-14	4	7	3.4	4.1
-1	5	7	25.8	23.8
-3	5	7	6.4	7.3
-9	5	7	15.0	14.3
-7	5	7	5.8	6.2
-4	6	7	11.7	11.9
-6	6	7	6.3	6.3
-10	6	7	9.7	9.1
-12	6	7	3.2	3.9
-1	7	7	4.2	2.8
-3	7	7	6.4	6.1
-5	7	7	4.7	4.5
-4	8	7	5.9	6.4
-6	8	7	6.3	6.5
-9	9	7	5.4	6.6
-1	1	8	14.8	19.6
-3	1	8	5.3	5.2
-7	1	8	7.4	7.9
-9	1	8	16.5	16.4
-11	1	8	12.0	11.3
-13	1	8	10.0	9.9
-2	2	8	3.3	3.8
-4	2	8	11.6	13.1
-2	2	8	12.2	12.5
-8	2	8	4.2	4.4
-10	2	8	10.8	12.1
-14	2	8	6.8	6.4
-1	3	8	35.7	41.1
-3	3	8	5.3	5.5
-7	3	8	8.2	8.6
-9	3	8	7.0	7.0
-11	3	8	7.2	7.2
-2	4	8	2.0	1.8
-4	4	8	20.6	19.0
-6	4	8	10.4	11.3
-10	4	8	12.5	11.3
-12	4	8	8.3	8.1
-14	4	8	4.6	5.5
-1	5	8	26.3	18.9
-3	5	8	8.4	7.4
-5	5	8	13.7	12.4
-7	5	8	3.5	3.7
-9	5	8	10.7	11.1
-11	5	8	7.3	7.1
-13	5	8	4.7	5.1
-2	6	8	7.2	6.3
-6	6	8	18.9	15.6
-6	6	8	10.8	8.0
-8	6	8	8.5	9.8
-10	6	8	2.6	2.4
-3	7	8	3.3	3.0
-5	7	8	11.6	9.1
-7	7	8	4.0	3.6
-9	7	8	4.8	4.4
-2	8	8	10.3	8.4
-6	8	8	3.3	3.7

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

Cruickshank suggests that useful constants have been found to be $A \simeq 2F_{min}$, $B = 1$ and $C \simeq 2F/_{max}$. The final values used were $A = 1.069$, $B = -0.143$ and $C = 0.074$. The introduction of negative constants causes the weight/F_{obs} curve to pass through a maximum, and prevents an excessively high weight being placed on extremely weak reflexions where the experimental error is very large.

In the final stages, three reflexions (8,0,4; 11,3,3; and −9,1,6) were excluded from the matrix but not from the calculation of R. The final R value was 7.9% after 44 cycles of full-matrix least-squares refinement based on 867 independent observed reflexions.

The final atomic coordinates are given in Table 1. Anisotropic temperature factors given by the equation

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

are shown in Table 2 and the calculated positions of hydrogen atoms are listed in Table 3. Values of observed and calculated structure amplitudes are listed in Table 4, and an agreement analysis is given in Table 5.

Table 5. *Agreement analysis*

F_{obs}	Number of planes	R	Sin θ	Number of planes	R	Zone	Number of planes	R
0– 4	46	14·3%	0·0–0·1	0		$hk0$	64	7·9%
4– 8	184	7·9	0·1–0·2	4	11·6%	$hk1$	71	7·6
8–12	164	6·9	0·2–0·3	24	9·9	$hk2$	97	8·4
12–16	119	8·6	0·3–0·4	51	8·1	$hk3$	68	8·2
16–20	80	9·0	0·4–0·5	86	8·6	$hk4$	106	6·7
20–24	59	8·1	0·5–0·6	111	7·5	$hk5$	75	8·7
24–28	54	9·7	0·6–0·7	155	8·2	$hk6$	110	8·3
28–32	35	8·3	0·7–0·8	152	10·5	$nk7$	71	6·2
32–36	26	8·8	0·8–0·9	159	8·8	$hk8$	79	10·1
36–40	22	6·6	0·9–1·0	125	6·4	$h0l$	93	8·3
40–44	8	6·2				$h1l$	33	6·3
44–48	7	4·9						
48–52	12	4·6						
52–56	8	9·8						
56–60	11	8·9						
60–64	4	12·7						
64–68	8	8·5						
68–72	3	10·1						
72–76	5	9·2						
>76	12	13·2						

Discussion

A view of the structure is given in Fig.1. The bond lengths and angles together with their estimated standard deviations are listed in Tables 6 and 7. A problem arises over the treatment of the standard deviation of the x and z coordinates of atom S(1), and consequently in the calculation of standard deviations of bond lengths and angles involving S(1). Since the x and z coordinates for S(1) have been fixed to define the origin of the cell they should have no error, but the standard deviations of the other atomic positions should be increased accordingly. The X-ray 63 programs do not allow for this, and to obtain a better estimate of the errors in bond lengths and angles involving S(1) standard deviations have been included for x and z.

Table 6. *Bond lengths and their standard deviations*

	Distance	σ
S(1)—S(2)	2·02 Å	0·005 Å
S(1)—C(1)	1·84	0·013
S(2)—C(8)	1·85	0·016
C(1)—C(2)	1·49	0·018
C(8)—C(9)	1·50	0·016
C(2)—C(3)	1·38	0·017
C(3)—C(4)	1·35	0·021
C(4)—C(5)	1·35	0·023
C(5)—C(6)	1·36	0·021
C(6)—C(7)	1·40	0·017
C(7)—C(2)	1·36	0·018
C(9)—C(10)	1·43	0·019
C(10)–C(11)	1·38	0·021
C(11)–C(12)	1·40	0·020
C(12)–C(13)	1·37	0·020
C(13)–C(14)	1·39	0·023
C(14)–C(9)	1·35	0·016

Equations to the planes through the atoms C(1), S(1), S(2) and through S(1), S(2), C(8), and the best least-squares planes through the benzene rings have been

Table 7. *Bond angles and their standard deviations*

	Angle	σ
S(2)—S(1)—C(1)	103·3°	0·4°
S(1)—S(2)—C(8)	102·9	0·5
S(1)—C(1)—C(2)	114·3	1·0
S(2)—C(8)—C(9)	112·3	1·2
C(1)—C(2)—C(3)	122·6	1·2
C(1)—C(2)—C(7)	119·0	1·1
C(3)—C(2)—C(7)	118·4	1·2
C(2)—C(3)—C(4)	122·6	1·3
C(3)—C(4)—C(5)	118·7	1·3
C(4)—C(5)—C(6)	120·9	1·5
C(5)—C(6)—C(7)	120·1	1·4
C(6)—C(7)—C(2)	119·3	1·1
C(8)—C(9)—C(10)	119·7	1·2
C(8)—C(9)—C(14)	122·1	1·2
C(10)—C(9)—C(14)	117·9	1·2
C(9)—C(10)—C(11)	117·8	1·2
C(10)–C(11)–C(12)	123·4	1·3
C(11)–C(12)–C(13)	116·9	1·3
C(12)–C(13)–C(14)	120·5	1·5
C(13)–C(14)–C(9)	123·3	1·3

calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) and are given in Table 8.

The central part of the molecule C(1)–S(1)–S(2)–C(8) adopts a skewed non-planar configuration like that found in hydrogen peroxide (Abrahams, Collin & Lipscomb, 1951), hydrogen disulphide (Stevenson & Beach, 1938; Wilson & Badger, 1949), dimethyl disulphide (Stevenson & Beach, 1938) and diphenyl disulphide (Lee & Bryant, 1969). The observed S–S bond length of 2·02 Å may have 23% of double bond character if the Pauling (1960) value of 2·08 Å is taken as the length of a pure single bond. The dihedral angle between the planes containing C(1), S(1), S(2) and S(1), S(2), C(8) is 92·1°. According to Hordvik (1966) a relationship exists between bond length and dihedral angle. A dihedral angle of 0° is associated with the maximum repulsion between non-bonding orbitals on the sulphur atoms, and a dihedral angle of 90° with

the optimum π overlap of orbitals. With a dihedral angle of 90° the orientation of the orbitals is favourable for overlap between filled p orbitals on one atom with empty $d_{x^2-y^2}$ and d_{z^2} orbitals on the other atom. From an empirical bond length/dihedral angle curve Hordvik relates the observed S–S bond of 2·02 Å with a dihedral angle of 92°, in excellent agreement with the value measured. This S–S bond length may be compared with 2·03 Å in diphenyl disulphide (Lee & Bryant, 1969) and 2·04 Å in dimethyl disulphide (Stevenson & Beach, 1938). The S–S bond lengths in diphenyl and dibenzyl disulphides differ by two standard deviations. Though the difference in length of 0·01 Å is small, it is regarded as significant, and is in accord with the findings of Allum & Forbes (1967), that the anti-wear properties of organic disulphides in lubricating oils depend on the strength of the S–S bond, and increase along the series: n-butyl < allyl < benzyl < phenyl.

The bond angles S(2)–S(1)–C(1) and S(1)–S(2)–C(8) of 103·3 and 102·9° respectively indicate that the outer electrons on the sulphur atoms are roughly sp^3 hybridized, but that considerable distortion arises from the repulsions between the lone pairs of electrons exceeding that between the bonding pairs of electrons. A review by Abrahams (1956) states that the valency angle for two-bonded sulphur is normally tetrahedral or slightly less. It is difficult to see how sp^3 hybrid orbitals could be involved in π bonding in this compound. If the bonds formed by the sulphur atoms utilized pure p orbitals, as suggested by Price & Oae (1962), then the dihedral angle would be expected to be close to 90°, and the p orbital not involved in σ bonding could participate in $p\pi$–$d\pi$ bonding. Though $p\pi$–$d\pi$ bonding occurs between S and O (Cruickshank, 1961), it is not possible to reconcile the bond angles of 103·3 and 102·9° in dibenzyl disulphide with the use of pure p orbitals.

The same factors which cause a dihedral angle of about 90° in H_2O_2 are probably responsible for the dihedral angle in disulphides. According to the molecular orbital description of the O_2 molecule, the antibonding π^*2py and π^*2pz orbitals are both singly occupied by electrons, thus weakening the O–O bond. If these singly occupied antibonding orbitals are used for bonding to hydrogen in H_2O_2 then a dihedral angle of 90° would be expected. In F_2O_2, the high electronegativity of F tends to remove electrons from the antibonding oxygen orbitals, thus shortening and strengthening the O–O bond (Jackson, 1962). The same reasoning would explain the very short S–S distance of 1·888 Å in S_2F_2 (Kuczkowski, 1964).

The C–S bond lengths of 1·84 and 1·85 Å with standard deviations of 0·016 and 0·016 Å are significantly longer than the usually accepted values of 1·812 Å (Cox & Jeffrey, 1951), 1·81 (5) Å (Sutton, 1958), and the values of 1·79 and 1·81 Å in diphenyl disulphide (Lee & Bryant, 1969). The reason for these weak bonds is not apparent, but it confirms the findings of Allum & Ford (1965), that the extreme pressure activity of organic disulphides in lubricating oils is related to the strength of the S–C bond, and increases along the series: phenyl < n-butyl < sec-butyl < tert-butyl < benzyl.

The sum of the three bond angles round C(2) is 360·0°, and those round C(9) add up to 359·7°, confirming a planar distribution of bonds and sp^2 hybridization. The range of bond lengths in the benzene rings is 1·35–1·43 Å, but none of these exceeds two standard deviations from the expected value of 1·39 Å. The rings are planar (maximum deviation from plane 0·019 Å) and make an angle of 90·9° with each other.

Ignoring contacts between hydrogen atoms, there are no intermolecular contacts below 3·5 Å. Disregarding the hydrogen atoms, intramolecular distances below 3·5 Å are listed in Table 9. Most of these are unavoidable diagonals across benzene rings, but the distances C(2)···S(1)=2·80 and C(9)···S(2)=2·79 Å are short, and account for the bond angles at C(1) and C(8) increasing from tetrahedral to 114·3 and 112·3° respectively. The distances C(3)···S(1)=3·44 and C(10)···S(2)=3·41 Å are of interest, and confirm the sugges-

Table 8. *Equations to planes*

Atoms in plane	Equation
C(1), S(1), S(2)	$9·16X - 5·99Y - 0·38Z = -0·07$
C(8), S(2), S(1)	$9·40X - 5·86Y - 0·43Z = 0·06$

Angle between above two planes = 92·1°

C(2), C(3), C(4), C(5), C(6), C(7)	$3·33X + 5·75Y + 7·02Z = 2·21$
C(9), C(10), C(11), C(12), C(13), C(14)	$3·24X - 5·80Y + 6·98Z = -2·21$

Angle between planes through the two benzene rings = 90·9°
X, Y and Z refer to the unit cell axis a, b and c.

Distances of atoms from planes

Atom	Distance from plane	Atom	Distance from plane
C(2)	0·005 Å	C(9)	−0·016 Å
C(3)	−0·007	C(10)	0·010
C(4)	0·002	C(11)	−0·007
C(5)	0·006	C(12)	0·008
C(6)	−0·008	C(13)	−0·015
C(7)	0·003	C(14)	0·019

tion that the van der Waals radius of S should be 1·72–1·73 Å (Fava Gasparri, Nardelli & Villa, 1967; Nardelli, Fava Gasparri, Giraldi Battistina & Domiano, 1966; Ždanov & Zvonkova, 1950; Van der Helm, Lessor & Merritt, 1950; Lee & Bryant, 1969), rather than the Pauling (1960) value of 1·85 Å. Accepting this smaller van der Waals radius of 1·72 plus 1·70 Å for half the thickness of an aromatic ring, these contacts are normal. The hydrogen atoms are not favourably placed nor at a suitable distance for hydrogen bonding to sulphur.

The importance of correlation coefficients is discussed by Geller (1961) who claims that high correlations depend on the trial structure including all parameters and atomic scattering factors, and partly on the number and extent of the data, but are essentially independent of the quality of the data.

Table 9. *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)	2·80 Å
S(1)	···C(3)	3·44
S(1)	···C(8)	3·03
S(2)	···C(1)	3·03
S(2)	···C(9)	2·79
S(2)	···C(10)	3·41
C(1)	····C(3)	2·52
C(1)	····C(7)	2·45
C(2)	····C(4)	2·40
C(2)	····C(5)	2·74
C(2)	····C(6)	2·38
C(3)	····C(5)	2·32
C(3)	····C(6)	2·70
C(3)	····C(7)	2·35
C(4)	····C(6)	2·36
C(4)	····C(7)	2·76
C(5)	····C(7)	2·39
C(8)	····C(10)	2·54
C(8)	····C(14)	2·50
C(9)	····C(11)	2·41
C(9)	····C(12)	2·82
C(9)	····C(13)	2·41
C(10)	···C(12)	2·45
C(10)	···C(13)	2·78
C(10)	···C(14)	2·38
C(11)	···C(13)	2·36
C(11)	···C(14)	2·70
C(12)	···C(14)	2·39

Similar difficulties in least-squares refinement of the structure of guanidinium aluminum sulphate have been reported by Geller & Katz (1962), and by Lingafelter, Oriolo, Schein & Stewart (1966) though in addition they obtained some negative temperature factors. In this case the accurate remeasurement of diffraction data and application of absorption corrections allowed the refinement to proceed without difficulty despite the large values of the correlation coefficients (Schein, Stewart & Lingafelter, 1966).

These difficulties and the large correlation coefficients were attributed to the presence of a pseudo centre of symmetry. In a similar way the difficult re-

finement and high correlations in dibenzyl disulphide are probably due to the pseudo twofold axis of symmetry in the molecule.

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