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The Crystal and Molecular Structure of Azobenzene-2-Sulphenyl Cyanide

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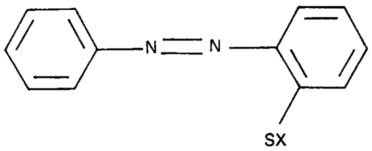
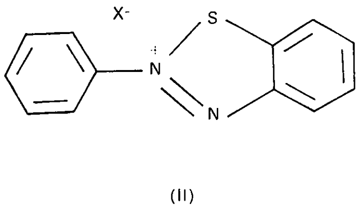
Azobenzene-2-sulphenyl cyanide, $C_6H_5N{:}NC_6H_4SCN$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell of dimensions $a=12{\cdot}99$, $b=22{\cdot}01$ and $c=3{\cdot}79$ Å. The structure has been determined from two-dimensional X-ray intensity data. The approximate structure has been obtained by optical-transform methods in conjunction with a Patterson projection and has been refined by Fourier and difference Fourier syntheses. The non-ionic nature of the S–CN linkage in the crystalline state of azobenzene-2-sulphenyl cyanide has been established, supporting the findings of the absorption spectra of the compound in the ultraviolet and visible regions. The refined structure has shown that the molecule is non-planar.

Introduction

Important features of structural interest in azobenzene-2-sulphenyl derivatives, which form a special group of compounds within the *ortho*-mercaptoazo compounds, have been pointed out by Burawoy, Liversedge, Vellins, Bartindale & Farrow (1954). A detailed analysis of ultraviolet and visible-light absorption spectra of these compounds made by these workers, using different solvents, has suggested structure (I) for non-ionic, and structure (II) for ionic members of the series. It is also suggested that in the case of halides there are indications of an equilibrium between ionic and non-ionic isomers in solution. These findings, however, do not throw any light on the structures of azobenzene-2-sulphenyl derivatives in the solid state. With the exception of a preliminary study of the structure of azobenzene-2-sulphenyl chloride (Burawoy *et al.*, 1954;



(I)



(II)

Woolfson, 1957), no detailed analysis of any member of this series appears to have been reported. It has therefore been considered worth while to undertake X-ray analysis of the compounds, and crystallographic data for some of these have already been reported by several workers in this department (Chaudhuri, Kakati & Bhattacharyya, 1963; Bhattacharyya, Talukdar & Chaudhuri, 1964; Barman & Chaudhuri, 1967). The detailed analysis of azobenzene-2-sulphenyl cyanide is reported here.

Experimental details

Crystals of azobenzene-2-sulphenyl cyanide suitable for X-ray study were obtained by slowly cooling a saturated solution of the compound in warm ethanol. They were needle-shaped and elongated along the *c*-axis. The density was measured by flotation in aqueous potassium iodide and unit-cell dimensions were measured from oscillation and Weissenberg photographs which had been calibrated against powder lines of silver ($a=4\cdot0862$ Å). The crystal data are:

Formula, $C_6H_5N:NC_6H_4SCN$, $M=239\cdot4$, m.p.$=99°$. Orthorhombic, $a=12\cdot99\pm0\cdot03$, $b=22\cdot01\pm0\cdot05$, $c=3\cdot79\pm0\cdot02$ Å, $D_m=1\cdot39$ g.cm^{-3}, $Z=4$, $D_c=1\cdot42$ g.cm^{-3}, $F(000)=496$. Space group, $P2_12_12_1$. Absorption coefficient for X-rays ($\lambda=1\cdot542$ Å) $\mu=24\cdot5$ cm^{-1}. Absent spectra: $h00$ when h is odd, $0k0$ when k is odd and $00l$ when l is odd.

Reflexions $hk0$ and $0kl$ were recorded on multiple-film Weissenberg photographs with copper $K\alpha$ radiation; the cross-sections of the specimens perpendicular to the axes of rotation were 0·14 mm × 0·07 mm for the *c* axis and 0·12 mm × 0·09 mm for the *a* axis. Intensities were measured by visual comparison with crystal-reflected calibration spots of known relative exposures. In this way intensities of 212 $hk0$ and 73 $0kl$ reflexions were estimated. Absorption correction was considered unnecessary owing to the small sizes of the crystal specimens chosen, but Lorentz and polarization factors were applied.

Structure analysis

Projection along [001]

Determination of trial xy coordinates

Approximate *x* and *y* coordinates were obtained by optical-transform methods (Hanson, Lipson & Taylor, 1953) supported by a Patterson projection along [001]. Inspection of the $hk0$ section of the weighted reciprocal lattice of azobenzene-2-sulphenyl cyanide (Fig. 1), drawn with weights proportional to approximate unitary structure factors, showed six distinct groups of strong reflexions lying very nearly in the benzene circle (Taylor & Lipson, 1964). These satisfied the necessary geometrical condition, conforming to six characteristic peaks in the transform of a benzene ring, and gave an indication that, in the projection of the unit cell contents along the *c*-axis, the benzene rings had very nearly parallel orientations even though the plane group *pgg* of the projection contained four molecules of different orientations. Such a situation arose in the case of 5-methoxy-2-nitrophenol (Crowder, Morley & Taylor, 1959). The final analysis of the structure of azobenzene–2-sulphenyl cyanide showed that all the benzene rings in the projections are not exactly parallel, but the departure from exact parallelism was very small.

The recognition of the approximate orientation of the benzene-ring configuration revealed the approximate shape and orientation of the representative molecule in the projection. Assuming standard bond

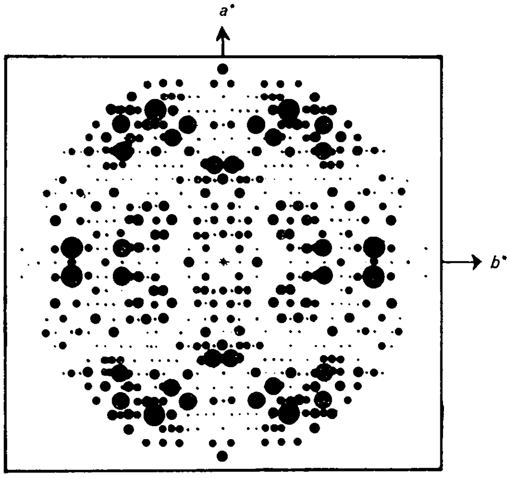


Fig. 1. $hk0$ section of the weighted reciprocal lattice of azobenzene-2-sulphenyl cyanide with weights proportional to approximate unitary structure factors.

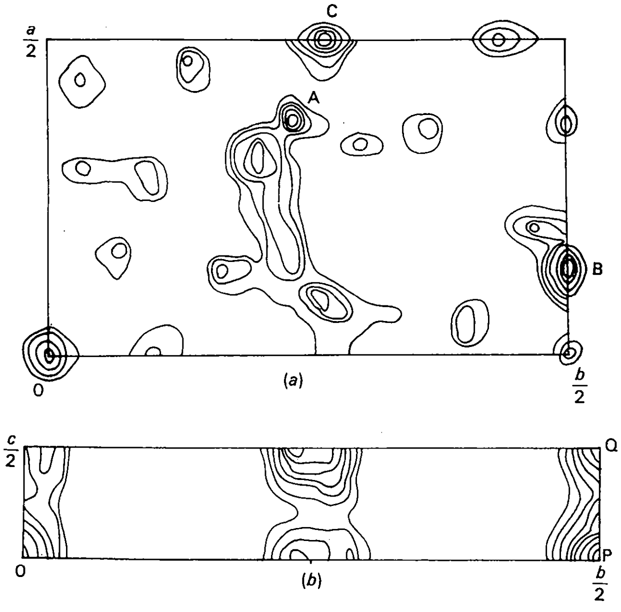


Fig. 2. (*a*) Patterson projection on (001). (*b*) Patterson projection on (100).

lengths and bond angles, a molecular model was eventually obtained by comparing the $hk0$ weighted reciprocal lattice section with the optical transforms of a few trial models of the molecule. Both *cis* and *trans* configurations of the molecule were tried, but the *cis* form was very easily discarded.

A Patterson projection [Fig. 2(a)] along [001] displayed S–S rotation peak A at $(2x,2y)$ and glide-reflexion peaks (Buerger, 1959) B and C at $(\frac{1}{2}-2x,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2}-2y)$, corresponding to the fourfold position of the sulphur atom in the plane group *pgg*. The fractional parameters ($x/a=0{\cdot}19$ and $y/b=0{\cdot}12$) of the representative sulphur atom of the equivalent set of four atoms were easily identified. A two-dimensional Fourier series was summed with phases based on the parameter of the sulphur atom. The resulting electron-density distribution was, however, not found to be good enough for recognizing the sites of the light atoms. From the location of the sulphur atom and of the molecule whose shape and orientation was already known from optical-transform considerations, a trial structure was postulated; it was tested optically and the match between the optical transform and the $hk0$ section of the weighted reciprocal lattice was considered reasonable enough for refining the structure by Fourier methods.

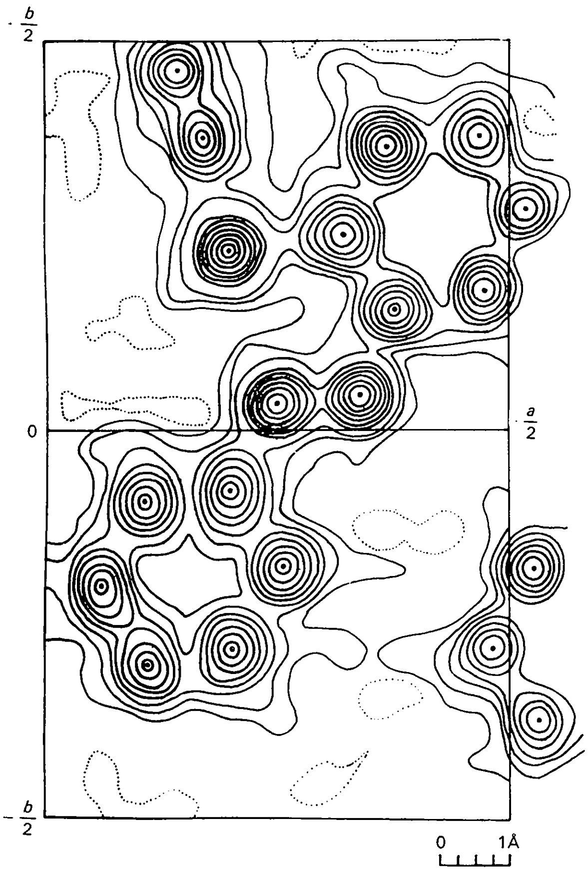


Fig. 3. Electron-density projection on (001). Contours are drawn at intervals of 0·5 e.Å^{-2}; the 1 e.Å^{-2} contour is dotted.

Refinement of the projection along [001]. *Hydrogen atoms*

In the initial stages of refinement the phase angles were determined optically (Hanson *et al.*, 1953) to cut down computational work. This procedure eventually permitted inclusion of 180 reflexions in the synthesis which revealed clearly all the atoms in the electron-density projection.

Fig. 3 gives the final (fourth) $F_o(hk0)$ synthesis which includes all the 216 experimentally observed reflexions with phases determined from calculated structure factors. In calculating $hk0$ structure factors, the origin of coordinates is chosen on the screw axis at $(\frac{1}{4}a,0,0)$ referred to the origin adopted in *International Tables for X-ray Crystallography* (1952), since this choice places the origin at the centre of symmetry of the projection along [001]. The values of the final atomic coordinates in Table 4 refer to this origin. (However, for evaluating electron density distributions of the a-axis projection, the phases of the $0kl$ structure factors, as given in Table 3, are calculated taking the origin of coordinates at $(0,-\frac{1}{4}b,0)$ with respect to the origin of the c-axis projection.) The agreement residual derived at this stage using the same isotropic temperature factor, 4·1 Å^2, for all the atoms is 21%, the accidentally absent reflexions being excluded. The agreement between the $hk0$ weighted reciprocal lattice section and the optical transform of four molecules with coordinates derived from the final $F_o(hk0)$ synthesis is demonstrated in Fig. 4. The atomic scattering factors used for structure factor calculation throughout the work are those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

A difference Fourier synthesis (Fig. 5) based on all the observed $hk0$ reflexions suggested small adjustments in the coordinates of a few atoms. The calculated shifts (Cochran, 1951) were 0·062, 0·041, 0·069, 0·093, 0·062 and 0·054 Å for the positions of the atoms N(1), N(2), N(3), C(3), C(8) and C(10) respectively. Moreover, the $(\varrho_o-\varrho_c)$ map showed some peaks which could be attributed to the hydrogen atoms, as the peaks appeared where the hydrogen atoms were expected. The positions of H(1), H(2), H(3), H(4), H(5), H(7) and H(8) were postulated taking the $(\varrho_o-\varrho_c)$ map as guide and assuming a C–H distance of 1·09 Å. Two out of a total of nine hydrogen atoms in the single molecule of azobenzene-2-sulphenyl cyanide were not revealed in the map. Their positions were postulated assuming normal C–H distances. A quick test of the correctness of the location of the hydrogen atoms was made by the optical-transform technique (Pinnock & Lipson, 1954) in which the transform of the hydrogen atom configuration alone was compared with a weighted reciprocal-lattice section drawn with weights proportional to (F_o-F_c) values, taking only the low-angle reflexions. The inclusion of the hydrogen-atom param-

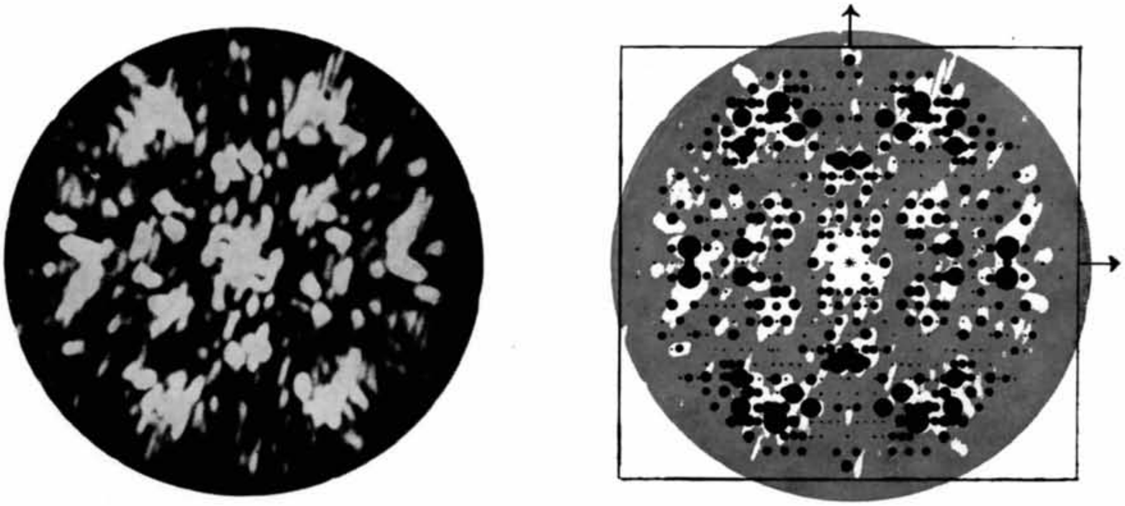


Fig. 4. The optical agreement with coordinates derived from final $F_o(hk0)$ synthesis. On the left is the optical transform of the contents of a unit-cell projected along [001]; on the right Fig. 1 is superimposed.

eters in the structure-factor calculation and the minor adjustments in the coordinates of the atoms as suggested by the difference electron density map reduced the agreement residual to 18%. McWeeny's (1951) scattering-factor curve for hydrogen was used and the same isotropic temperature factor as that of the heavy atoms was chosen. Adjustments of individual isotropic temperature factors for some atoms were also suggested and the pattern of the difference map around the sulphur atom appeared to be quite characteristic of anisotropic thermal motion (Cochran, 1951), indicating the direction of maximum vibration to be inclined at an angle of nearly 35° to the *a*-axis. The values of the temperature coefficients are given in Table 1. The adjustment of individual isotropic and anisotropic temperature factors further reduced the R index to 17%.

Table 1. *Temperature coefficients used in the final calculation of hk0 structure factors*

	B(Å^2)		B(Å^2)
S	max. 3·4	C(9)	4·9
	min. 1·8	C(10)	4·1
C(1)	4·1	C(11)	5·1
C(2)	4·1	C(12)	4·6
C(3)	4·1	C(13)	5·0
C(4)	4·1	N(1)	4·1
C(5)	4·7	N(2)	4·1
C(6)	5·0	N(3)	4·1
C(7)	4·1		
C(8)	4·1		

For a few strong low-angle reflexions the calculated structure factors were found to be consistently higher than the observed values, indicating a secondary extinction effect. These reflexions are listed in Table 2. An empirical correction for secondary extinction was applied to these reflexions, as described by Pinnock, Taylor & Lipson (1956). With this correction the overall agreement came down to 15%. The unobserved reflexions were also included in the R index calculation, with a given value of half the least observable value in their respective regions. The values of observed and calculated structure factors are shown in Table 3.

Table 2. *Reflexions affected by extinction*

*hk*0	F_c	F_o
120	57	41
200	78	54
230	69	48
330	70	49
490	47	37

The projection along [100]

Determination of the trial z coordinate

As in the case of the [001] projection, the approximate structure of the [100] projection was deduced from optical-transform methods in conjunction with a Patterson projection. Assuming normal bond distances and angles, a wire model of azobenzene-2-sulphenyl cyanide of *trans* configuration was constructed and the model so orientated that its shadow, cast on the electron-density projection along [001] by a beam of light parallel to the [001] axis, fitted fairly well. The shadow produced by a second beam of light parallel to the [100] axis then gave the approximate shape of the molecule on the (100) plane. Out of a few alternative models that were obtained in this way, corresponding to different possible orientations of the benzene rings, one was selected that gave an optical transform showing the best match with the 0*kl* weighted reciprocal-lattice section. The problem of locating the molecule was solved by Patterson synthesis. Inspection of the Patterson projection [Fig. 2(*b*)] along [100] indicated 0·250 and 0 as the possible approximate values of the z parameter of the representative sulphur atom, corresponding to glide-reflexion peaks P and Q displayed on the line $y=\frac{1}{2}$. Assuming the y parameter from the [001] projection, these locations were subjected to an optical-transform test of four molecules and the sulphur position (0·361, 0·250) was readily selected. A structure factor calculation with this model gave an agreement residual of 31%; the y parameters, however, had been assumed from the [001] projection.

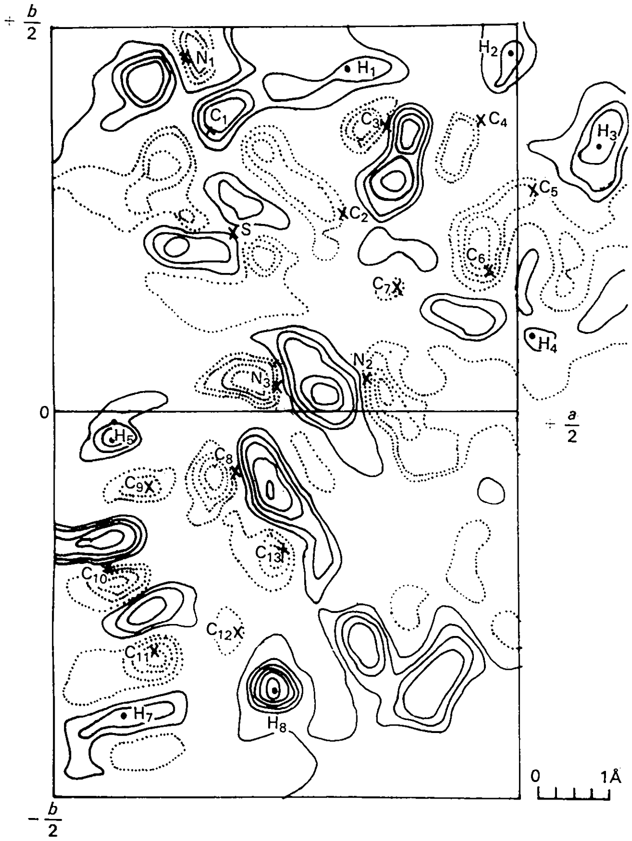


Fig. 5. Difference electron density projection on (001), showing the resolution of the hydrogen atoms and anisotropy in the thermal vibration of the sulphur atom. Contours are drawn at intervals of 0·1 e.Å^{-2}. Negative contours are dotted.

Table 3. *Observed and calculated structure factors (origin on 2_1 axis parallel to the c axis for hk0 structure factors and on 2_1 axis parallel to the a axis for 0kl structure factors)*

* Indicates structure factors corrected for extinction.

h	k	l	F_o	F_c
0	2	0	33.9	40.6
0	4	0	90.0	-97.1
0	6	0	9.9	12.9
0	8	0	27.9	38.9
0	10	0	24.6	26.5
0	12	0	18.4	-14.7
0	14	0	22.3	-29.1
0	16	0	-	3.0
0	18	0	10.1	-4.7
0	20	0	7.3	-5.8
0	22	0	-	4.0
0	24	0	-	-2.4
0	26	0	6.1	6.2
*2	0	0	87.0	-80.0
4	0	0	-	-3.0
6	0	0	40.3	41.3
8	0	0	8.4	12.9
10	0	0	6.7	6.2
12	0	0	5.7	10.8
14	0	0	10.3	10.9
16	0	0	5.3	4.6
1	1	0	6.5	-8.0
*1	2	0	59.4	-57.7
1	3	0	10.4	9.1
1	4	0	26.2	30.7
1	5	0	13.6	-11.5
1	6	0	-	-4.0
1	7	0	11.0	4.4
1	8	0	30.6	26.6
1	9	0	21.1	16.4
1	10	0	44.5	48.7
1	11	0	24.7	-24.5
1	12	0	44.0	-46.0
1	13	0	11.8	-10.6
1	14	0	9.2	9.8
1	15	0	12.6	-14.7
1	16	0	15.6	10.9
1	17	0	13.8	14.1
1	18	0	34.3	40.6
1	19	0	11.2	16.6
1	20	0	11.7	-15.6
1	21	0	-	4.6
1	22	0	-	-3.3
1	23	0	-	-2.0
1	24	0	5.7	2.5
1	25	0	6.8	3.6
2	1	0	28.2	25.3
2	2	0	36.7	-43.7
*2	3	0	66.3	68.3
2	4	0	-	-3.8
2	5	0	14.3	13.9
2	6	0	14.7	-11.7
2	7	0	55.2	61.5
2	8	0	44.0	-43.2
2	9	0	6.0	2.2
2	10	0	7.4	-9.0
2	11	0	9.5	-11.7
2	12	0	23.3	22.2
2	13	0	5.9	9.3
2	14	0	14.2	13.9
2	15	0	18.9	20.0
2	16	0	9.5	-9.0
2	17	0	7.0	5.5
2	18	0	6.5	-7.4
2	19	0	18.0	-19.8
2	20	0	11.3	16.6
2	21	0	-	2.2
2	22	0	6.3	9.8
3	1	0	41.1	-43.8
3	2	0	14.8	15.5
*3	3	0	64.0	69.4
3	4	0	10.3	12.8
3	5	0	9.5	8.5
3	6	0	33.3	-32.2
3	7	0	-	-1.3
3	8	0	31.5	29.0
3	9	0	9.0	-8.5
3	10	0	42.6	40.4
3	11	0	26.9	25.8
3	12	0	7.2	7.2
3	13	0	15.8	16.1
3	14	0	10.5	-11.7
3	15	0	6.6	5.9
3	16	0	8.1	8.2
3	17	0	14.5	-14.9
3	18	0	-	1.2
3	19	0	8.8	-7.4
3	20	0	16.1	19.6
3	21	0	-	2.1
3	22	0	-	5.0
3	23	0	-	0.7
3	24	0	-	-6.0
3	25	0	-	4.6
3	26	0	6.9	1.3
4	1	0	43.3	-36.4
4	2	0	28.5	29.2
4	3	0	18.6	17.4
4	4	0	26.8	-28.1
4	5	0	6.8	-12.2
4	6	0	4.6	3.2
4	7	0	45.3	-43.1
4	8	0	22.7	25.0
*4	9	0	40.0	-46.5
4	10	0	18.3	19.7
4	11	0	23.5	22.2
4	12	0	-	0.8
4	13	0	14.5	15.2
4	14	0	-	4.6
4	15	0	24.2	-29.9
4	16	0	-	3.0
4	17	0	4.5	-9.5
4	18	0	-	-2.0
4	19	0	9.9	10.9
4	20	0	-	0.9
4	21	0	5.5	6.7
4	22	0	-	-5.0
4	23	0	-	2.2
4	24	0	4.0	0.1
4	25	0	-	-3.2
4	26	0	5.4	-3.0
5	1	0	10.7	11.2
5	2	0	46.9	47.2
5	3	0	14.5	-17.7
5	4	0	5.7	-3.5
5	5	0	21.0	-24.9
5	6	0	7.3	-4.1
5	7	0	-	-0.7
5	8	0	17.7	-19.7
5	9	0	15.2	18.2
5	10	0	6.8	4.7
5	11	0	6.6	8.7
5	12	0	-	4.1
5	13	0	24.2	-27.7
5	14	0	5.2	5.7
5	15	0	-	3.3
5	16	0	5.5	-6.6
5	17	0	15.9	16.8
5	18	0	4.3	6.9
5	19	0	-	-2.7
5	20	0	5.6	-5.6
5	21	0	6.9	-12.9
5	22	0	-	-0.6
5	23	0	-	3.1
5	24	0	-	1.8
5	25	0	-	-2.1
5	26	0	4.7	-2.7
6	1	0	10.0	-8.4
6	2	0	24.8	-20.7
6	3	0	26.3	-27.0
6	4	0	17.9	-16.6
6	5	0	19.0	18.3
6	6	0	-	1.0
6	7	0	7.8	4.5
6	8	0	14.5	13.5
6	9	0	-	-3.0
6	10	0	-	2.0
6	11	0	7.6	-7.6
6	12	0	14.6	-11.9
6	13	0	-	1.3
6	14	0	8.3	-7.9
6	15	0	11.1	13.9
6	16	0	3.0	11.0
6	17	0	-	3.5
6	18	0	-	-2.9
6	19	0	10.4	-14.8
6	20	0	6.6	-10.0
6	21	0	-	-5.3
6	22	0	-	3.0
6	23	0	6.0	8.5
7	1	0	52.1	-49.3
7	2	0	45.9	-46.8
7	3	0	10.9	9.4
7	4	0	-	0.5
7	5	0	19.7	22.9
7	6	0	15.2	14.8
7	7	0	15.1	-13.9
7	8	0	14.3	11.6
7	9	0	6.6	-3.4
7	10	0	11.4	-2.5
7	11	0	-	2.8
7	12	0	14.6	-14.5
7	13	0	15.4	15.7
7	14	0	16.1	16.1
7	15	0	-	-2.0
7	16	0	9.9	10.4
8	1	0	-	-2.2
8	2	0	-	-0.2
8	3	0	11.3	13.0
8	4	0	27.8	26.6
8	5	0	-	-0.3
8	6	0	-	3.8
8	7	0	10.3	-9.4
8	8	0	24.2	-23.3
8	9	0	13.3	-14.0
8	10	0	7.5	-10.3
8	11	0	16.1	17.1
8	12	0	25.3	27.9
8	13	0	10.5	12.6
8	14	0	12.5	16.7
8	15	0	-	-4.0
8	16	0	12.0	-11.4
8	17	0	6.8	5.3
8	18	0	9.4	7.3
8	19	0	4.2	5.0
8	20	0	-	3.2
8	21	0	-	0.8
8	22	0	5.6	5.7
9	1	0	8.9	6.4
9	2	0	-	5.2
9	3	0	10.4	8.0
9	4	0	-	2.6
9	5	0	9.4	6.4
9	6	0	37.3	-42.1
9	7	0	13.1	8.5
9	8	0	10.0	-10.4
9	9	0	-	3.5
9	10	0	11.9	11.4
9	11	0	15.5	11.1
9	12	0	-	0
9	13	0	-	2.0
9	14	0	14.3	-17.7
9	15	0	-	-0.3
9	16	0	7.5	-6.6
9	17	0	-	2.3
9	18	0	-	1.9
9	19	0	-	0.2
9	20	0	8.2	12.2
10	1	0	12.0	10.5
10	2	0	-	2.2
10	3	0	-	1.0
10	4	0	27.6	-27.2
10	5	0	8.6	-5.2
10	6	0	-	-2.8
10	7	0	12.3	3.3
10	8	0	13.2	15.7
10	9	0	17.4	-18.6
10	10	0	11.5	-14.6
10	11	0	-	-4.0
10	12	0	17.8	-22.2
10	13	0	5.7	2.5
10	14	0	-	-1.9
10	15	0	7.0	-6.4
10	16	0	6.7	5.4
10	17	0	-	3.5
10	18	0	7.0	7.2
11	1	0	10.9	13.6
11	2	0	9.6	-9.7
11	3	0	9.6	-8.2
11	4	0	6.1	-6.2
11	5	0	-	-1.1
11	6	0	18.9	18.3
11	7	0	-	-2.0
11	8	0	24.5	-28.7
11	9	0	-	-4.1
11	10	0	6.8	4.9
11	11	0	6.9	8.9
11	12	0	9.4	-10.1
11	13	0	9.5	-13.5
11	14	0	-	3.9
11	15	0	-	0.8
11	16	0	5.5	8.1
12	1	0	-	1.7
12	2	0	-	4.0
12	3	0	8.0	-7.0
12	4	0	10.3	14.8
12	5	0	10.7	9.9
12	6	0	6.5	6.2
12	7	0	7.6	7.7
12	8	0	-	3.0
12	9	0	-	-2.3
12	10	0	-	-2.2
12	11	0	9.9	-10.4
12	12	0	-	1.0
12	13	0	-	0.2
12	14	0	-	0.9
12	15	0	6.6	6.8
13	1	0	10.1	-12.5
13	2	0	-	0.6
13	3	0	-	-0.6
13	4	0	-	-0.6
13	5	0	8.0	8.2
13	6	0	-	-2.8
13	7	0	6.8	-9.7
13	8	0	-	-2.8
13	9	0	5.4	-5.7
13	10	0	-	-1.2
13	11	0	5.8	7.2
13	12	0	6.7	-7.1
13	13	0	8.5	6.6
14	7	0	7.6	-7.3
14	8	0	-	3.0
14	9	0	-	4.2
14	10	0	-	-0.8
14	11	0	8.8	-6.9
15	1	0	6.9	9.1
15	2	0	4.9	3.2
15	3	0	-	-4.1
15	4	0	-	-1.0
15	5	0	7.1	-6.6
15	6	0	4.8	-3.8
15	7	0	-	3.9
15	8	0	-	2.2
15	9	0	7.7	10.0
15	10	0	4.4	2.7
0	0	2	16.2	-10.0
0	0	4	4.5	5.8
0	2	0	44.9	-40.6
0	4	0	90.0	-96.6
0	6	0	12.1	-13.0
0	8	0	36.2	33.4
0	10	0	28.2	-24.4
0	12	0	20.5	-16.9
0	14	0	25.0	25.3
0	16	0	-	3.0
0	18	0	11.4	7.2
0	20	0	7.4	-4.3
0	22	0	-	-4.0
0	24	0	4.7	-6.8
0	26	0	9.0	-6.3
0	1	1	6.5	-16.1
0	2	1	31.2	28.0
0	3	1	8.9	-10.2
0	4	1	29.6	32.0
0	5	1	10.6	-7.6
0	6	1	37.2	-45.8
0	7	1	9.8	-12.3
0	8	1	13.3	12.1
0	9	1	7.1	-5.5
0	10	1	15.1	12.3
0	11	1	23.3	-23.3
0	12	1	15.0	-14.7
0	13	1	14.7	11.9
0	14	1	25.2	-26.0
0	15	1	8.3	-3.0
0	16	1	14.6	14.6
0	17	1	28.7	26.8
0	18	1	15.4	14.9
0	19	1	13.1	-11.6
0	20	1	7.8	-7.8
0	21	1	-	2.0
0	22	1	4.1	8.4
0	23	1	4.0	2.4
0	24	1	6.4	7.5
0	1	2	11.5	-11.8
0	2	2	-	1.3
0	3	2	2.7	6.3
0	4	2	41.7	54.7
0	5	2	3.7	-10.9
0	6	2	21.0	-27.2
0	7	2	-	-3.0
0	8	2	19.3	-21.0
0	9	2	8.0	4.4
0	10	2	9.9	17.0
0	11	2	11.4	12.7
0	12	2	7.9	8.4
0	13	2	14.4	-10.6
0	14	2	5.4	-5.0
0	15	2	-	2.5
0	16	2	7.7	-6.1
0	17	2	15.7	11.7
0	18	2	12.9	9.2
0	19	2	5.3	-7.9
0	20	2	-	-2.7
0	21	2	3.3	-1.4
0	22	2	7.5	-3.0
0	23	2	2.3	-1.6
0	24	2	4.3	-3.3
0	1	3	-	1.9
0	2	3	10.6	-8.6
0	3	3	-	-3.1
0	4	3	14.6	7.8
0	5	3	4.2	4.0
0	6	3	6.2	4.9
0	7	3	4.8	1.0
0	8	3	8.3	-10.0
0	9	3	8.0	-7.6
0	10	3	11.1	-10.9
0	11	3	-	0
0	12	3	6.5	6.7
0	13	3	4.8	3.4
0	14	3	-	3.1
0	15	3	2.9	-1.0
0	16	3	4.8	-5.2
0	17	3	5.0	-1.9
0	18	3	-	2.7
0	19	3	-	-3.4
0	20	3	7.8	9.3
0	1	4	-	4.0
0	2	4	2.9	-1.9
0	3	4	-	1.0
0	4	4	-	-2.9
0	5	4	-	3.0
0	6	4	-	-3.3
0	7	4	-	3.8
0	8	4	6.2	9.2
0	9	4	-	1.0
0	10	4	-	-2.2
0	11	4	-	-3.1
0	12	4	3.9	-4.8

As stated earlier, in calculating the $0kl$ structure factors, the origin of the coordinates was taken at $(0, -\frac{1}{4}b, 0)$ with respect to the origin chosen for the c-axis projection.

Refinement of the projection along [100]

Refinement by Fourier and difference Fourier syntheses brought the R index down to 21%. The interpretation of the difference electron-density map did not help in the adjustment of individual temperature factors and location of hydrogen atoms. The same isotropic temperature parameter $B = 4{\cdot}1$ Å^2 was therefore used for all the atoms and the z coordinates of the hydrogen atoms were calculated from x and y coordinates obtained from the [001] projection, assuming C–H distances to be 1·09 Å. Inclusion of the hydrogen parameters in the structure factor calculation reduced the R index to 20%.

The observed and calculated structure factors are listed in Table 3 and the final F_o synthesis of the $0kl$ reflexions is shown in Fig. 6.

Atomic coordinates and estimation of accuracy

The final atomic coordinates are listed in Table 4.

Table 4. *Final atomic coordinates*

	x (Å)	y (Å)	z (Å)
C(1)	2·213	4·045	0·388
C(2)	4·075	2·839	1·575
C(3)	4·750	4·015	1·450
C(4)	6·000	4·138	2·135
C(5)	6·725	3·138	2·700
C(6)	6·095	1·975	2·863
C(7)	4·825	1·788	2·213
C(8)	2·550	−0·838	1·988
C(9)	1·363	−1·038	1·288
C(10)	0·740	−2·225	1·288
C(11)	1·425	−3·388	1·800
C(12)	2·595	−3·138	2·463
C(13)	3·250	−1·950	2·558
N(1)	1·825	5·055	−0·123
N(2)	4·388	0·475	1·920
N(3)	3·250	0·365	2·345
S	2·530	2·550	0·983
H(1)	4·17	4·91	1·21
H(2)	6·47	5·07	2·42
H(3)	7·81	3·26	2·80
H(4)	6·71	1·09	3·00
H(5)	0·84	−0·14	0·95
H(6)	−0·30	−2·34	0·98
H(7)	0·99	−4·34	1·49
H(8)	3·11	−3·97	2·93
H(9)	4·29	−1·82	2·87

The standard deviations in the coordinates have been estimated from the differences between observed and calculated F values using the method described by Cruickshank (1949). The average values of $\sigma(x)$ and $\sigma(y)$ for the carbon atoms are calculated from well-resolved peaks. Owing to poor resolution of the electron-density projection along [100], the average $\sigma(z)$ for the light atoms has been obtained only from three resolved carbon atoms. The $\sigma(z)$ value is thus a definite underestimate. The standard deviations obtained are:

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C	0·017	0·020	0·026
N	0·013	0·016	0·026
S	0·004	0·004	0·021

The intramolecular bond lengths and bond angles are listed in Table 5; the indicated errors in bond lengths are the standard deviations estimated according to the formula of Ahmed & Cruickshank (1953).

Table 5. *Values of bond lengths and bond angles*

Bond lengths		Bond angles	
N(1)≡C(1)	1·20 ± 0·03 Å	N(1)≡C(1)—S	148°
C(1)—S	1·89 ± 0·02	C(1)—S——C(2)	97
S——C(2)	1·68 ± 0·02	S——C(2)—C(3)	124
C(2)—C(3)	1·36 ± 0·05	C(2)—C(3)—C(4)	117
C(3)—C(4)	1·44 ± 0·03	C(3)—C(4)—C(5)	126
C(4)—C(5)	1·36 ± 0·03	C(4)—C(5)—C(6)	119
C(5)—C(6)	1·33 ± 0·03	C(5)—C(6)—C(7)	118
C(6)—C(7)	1·44 ± 0·03	C(6)—C(7)—C(2)	124

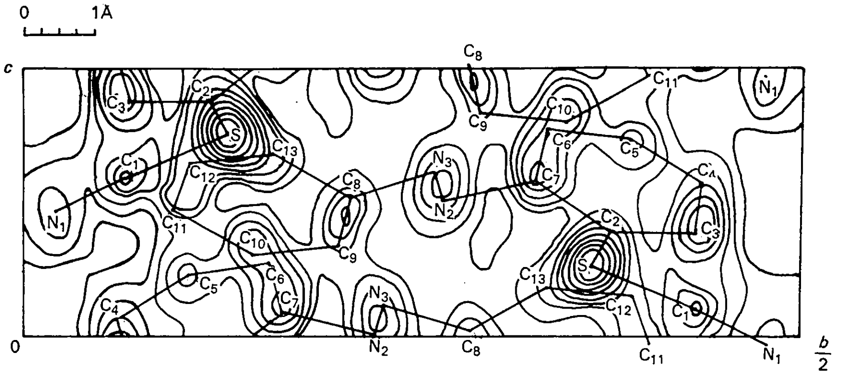


Fig. 6. Electron density projection on (100). Contours are drawn at intervals of 1 e.Å^{-2} at the carbon and nitrogen atoms and those at the sulphur atoms at intervals of 2 e.Å^{-2}.

Table 5 (*cont.*)

Bond lengths		Bond angles	
C(7)—C(2)	1·44 ± 0·03	C(6)—C(7)—N(2)	120
C(7)—N(2)	1·42 ± 0·03	C(7)—N(2)=N(3)	107
N(2)=N(3)	1·22 ± 0·02	N(2)=N(3)—C(8)	116
N(3)—C(8)	1·44 ± 0·02	N(3)—C(8)—C(9)	131
C(8)—C(9)	1·39 ± 0·03	C(13)-C(8)—C(9)	120
C(9)—C(10)	1·34 ± 0·03	C(8)—C(9)—C(10)	121
C(10)-C(11)	1·44 ± 0·03	C(9)—C(10)-C(11)	119
C(11)-C(12)	1·37 ± 0·03	C(10)-C(11)-C(12)	115
C(12)-C(13)	1·36 ± 0·03	C(11)-C(12)-C(13)	127
C(13)-C(8)	1·43 ± 0·03	C(12)-C(13)-C(8)	115

The configuration of the azobenzene-2-sulphenyl cyanide molecule and the arrangement of the molecules in the crystal lattice are indicated in Fig. 7. The packing is consistent with intermolecular binding by van der Waals forces, the shortest intermolecular approach being 3·52 Å.

Geometry of the azobenzene-2-sulphenyl cyanide molecule

The equations to the best plane through the aromatic rings C(2)C(3)C(4)C(5)C(6)C(7) and C(8)C(9)C(10)-C(11)C(12)C(13), derived by the method of least-squares are respectively:

$$-0{\cdot}720x+0{\cdot}546y+1{\cdot}512z=1$$

$$-0{\cdot}362x-0{\cdot}007y+0{\cdot}877z=1\ .$$

The displacements of the atoms in the aromatic rings from their corresponding mean planes are shown in Table 6.

Table 6. *Perpendicular distances of the atoms in the aromatic rings from their corresponding mean planes*

	Distance (Å)		Distance (Å)
C(2)	−0·002	C(8)	−0·196
C(3)	−0·002	C(9)	−0·375
C(4)	0·094	C(10)	−0·129
C(5)	−0·003	C(11)	0·091
C(6)	0·001	C(12)	0·256
C(7)	−0·086	C(13)	0·084

The atoms in the ring C(2)C(3)C(4)C(5)C(6)C(7) are very close to the mean plane, whereas in the case of the ring C(8)C(9)C(10)C(11)C(12)C(13) the displacements of the atoms C(8), C(9) and C(12) are appreciable. However, the accuracy of the atomic coordinates, particularly of the *z* coordinates, does not permit any emphasis to be placed on the distortion of the rings. The calculated angles of inclination of the rings C(2)C(3)C(4)C(5)C(6)C(7) and C(8)C(9)C(10)C(11)-C(12)C(13) to the (001) plane are 31° and 23° respectively in the same sense. This definitely indicates that the molecule of azobenzene-2-sulphenyl cyanide is not planar.

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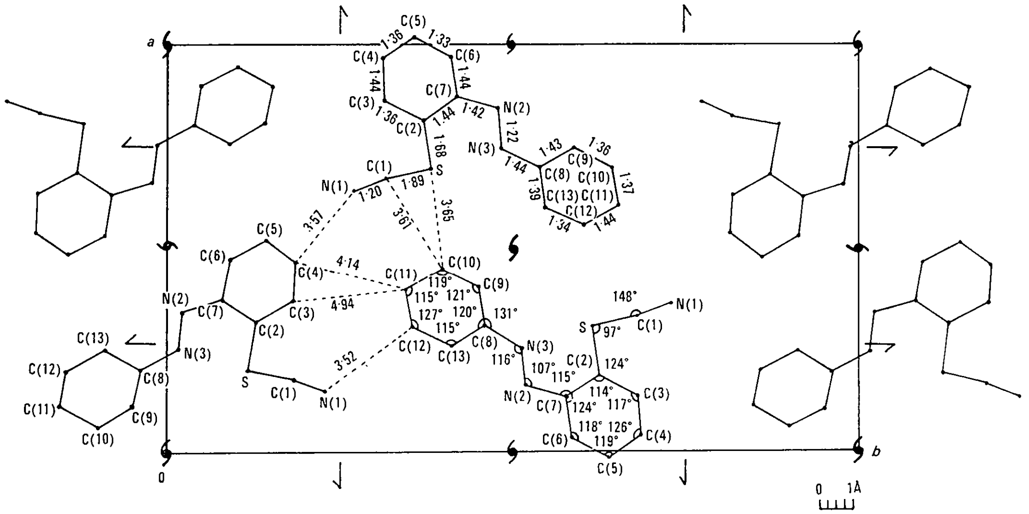

Fig. 7. Contents of a unit cell of azobenzene-2-sulphenyl cyanide viewed along the *c* axis. Intramolecular bond lengths, bond angles and intermolecular distances are indicated.

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The Crystal Structure of D,L-Arabinitol

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The crystal structure of D,L-arabinitol, $C_5H_7(OH)_5$, was derived from the three-dimensional E^2-1 Patterson function by means of minimum functions. The structure was refined anisotropically by least squares to an R value of 0·037 for 557 reflections. The lattice parameters are $a=9\cdot213(1)$, $b=4\cdot855(2)$ and $c=15\cdot490(2)$ Å ($Z=4$). The D and L molecules are related by glide planes in the space group $Pna2_1$. The molecule has a planar zigzag carbon chain with oxygen atoms above and below the plane. All oxygen atoms are involved in a three-dimensional hydrogen-bonding scheme consisting of chains coiled around the screw axes.

Introduction

Arabinitol (lyxitol) is an acyclic polyalcohol formerly known as arabitol. Since D-arabinitol is 40–60% as sweet as sucrose, and experiments have shown that little or none is assimilated in the body, this substance has been suggested as a sugar substitute in foods (Crick, 1958).

The D form occurs in lichens (Lindberg, Misiorny & Wachtmeister, 1953) as the free carbohydrate and also as the galactoside, umbilicin. Neither L- nor D,L-arabinitol is found naturally. The L form is prepared by the catalytic reduction (Prince & Reichstein, 1937) of β-L-arabinose, which is obtained from mesquite gum (Anderson & Sands, 1929), and crystallization of a solution of an equimolar mixture of the enantiomorphs yields D,L-arabinitol.

As can be seen from the Fischer formulas below (with the terminal hydroxyls turned to the right by convention), arabinitol lies in a configurational sequence of increasing chain length between erythritol (*meso*-erythritol) and mannitol and also between threitol and galactitol. The terminal hydroxyls in these polyols are found in two different staggered conformations. The hydroxyl either continues the carbon chain to give an 'extended' conformation or it turns away from the chain in what might be called a 'flexed' conformation. Erythritol and mannitol are flexed at both ends. Threitol has not been studied, but the hydroxyls at both ends of galactitol are extended, as is the ter-

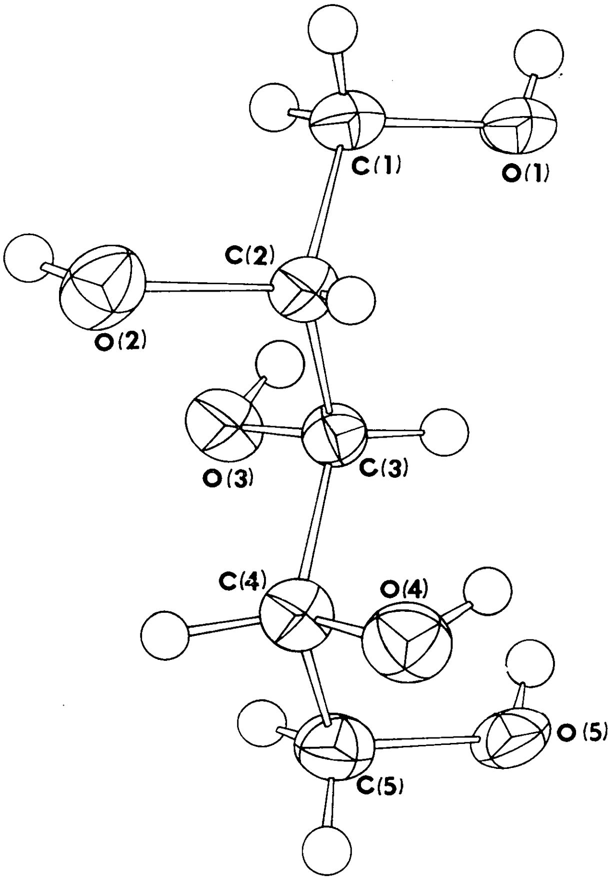

Fig. 1. D-Arabinitol molecule, showing atomic identification and thermal ellipsoids.

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