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A preliminary crystallographic examination of 1:4-dithian.

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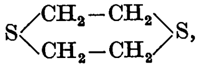
Goniometric and X-ray diffraction measurements have been made on dithian and its unit cell and space group have been determined.

1:4-Dithian,  $S\langle\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}\rangle S$, molecular weight 120·2, tends to crystallize in fern-like multiple growths from ethyl alcohol. Large, well-formed crystals suitable for goniometric examination can be obtained from carbon disulphide or ethyl ether. These are usually of tabular habit. A carbon disulphide–ligroin mixture yields either needle or plate-like crystals suitable for single-crystal X-ray diffraction analysis.

The crystal habit of this substance is not mentioned by Groth (1906–1919) but it was previously referred to in the literature by two early workers, Crafts (1862) and Husemann (1863), of whom only the former made actual measurements.

Goniometric examination and optical properties

The crystals were monoclinic and their habit, according to the Barker setting (Porter & Spiller, 1951) a combination of *m*(110), *r*(101) and *R*($\bar{1}$01). The usual tabular development has *R* large and *m* fairly small. Sometimes the crystals were elongated along the *b* axis with *R* and *r* equally developed. The face *a*(100) was occasionally observed as a minute bevel on the edge *Rr*.

The following are the mean angular measurements from a number of selected crystals observed on a two-circle goniometer:

	R′(10$\bar{1}$)	*a*(100)	*r*(101)	*m*(110)
φ	0°	50° 35′	98° 23′	50° 35′
ϱ	90°	90°	90°	34° 50′

These figures give

$$\beta = 92^\circ\ 26' \quad \text{and} \quad a:b:c = 1\cdot438:1:1\cdot242$$

with the following Barker classification angles: *cr* 39° 46′; *ra* 47° 48′; *am* 55° 10′; *bq* 38° 52′.

Both *R* and *r* show extinctions which are straight to the edge *Rr*. In convergent polarized light one optic axis can be seen emerging nearly perpendicular to the face *r*, the optic axial plane being perpendicular to the edge *Rr* and therefore coincident with the symmetry plane. When the crystal is observed on the face *R* the brushes of the other optic axis can be seen but not the axis itself.

The habit described by Crafts with *m* predominating was not observed, but the angular measurements are in good agreement:

	Crafts	Calculated from present data
mm	69° 44′	69° 40′
ar	47 59	47 48
mr	67 30	67 26
mR′	68 49	68 44

If the alternative setting is adopted making *R′* = *c*(001), *m*(110) and *r*($\bar{2}$01) this gives

$$\beta = 129^\circ\ 25' \quad \text{and} \quad a:b:c = 1\cdot860:1:1\cdot243\,.$$

X-ray diffraction examination

Difficulties arise in the single-crystal X-ray analysis of dithian owing to its great volatility. It can, however, be preserved long enough for examination by enclosure in thin-walled Lindemann glass capillaries.

Single-crystal rotation photographs showed a monoclinic cell, the needle axis being coincident with the *b* axis, with

$$a = 10\cdot09,\ b = 5\cdot46,\ c = 6\cdot74\ \text{Å},\ (a:b:c = 1\cdot85:1:1\cdot23),\quad \beta = 130^\circ\ 22',$$

figures which are in reasonable agreement with the goniometric results, bearing in mind the difficulties just mentioned. The wavelength of Cu $K\alpha$ radiation was taken as 1·542 Å.

Oscillation photographs showed *hkl* reflexions present in all orders, *h*0*l* halved for *h* odd, and 0*k*0 halved for *k* odd, indicating the space group C_{2h}^5–$P2_1/a$.

The density determined by flotation, 1·24 g.cm.$^{-3}$, leads to the conclusion that there are 2 molecules per unit cell. Since the space group $P2_1/a$ has four general positions, it follows that the molecule must have a centre of symmetry.

This conclusion accords with the work of Hassel & Viervoll (1947) who found, from an electron-diffraction study of the vapour, that the centrosymmetrical 'chair' (*trans*) ring is the most probable structure. Dipole-moment measurements of dithian in benzene solution by Calderbank & Le Fèvre (1949) also indicate a centrosymmetrical molecule.

The space group can alternatively be taken as $P2_1/n$, with

$$a = 7\cdot69,\ b = 5\cdot46,\ c = 6\cdot74\ \text{Å},\ (a:b:c = 1\cdot41:1:1\cdot23),\quad \beta = 91^\circ\ 32'.$$

Table 1 gives the powder-pattern spacings and visually estimated relative intensities, using Cu $K\alpha$ radiation.

Table 1. *Powder-pattern spacings and relative intensities for* 1:4-*dithian*

d (Å)	Relative intensity
5·32	14
4·53	46
3·95	28
3·67	32
3·35	11
3·14	15
2·75	7
2·66	7
2·53	10
2·37	1
2·20	5
2·11	5
2·03	1
1·977	1
1·902	5
1·772	6
1·657	3
1·572	3
1·414	1
1·340	2
1·274	2
1·204	1
1·151	1

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The crystal structure of high cyclobutane.*

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According to Rathjens & Gwinn (1953), cyclobutane melts at 182° K. and has a transition point at about 145° K. We have investigated the structures of the two solid forms by the X-ray diffraction method.

Samples provided by Dr Rathjens were sealed in Pyrex capillaries, mounted in the camera, and cooled in the usual way with a stream of cold nitrogen gas. Powder patterns of the low-temperature form contain many lines. The structure is not cubic and has not been solved. Powder patterns of the high form show only a single line, which is assigned to 110 on the basis of the single-crystal work.

Slow freezing resulted in single crystals of the high form whose orientations seemed to be random in the capillary. Rotation photographs of four such crystals at about 173° K. (axes of rotation approximately [100], [311], [531] and [441], respectively) show the unit cell to be body-centered cubic, with

$$a = 6{\cdot}06 \pm 0{\cdot}03\ \text{Å}\ (\lambda\ \text{Cu}\ K\alpha = 1{\cdot}542\ \text{Å})\,.$$

Though only reflections of the forms {110} and {200} are observed, the interpretation is unique because the crystals were misaligned enough to permit independent observation of 'coincident' reflections in nearly every case so that the multiplicities of the forms were determined. The distribution of the spots among the various layer lines was also checked in each case. This unit cell, with two molecules, corresponds to a calculated density of $0{\cdot}84 \pm 0{\cdot}01$ g.cm.$^{-3}$.

If the origin is chosen at the center of gravity of one molecule, then the second molecule must be at the body center. To achieve cubic symmetry, these molecules must have rotational disorder, either static or dynamic. The rapid decrease of intensity with increasing Bragg angle is explained by rotational disorder which approaches spherical symmetry. The calculations were based on the molecular dimensions deduced by Dunitz & Schomaker (1952) by electron diffraction of the gas. Since the intermolecular distance, 5·25 Å between centers, is substantially smaller than the largest van der Waals diameter of cyclobutane, the rotations are expected to be hindered.

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Unit-cell dimensions and space groups of synthetic peptides. II. Glycyl-L-alanine, glycyl-L-alanine hydrochloride, glycyl-L-alanine hydrobromide and glycyl-L-tryptophane.

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As part of the research programme on the structures of crystalline peptides recently begun by the Wool Industries Research Association (Tranter, 1952) preliminary X-ray data have now been obtained for glycyl-L-alanine, the hydrochloride and hydrobromide derived from this peptide and for glycyl-L-tryptophane.

Source of peptides

*Glycyl-*DL*-alanine* was readily synthesized by the chloroacetyl method first described by Fischer & Otto (1903) and the purity of the final product was checked chromatographically. In the meanwhile, preliminary X-ray data for this material had appeared (Pasternak & Leonard, 1952), and it was therefore decided to examine the optically active dipeptide instead. Attempts to prepare it by the same method were not very successful and glycyl-L-alanine was finally obtained in the pure state by the 'carbobenzoxy' method (Bergmann & Zervas, 1932). After removal of the 'protective' grouping by catalytic hydrogenation the free peptide crystallized from water more easily than the DL-isomer in the form of large needles.