

## The Crystal Structure of Di- $\mu$ -bromo- $\mu$ -1,2-cyclohexylenetetra-bromoditellurium, $\text{Te}_2\text{Br}_6\text{C}_6\text{H}_{10}$

A. C. HAZELL

*Department of Inorganic Chemistry, University of Århus, DK-8000 Århus C, Denmark*

The product of the reaction between tellurium tetrabromide and cyclohexene has been shown by X-ray diffraction to be di- $\mu$ -bromo- $\mu$ -1,2-cyclohexylenetetra-bromoditellurium,  $\text{Te}_2\text{Br}_6\text{C}_6\text{H}_{10}$ . The tellurium atoms are surrounded by 4 bromine atoms in a plane and by one carbon atom at the apex of the pyramid. The two tellurium atoms are linked by two bromine atoms and the cyclohexane group. The mean value of the bridging Te-Br bonds is 2.880 Å, e.s.d. 0.006 Å, and of the terminal Te-Br bonds 2.542 Å, e.s.d. 0.006 Å. The dihedral angle between the planes defined by a tellurium atom and the bridging bromine atoms is 132°.

Intensity data were collected on a semi-automatic diffractometer using  $\text{MoK}\alpha$ -radiation. The final  $R$ -value obtained was 0.059 for 77 parameters and 574 reflections for which  $I > 3\sigma(I)$ ; the weighted  $R$ -value was 0.061.

Tellurium tetrabromide has been shown<sup>1</sup> to react with cyclohexene to form a colourless crystalline compound to which the formula  $(\text{TeBrC}_6\text{H}_{10})_n$  was tentatively proposed. The crystal structure of the compound has been determined to elucidate the nature of the compound and has shown it to be di- $\mu$ -bromo- $\mu$ -1,2-cyclohexylenetetra-bromoditellurium,  $\text{Te}_2\text{Br}_6\text{C}_6\text{H}_{10}$ . Since hydrogen atoms could not be located, nor the geometry of the  $\text{C}_6$ -ring be determined accurately, there is no proof as to the number of hydrogen atoms.

### EXPERIMENTAL

The crystals which were recrystallised from cyclohexene were kindly provided by Professor E. E. Aynsley.

Limited intensity data were originally collected by visual estimation of Weissenberg photographs recorded with  $\text{CuK}\alpha$ -radiation. These data were badly affected by absorption errors. New data was collected using a linear diffractometer of the Arndt-Phillips<sup>2</sup> design and  $\text{MoK}\alpha$ -radiation. Balanced filters ( $\text{ZrO}$ ,  $\text{SrO}_2$ ) were used in conjunction with a scintillation counter and a pulse height analyser. The background-peak-background technique was used. Layers  $k = 0$  to  $k = 15$  were recorded.

A total of 2385 independent reflections were measured of which 574 had  $I > 3\sigma_c(I)$  where  $\sigma_c(I)$  is the square root of the total number of counts for an intensity  $I$ . For the

majority of the reflections, symmetry related reflections were measured. Four standard reflections, 400, 600, 800, and 404 were measured. Since the intensities of these varied differently as a function of the radiation received by the crystal the weighted mean value was used to scale the intensities.

The crystal used for intensity data was 0.138 mm in the [100] direction, 0.308 mm in the [010] direction, 0.092 mm in the [001] direction. Intensities were corrected for absorption using the Gaussian-quadrature method as described by Wells.<sup>3</sup>

## CRYSTAL DATA

$\text{C}_6\text{H}_{10}\text{Te}_2\text{Br}_6$ ,  $M = 816.9$ . Orthorhombic  $a = 14.436 \text{ \AA}$ ,  $b = 12.374 \text{ \AA}$ ,  $c = 8.936 \text{ \AA}$ .  $U = 1596 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 3.40$ ,  $F(000) = 1160$ .

The compound crystallises as colourless needles elongated in the [010] and bounded by {101} and terminated by {010}, cleavage is perpendicular to the [010] direction. This morphology violates the Donnay-Harker law.<sup>4</sup>

The possible space-groups are  $Pnma$  ( $D_{2h}$ ,<sup>6</sup> No. 62) or  $Pn2_1a$  ( $C_{2v}$ ,<sup>9</sup> No. 33).

Atomic coordinates and thermal parameters are given in Tables 1 and 2. Observed and calculated structure factors are compared in Table 3.

Table 1. Atomic coordinates as fractions of cell edges, the estimated standard deviations  $\times 10^4$  are given in brackets.

	$x$	$y$	$z$
Te 1	0.1373 (4)	0.25	0.0032 (8)
Te 2	-0.0015 (4)	0.25	0.3691 (8)
Br 1	0.1188 (4)	0.0906 (5)	0.2345 (9)
Br 2	0.1378 (5)	0.0990 (5)	-0.1907 (9)
Br 3	-0.1081 (2)	0.1036 (3)	0.4680 (4)
C 1	-0.2139 (35)	0.25	-0.0105 (56)
C 2	-0.1609 (31)	0.25	-0.1469 (57)
C 3	-0.1650 (28)	0.25	0.1493 (62)
C 4	-0.0574 (30)	0.25	-0.1339 (54)
C 5	-0.0647 (30)	0.25	0.1381 (56)
C 6	-0.0146 (29)	0.25	0.0053 (64)

Table 2. Thermal vibration parameters (in  $\text{\AA}^2 \times 10^{-4}$ ) and, in brackets, their estimated standard deviations.

	$u_{11}$	$u_{22}$	$u_{33}$	$u_{12}$	$u_{13}$	$u_{23}$
Te 1	227 (27)	441 (25)	373 (40)	0	30 (28)	0
Te 2	280 (30)	515 (27)	238 (34)	0	-17 (28)	0
Br 1	401 (40)	566 (35)	567 (50)	75 (34)	10 (39)	155 (40)
Br 2	492 (42)	606 (36)	606 (52)	-8 (35)	160 (40)	-201 (44)
Br 3	620 (24)	521 (16)	452 (25)	-47 (17)	97 (21)	46 (20)
C 1	772 (378)	1137 (389)	36 (284)	0	-18 (289)	0
C 2	649 (329)	46 (148)	623 (400)	0	26 (321)	0
C 3	121 (235)	1088 (368)	635 (448)	0	-221 (285)	0
C 4	546 (320)	412 (231)	329 (324)	0	-376 (282)	0
C 5	188 (263)	3055 (810)	128 (312)	0	-477 (264)	0
C 6	176 (258)	1904 (577)	457 (370)	0	160 (274)	0



The morphology does not follow the Donnay-Harker law<sup>4</sup> a fact which in some cases makes it possible to locate approximate positions for the centres of molecules.<sup>5,6</sup> The position found, (0,1/4,0), did not, at the time, seem to be consistent with information from the Patterson function.

Direct methods were then applied and the signs of 300 reflections determined using Danielsen's<sup>7</sup> program SYMBAD, the space-group was assumed to be  $Pnma$ . The E-map contained 16 peaks of height greater than 150. The two largest peaks were taken to represent tellurium atoms, the fifth highest peak was taken to be Br 1 as this was placed so as to give Te-Br distances of about 2.8 Å and to form bridge atoms between the tellurium atoms. An electron density map calculated on the basis of these atoms showed two more bromine atoms in positions corresponding to the 8th and the 13th highest peaks on the E-map.

This model refined to an  $R$ -value of 0.15, a difference map, showed peaks corresponding to the 6 carbon atoms cyclohexene ring which is bonded to both tellurium atoms as shown in Fig. 2. The carbon-peaks, however, were all in the plane  $y=0.25$  which is a mirror plane if the space-group is  $Pnma$ .

#### REFINEMENT

Block-diagonal least-squares refinement was carried out for the 574 reflections with  $I > 3\sigma(I)$  giving  $R=0.059$  for 77 parameters and a weighted  $R$ -value of 0.061. The parameters refined were atomic coordinates, thermal parameters, an overall scale factor, and an isotropic extinction factor.

None of the attempts at refinement in the non-centrosymmetric space-group  $Pn2_1a$  gave a significant improvement in the  $R$ -value, neither did refinement in  $Pnma$  assuming the cyclohexane groups to be disordered. The results given in Tables 1-3 are those from refinement in  $Pnma$  with the carbon atoms held at  $y=1/4$ .

#### COMPUTATIONAL DETAILS

Block-diagonal least-squares refinements were carried out using the programs of Cruickshank *et al.*<sup>8</sup> (on the University of Durham Pegasus computer) and later that of Grønbaek Hazell.<sup>9</sup> The weighting scheme used for the final stages of refinement was  $w=1/\sigma^2$  where  $\sigma = \sqrt{\sigma(F_c^2) + (A+1)F_{\text{obs}}^2 - |F_{\text{obs}}|}$ . The constant  $A$  was automatically selected so that  $\langle |F_{\text{obs}}| - |F_{\text{calc}}| \rangle$  varied as little as possible with  $|F_{\text{obs}}|$ . An isotropic extinction factor,<sup>10</sup>  $g$ , was included in the least-squares refinement in the manner proposed by Larson.<sup>11</sup> The final value of  $A$  was 0.038 and of  $g$   $7.8 \times 10^{-8}$ . The atomic scattering factors used for tellurium and for bromine were the mean of the values calculated by Cromer and Waber<sup>12</sup> from relativistic Dirac-Slater wave functions and of those calculated by Cromer and Mann<sup>13</sup> from Hartree-Fock wave functions. For the carbon atoms the scattering factors used were those of *International Tables*.<sup>14</sup> The tellurium and the bromine scattering factors were corrected for the real part<sup>15</sup> of the anomalous scattering correction. The signs of the 300 reflections used to calculate the E-map were determined by the multi-solution method of Germain and Woolfson<sup>16</sup> using Danielsen's Algol program SYMBAD.<sup>7</sup>

## DISCUSSION

The molecule is shown in Fig. 1. The bond distances are given in Tables 4 and 5; the values are not corrected for thermal vibration. The dihedral angle between the planes defined by Te 1, Br 1, and Br 1' and by Te 2, Br 1, and Br 1' is 132°. Each tellurium atom is surrounded by 4 bromine atoms in a plane and by one carbon atom at the apex of the pyramid. The tellurium atoms do not lie exactly in the planes of the bromine atoms but are displaced 0.117 Å, for Te 1, and 0.093 Å, for Te 2, away from the carbon atoms. The tellurium atoms can be thought of as being  $5s5p^35d^2$  hybridised, the lone pair being *trans* to the carbon atom.

Table 4. Bond distances, in Å, and their estimated standard deviations. The bond lengths are not corrected for thermal vibration.

	<i>l</i>	$\sigma(l)$		<i>l</i>	$\sigma(l)$
Te 1—Br 1	2.870	0.009	C 1—C 2	1.44	0.07
Te 2—Br 1	2.890	0.008	C 1—C 3	1.59	0.07
Te 1—Br 2	2.548	0.009	C 2—C 4	1.50	0.06
Te 2—Br 3	2.536	0.006	C 3—C 5	1.45	0.06
Te 1—C 6	2.191	0.042	C 4—C 6	1.39	0.07
Te 2—C 5	2.256	0.049	C 5—C 6	1.39	0.07

Table 5. Bond angles, in degrees, and their estimated standard deviations. No corrections have been made for thermal vibration. Atoms which are primed are related to the corresponding unprimed atom by reflection through the mirror plane at  $y=1/4$ .

	$\theta$	$\sigma(\theta)$		$\theta$	$\sigma(\theta)$
Br 1—Te 1—Br 2	89.2	0.21	Br 1—Te 2—C 5	82.1	0.86
Br 1—Te 1—Br 1'	86.9	0.34	Br 3—Te 2—C 5	94.2	0.83
Br 2—Te 1—Br 2'	94.2	0.40	C 1—C 2—C 4	117.6	4.29
Br 1—Te 2—Br 3	91.2	0.14	C 2—C 4—C 6	120.9	4.22
Br 1—Te 2—Br 1'	86.1	0.30	C 4—C 6—C 5	122.3	3.98
Br 3—Te 2—Br 3'	91.1	0.26	C 6—C 5—C 3	125.3	4.51
Te 1—Br 1—Te 2	83.5	0.21	C 5—C 3—C 1	112.3	4.22
Br 1—Te 1—C 6	84.3	1.11	C 3—C 1—C 2	121.7	4.11
Br 2—Te 1—C 6	90.5	1.05			

The bridging Te—Br distance has a mean value of 2.880 Å, e.s.d. 0.006 Å, which is significantly longer than the terminal Te—Br distances which have a mean value of 2.542 Å, e.s.d. 0.006 Å. This latter distance is fairly close to the value of 2.50 Å obtained from the single bond radii<sup>17</sup> but is considerably shorter than that found in the  $\text{TeBr}_6^{2-}$  ion (2.70 Å) where the tellurium atom is either described<sup>18</sup> as being  $5p^35d^26s$  hybridised or the bonding is presumed<sup>19-21</sup> to arise from the use of *p*-orbitals only. As is usual in halogen bridged compounds, e.g. the aluminium trichloride dimer,<sup>22</sup> the bridging bonds are longer than the terminal bonds.

The molecules are packed (see Fig. 2) so that their centroids are close to (0,1/4,0) as had been predicted from the morphology. The centroid of the molecule is not coincident with the centre of gravity. Since the structure of

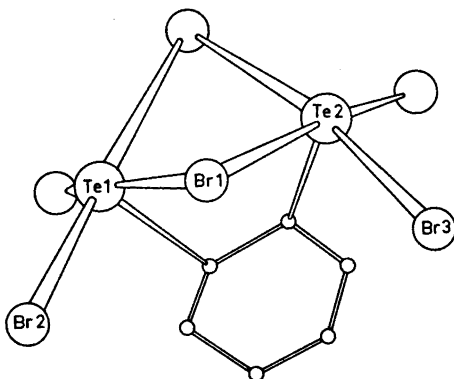


Fig. 1. The molecule of  $\text{Te}_2\text{Br}_6\text{C}_6\text{H}_{10}$ . The small circles represent carbon atoms.

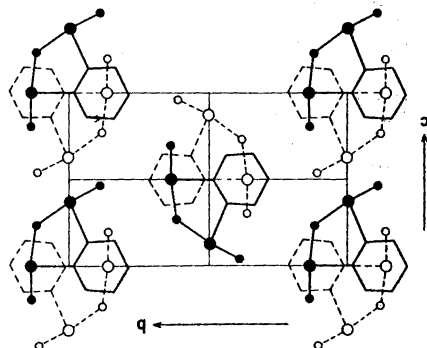


Fig. 2. Projection down the  $b$ -axis to show the packing. The molecules drawn with full lines have their centres at  $y=1/4$ , those drawn with broken lines have centres at  $y=3/4$ .

the molecule was so different from models which could be postulated from the assumed chemical formula, it was not possible to use the knowledge of the position of the centroid in determining the structure.

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