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Two-dimensional refinement of the crystal structure of tellurium.

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A two-dimensional refinement of the structure of tellurium has been completed by single-crystal and counter techniques. The bond length determined is 2·835 (σ=0·002) Å; the bond angle is 103·2° (σ=0·1°) and the next nearest neighbor distance is 3·495 (σ=0·003) Å. The thermal motion in the plane perpendicular to the *c* axis is rather isotropic.

In a recent redetermination of the structure of trigonal selenium (Cherin & Unger, 1966), the interatomic distances were found to be significantly different from those previously determined by Bradley (1924). Therefore, it was felt that the structure of tellurium, also determined by Bradley (1924) should be redefined with the use of modern techniques of collecting and analyzing data.

Tellurium crystallizes in the trigonal system in the space group $P3_121$ or $P3_221$. The hexagonal unit-cell dimensions, as determined by Swanson & Tatge (1951) are a=4·4572, c=5·9290 Å. The observed density is 6·25 g.cm^{-3}, and the X-ray density is 6·2259 g.cm^{-3}. There are three atoms in the unit cell which are part of an infinite chain parallel to the *c* axis. There is one atom per asymetric unit, which lies on a twofold axis. Therefore, only one position parameter need be determined. For this purpose two-dimensional data (*hk*0) are adequate, although they do not enable U_{33}, the r.m.s. vibrational amplitude component parallel to **c**, to be determined.

The stationary-counter stationary-crystal method, as described by Alexander & Smith (1962), was used with single tellurium crystals grown from the vapor (Keezer, 1962). The crystal was aligned along its needle axis (*c* axis); two-dimensional data (*hk*0) were collected with the use of a General Electric Goniostat and Mo $K\alpha$ (Zr filtered) radiation. The intensity of each reflection was recorded three times, and a full set of equivalent reflections was measured. The standard deviations of these measurements were used to calculate the weights of the ensuing least-squares analysis.

An anomalous dispersion correction was applied directly to the observed structure factors, a procedure which is valid in the case where all atoms are of the same kind. The relationship used was as follows:

$$F_{\rm corr}=F_o/[(1+\delta_1)^2+\delta_2^2]^{\frac{1}{2}}\ ,$$

where

$$\delta_1=\Delta f'/f_0\ ,\quad \delta_2=\Delta f''/f_0\ .$$

The quantities f_0, $\Delta f'$, and $\Delta f''$ were taken *International Tables for X-Ray Crystallography* (1962).

A least-squares analysis was carried out with the program ORFLS written by Busing, Martin & Levy (1962). The refinement was initiated with the positional parameter reported by Bradley (1924). The refinement converged quickly, and after five cycles R dropped to 6·0%. (An absorption correction had been applied assuming the crystal was cylindrical with a diameter of 0·1 mm.) The estimated diameter was then permitted to vary by 10%. The result which had both the smallest standard deviations and the lowest value of R, defined as $\sum\limits_n ||F_o|-|F_c||/\sum\limits_n |F_o|$ (only observed reflections were used in the refinement), was chosen as the final refinement; the final R was 5·0%. Throughout the absorption variation procedure the x parameter never changed by more than 0·0001.

The thermal and position parameters are given in Table 1. The observed and calculated structure factors are given in Table 2. The bond length we determined is 2·835 (σ=0·002) Å. This is significantly different from the length previously reported (Bradley, 1924), but the bond angle of 103·2° (σ=0·1°) is only slightly greater than that reported earlier. Within the limits of experimental error, the tellurium bond angle is identical with that found in trigonal selenium (Cherin & Unger, 1966). The similarity of the r.m.s. amplitudes indicates that, as in selenium, the vibrational motion is rather isotropic in the plane perpendicular to **c**.

Several important coordination distances are given in Fig. 1. The next nearest neighbor distance along the chain is 4·445 (σ=0·001) Å. The nearest approach of atoms on

Table 1. *Position and thermal parameters in tellurium*

	Cherin & Unger (1967)	Bradley (1924)
x	0·2633 (σ=0·0005)	0·269
Bond length (Å)	2·835 (σ=0·002)	2·869
Bond angle	103·2° (σ=0·1°)	102·2°
U_{11}	0·0916 (σ=0·0015)	
U_{22}	0·0871 (σ=0·0014)	
r.m.s. Amplitude of vibration (parallel to **a**) (Å)	0·172 (σ=0·002)	
r.m.s. Amplitude of vibration perpendicular to **a**) (Å)	0·167 (σ=0·002)	
R	5·0%	

Table 2. *Observed and calculated structure amplitudes in tellurium*

hkl	F_o	F_c	*hkl*	F_o	F_c
100	26·60	22·27	120	31·15	30·98
200	21·52	18·99	130	12·51	11·99
300	21·43	20·51	140	4·39	4·31
400	24·97	25·62	150	10·73	10·88
600	1·81	2·06	160	2·87	3·17
700	3·44	3·54	230	17·57	17·50
800	2·34	2·16	240	5·05	5·11
110	47·64	52·78	250	4·90	4·78
220	14·23	14·05	260	2·40	2·47
330	7·19	7·53	340	5·05	5·13
440	4·85	4·68	360	2·41	2·21

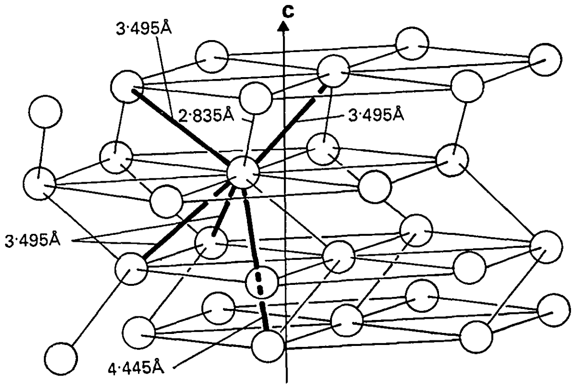

Fig. 1. Interatomic distances in tellurium.

neighboring chains is 3·495 ($\sigma=0\cdot003$) Å. This is considerably closer than the 4·40 Å predicted on the basis of van der Waals interactions alone (Von Hippel, 1948). The same 'contraction' was observed in trigonal selenium (Cherin & Unger, 1966). However, this effect is more pronounced in tellurium.

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The crystal structure of 2,2′-diaminodiphenyl disulphide.

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2,2′-Diaminodiphenyl disulphide crystallizes in space group *Pbca* with $a=8\cdot211$, $b=13\cdot144$, $c=22\cdot766$ Å and $Z=8$. The crystal structure was solved and the molecular conformation determined without emphasis on high accuracy. The dihedral angle across the S–S bond is 87°, those across the S–C bonds are 86 and 85° respectively. There is suggestive evidence that hydrogen bonds between the amino groups tie the molecules to chains roughly parallel to the *b* axis.

During the course of investigations on thioaromatic compounds, carried out in this laboratory, interest arose in the molecular conformation of 2,2′-diaminodiphenyl disulphide, $H_2N\text{–}C_6H_4\text{–}S\text{–}S\text{–}C_6H_4\text{–}NH_2$.

Experimental

The substance was obtained in the form of thin, yellow platelets, whose X-ray powder diagram was indexed on the basis of a hexagonal unit cell: $a=13\cdot144\pm0\cdot005$, $c=8\cdot211\pm0\cdot004$ Å (λ Cu $K\alpha_1=1\cdot54050$ Å).

Single-crystal X-ray diffraction data revealed that the structure is in fact orthorhombic: $a=8\cdot211$, $b=13\cdot144$, $c=22\cdot766$ Å; $c/b=\sqrt{3}$. The space group, *Pbca*, is uniquely determined by systematic absences. The general position is eightfold; with $Z=8$ the calculated density is $d_x=1\cdot34$ g.cm^{-3}, a normal value for this sort of compound.

Three-dimensional intensity data were collected by means of the PAILRED automatic diffractometer, using crystal-monochromatized Cu $K\beta$ radiation. The integrated intensities of 369 reflexions having $\sin\theta/\lambda\le0\cdot36$ Å^{-1} were measured and corrected for Lorentz and polarization effects, but not for absorption.

Structure determination

The positions of the sulphur atoms were derived directly from the sharpened Patterson map. Approximate coordinates of all carbon and nitrogen atoms were found by the use of combined Fourier and vector-search methods. In the ensuing full-matrix, least-squares refinement the quantity $\Sigma w(|F_o|-|F_c|)^2$ was minimized with respect to the coordinates of the above atoms, as well as their individual, isotropic *B* parameters. Only first derivatives of the structure factors were considered. Hydrogen atoms were excluded. The weighting scheme was based on counting statistics, a lower limit of 2% being set for the relative error in the measurement of strong reflexion intensities. The atomic scattering factors employed were from *International Tables of X-ray Crystallography* (1962).

The refinement yielded a final *R* index of 16·7% and a final *weighted R* index of 5·7%, defined as

$$R=\frac{\Sigma\,||F_o|-|F_c||}{\Sigma\,|F_o|}\quad\text{and}\quad R_w=\frac{F_c||\Sigma w||F_o|-|}{\Sigma w|F_o|}$$

respectively. The average coordinate shift in the last refinement cycle was about 0·04 times the estimated standard deviation; the largest relative shift was almost four times as large. The standard deviations were estimated from the least-squares residuals. They are given together with the atomic parameters in Table 1. Since absorption corrections were not applied, the *B* values quoted there have no direct physical meaning. Table 2 contains a list of observed and calculated structure factors.

Discussion

No attempts have been made in the present study to attain a high degree of accuracy, because this is not required for the determination of the molecular conformation. *A priori*, therefore, appreciable standard deviations of the coordinates were expected, but the magnitude of the estimated standard deviations (up to 0·6 Å) associated with the coordinates of C(*B*3), C(*B*5) and C(*B*6) exceeds all expectations and remains unexplained. Yet there are no indications that these atoms are wrongly sited, neither from the calculated values of R_w and of the *B* parameters, nor from the 3-D electron-density synthesis. Moreover, the positions of these atoms are within about 0·1 Å of those computed with the use of the most reliably determined structure parameters and assuming ring *B* to be a regular hexagon with sides of 1·39 Å.

In order to diminish the effect of the above inaccuracies the centres of gravity of the aromatic rings, *G*(*A*) and *G*(*B*), which can be located with greater precision than the individual carbon atoms, were taken as points of reference for subsequent calculations of bond distances and angles.