Crystal and Molecular Structure of α-Di-iodo(dimethyl)tellurium

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Crystals of the title compound are monoclinic, space group $P2_1/c$ with cell dimensions a = 9·439(1), b = 21·991(2) c = 12·217(1) Å, β = 107·63(1)°, and Z = 12. The structure was determined from three-dimensional X-ray data collected by counter methods and refined by full-matrix least-squares techniques to R 5·4% for 2191 observed reflections. Each tellurium atom has a distorted octahedral environment with two iodine atoms in a *trans*-arrangement, two methyl groups *cis*- to each other, and two contacts from iodine atoms attached to neighbouring molecules. Intramolecular Te–I bonds range from 2·854(3) to 2·994(3) Å and Te–C bonds range from 2·10(3) to 2·16(3) Å. The intermolecular Te · · · I contacts range from 3·659(3) to 4·030(3) Å. Differences in bond lengths and angles can be correlated with the differing distortions in the environment of each tellurium atom.

INITIAL chemical work [1,2] on di-iodo(dimethyl)tellurium suggested that the compound existed in α and β forms which were concluded to be *cis*- and *trans*-isomers of a square-planar structure. Subsequent investigation [3] suggested that these forms were covalent (α) and ionic (β) isomers. The ionic formulation $[TeMe_3^+][TeMeI_4^-]$ has already been confirmed by an X-ray crystal structure analysis.[4] Preliminary X-ray examination of the α form [5] revealed that there were twelve formula units in the cell and the simple molecular formula of Me_2TeI_2 was therefore questioned. We have carried out a structure determination of the α form in order to investigate its nature and also to compare it with the ionic form.

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EXPERIMENTAL

Crystals of the deep red, volatile α-dimethyltellurium di-iodide were sealed in capillaries and then examined under a polarizing microscope. A parallelepiped-shaped single crystal with dimensions 0·18 × 0·33 × 0·21 mm corresponding to the *a*, *b*, *c* directions was used throughout the work. Weissenberg photographs were taken, with the crystal mounted along *a*, of the zones 0*kl*—3*kl* (using Cr-K_α) and Mo-K_α precession photographs of the zones *h*0*l* and 0*kl* showed the Laue class was 2/*m*.

Crystal Data.—$C_2H_6I_2Te$, $M = 411{\cdot}4$, Monoclinic, $a = 9{\cdot}439(1)$, $b = 21{\cdot}991(2)$, $c = 12{\cdot}217(1)$ Å, $\beta = 107{\cdot}63(1)°$, $D_m = 3{\cdot}34$,[5] $Z = 12$, $D_c = 3{\cdot}39$, $F(000) = 2112$, $\lambda(\text{Mo-}K_\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo-}K_\alpha) = 113{\cdot}9$ cm^{-1}. Space group $P2_1/c$ from the systematic absences, *h*0*l* for $l = 2n + 1$ and 0*k*0 for $k = 2n + 1$.

Reflection intensities for the unique set of data were collected on a computer-controlled Picker four-circle diffractometer with the *a* axis approximately parallel to ϕ. Measurements were made using a 1·2° take-off angle with a symmetric θ—2θ scan of 2·0° width (corrected for dispersion effects) at 2° min^{-1}. Background counts of 10 s were measured at both scan limits. Cell constants were determined by applying a least-squares fit to 27 general high-angle ($35° < 2\theta < 45°$) reflections whose positions were accurately determined for Mo-K_{α_1} ($\lambda = 0{\cdot}70926$ Å) radiation.

Of the 3157 intensities recorded in the range $0 < 2\theta < 45°$, 2191 were $> 2{\cdot}5\sigma$ and were considered observed ($\sigma = \sqrt{N}$ where *N* is the scan count plus the total of both background counts normalized to the scan time). Three standard reflections were measured at least every 4 h and showed a fluctuation of ±2·5% over the entire data collection. As the crystal was mounted approximately parallel to *a*, each of the two arcs on the goniometer head was adjusted by *ca.* 6° such that the reflection 3,1,$\bar{1}$ was at χ 90°. It was then used to give an experimental absorption curve as a function of ϕ. Approximate absorption corrections [6] were applied to the intensity data according to this experimental curve and then Lorentz and polarization factors were applied to give structure factor moduli.

Structure Determination.—The structure was solved by tangent refinement methods using reflections with *E* values above 1·80 ($E_{\max}$ 3·65). The origin-determining reflections were 5,5,$\bar{1}\bar{1}$ (*E* 3·65), 7,0,$\bar{4}$ (*E* 3·42), and 7,12,$\bar{1}$ (*E* 2·90). Two additional reflections 5,11,$\bar{7}$ (*E* 3·57) and 3,11,$\bar{1}$ (*E* 3·14) were employed to help initiate phase assignments. Of the four combinations of their signs the positive value for 5,11,$\bar{7}$ and the negative for 3,11,$\bar{1}$ had the lowest R_k [7] value of 0·117. An *E* map using the signed 238 reflections revealed clearly all the nine heavy-atom positions in the asymmetric unit. Initial refinement commenced at *R* 0·223 which was reduced to 0·119 after four cycles of full-matrix least-squares refinement. An electron density difference map then yielded the six carbon atom positions. After their inclusion, two further cycles of refinement further reduced *R* to 0·105. A difference map showed anisotropic thermal motion about the six iodine atoms to be substantial; introduction of the appropriate variables led to *R* 0·072. A systematic statistical analysis of F_o and F_c showed extinction effects. Accordingly an isotropic secondary extinction coefficient E_c was included [8] such that the expression, $\Sigma\omega[F_o - F_c/(1 + E_c \times I)]^2$ where *I* is the uncorrected intensity [final value of E_c 0·000022(2)], was minimized. *R* was then 0·068. Parameters due to anisotropic thermal motion of the three tellurium atoms were then included in the refinement leading to *R* 0·063. At each stage the improvement obtained was justified on the basis of Hamilton's criterion.[9] Until this point, equal weights had been used, but analysis of the data showed that the lower and higher $|F_o|$ values were overweighted. A weighting scheme, where $\sigma = 440/F_o$ ($\omega = 1/\sigma^2$) for $F_o \leq 80$, $\sigma = 0{\cdot}502\sqrt{F_o}$ for $F_o > 150$, and $\sigma = 5{\cdot}5$ for $80 < F_o \leq 150$ was introduced. This weighting scheme was chosen such that the error of fit, defined as $[\Sigma\omega\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$ where $\Delta = |F_o| - |F_c|$, N_o is number of observations, and N_v the number of variables, was 1·0 and $\omega\Delta^2$ showed no trends as a function of F_o and sin θ/λ. Further refinement of the model with this weighting scheme led to *R* 0·054 and the weighted value *R′* 0·059. An electron density difference map computed after the refinement was complete showed peaks and troughs up to 0·70 eÅ^{-3}, the highest peak occurring 1·5 Å from Te(1) and the largest trough 1·8 Å from I(2).

Table 1 gives the final atomic parameters and Table 2 lists the interatomic distances and angles (and also contains values for Me_2TeCl_2 [10] for comparison). Standard errors estimated by least-squares procedures and including correlation effects and cell-dimension errors are given in parenthesis. The Figure shows the packing of the molecules within the unit cell viewed down an axis rotated 8° from *a** towards *a*.

TABLE 1

Final positional and thermal parameters

Atom	*x*	*y*	*z*	*B*(Å^2)
I(1)	0·1333(3)	0·1838(1)	0·5544(1)	*
I(2)	−0·4247(2)	0·1876(1)	0·6661(2)	*
I(3)	0·0099(2)	0·1044(1)	0·9152(2)	*
I(4)	0·6512(2)	0·0850(1)	1·0143(2)	*
I(5)	0·3404(2)	0·1644(1)	0·2534(1)	*
I(6)	0·2605(2)	−0·0402(1)	0·5318(2)	*
Te(1)	−0·1459(2)	0·1848(1)	0·6165(1)	*
Te(2)	0·3292(2)	0·0925(1)	0·9657(1)	*
Te(3)	0·2967(2)	0·0647(1)	0·3880(1)	*
C(1)	−0·0868(31)	0·2699(13)	0·7004(23)	5·0(6)
C(2)	−0·2511(30)	0·2225(13)	0·4513(23)	4·9(6)
C(3)	0·3029(28)	0·0600(12)	0·7978(22)	4·3(6)
C(4)	0·3406(31)	0·1853(14)	0·9288(24)	5·2(6)
C(5)	0·0634(33)	0·0645(14)	0·3016(26)	5·8(7)
C(6)	0·3353(29)	0·0008(13)	0·2663(23)	4·7(6)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	4·27(10)	7·00(12)	6·17(11)	−0·04(9)	2·25(9)	−0·43(10)
I(2)	4·77(10)	7·72(13)	6·17(12)	−0·12(10)	2·77(9)	0·15(10)
I(3)	4·50(10)	9·80(16)	7·07(13)	−0·71(11)	1·64(9)	−0·76(12)
I(4)	4·74(11)	6·38(13)	9·13(5)	0·16(10)	2·12(10)	0·37(11)
I(5)	7·68(13)	5·15(11)	4·81(11)	−0·49(10)	1·62(9)	−0·12(9)
I(6)	9·76(16)	5·73(12)	5·80(12)	−0·17(11)	3·47(11)	−0·76(10)
Te(1)	3·51(8)	4·61(10)	3·29(9)	−0·16(8)	0·82(7)	−0·19(8)
Te(2)	4·22(9)	4·37(10)	3·59(9)	−0·08(8)	1·37(7)	−0·12(8)
Te(3)	4·66(10)	4·43(10)	3·78(9)	−0·15(8)	1·29(8)	−0·73(8)

* Anisotropic thermal parameters (Å^2 × 10^2) used for iodine and tellurium atoms.

The motion of the iodine and tellurium atoms is mainly perpendicular to the Te–I bonds. While the anisotropic

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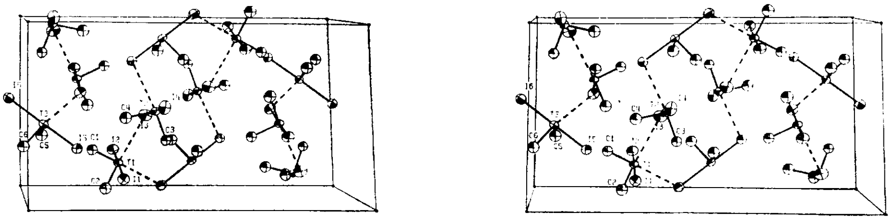

FIGURE 1 Stereomolecular packing diagrams viewed down an axis rotated by 8° from a^* towards a. Short intermolecular Te ··· I contacts within the unit cell are shown as dotted lines. Thermal ellipsoids contain 50% electron density of the atoms

TABLE 2

Interatomic distances (Å) and angles (°)

(*a*) Distances

Te(1)–I(1)	2·965(3) [a]	Te(2)–C(4)	2·10(3)
Te(1)–I(2)	2·885(3) [a]	Te(2) ··· I(4^{III})	3·912(3)
Te(1)–C(1)	2·12(3)	Te(2) ··· I(5^{IV})	3·826(3)
Te(1)–C(2)	2·13(3)		
Te(1) ··· I(3^{I})	3·919(3) [b]	Te(3)–I(5) [a]	2·854(3)
Te(1) ··· I(6^{II})	3·659(3)	Te(3)–I(6) [a]	2·994(3)
		Te(3)–C(5)	2·13(3)
Te(2)–I(3)	2·914(3) [a]	Te(3)–C(6)	2·16(3)
Te(2)–I(4)	2·934(3) [a]	Te(3) ··· I(1^{I})	3·907(3)
Te(2)–C(3)	2·12(3)	Te(3) ··· I(6^{II})	4·030(3)

(*b*) Angles

I(1)–Te(1)–I(2)	177·3(2)	I(3)–Te(2)–C(4)	90(1)
C(1)–Te(1)–C(2)	95(2)	I(3)–Te(2) ··· I(4)	97(1)
C(1)–Te(1) ··· I(3)	89(1)	I(3)–Te(2) ··· I(5)	84(1)
C(1)–Te(1) ··· I(6)	178(1)	I(4)–Te(2)–C(3)	89(1)
C(2)–Te(1) ··· I(6)	83(1)	I(4)–Te(2)–C(4)	89(1)
I(2) ··· Te(1) ··· I(3)	174(1)	I(4)–Te(2) ··· I(4)	85(1)
I(3) ··· Te(1) ··· I(6)	92(1)	I(4)–Te(2) ··· I(5)	96(1)
I(1)–Te(1)–C(1)	90(1)		
I(1)–Te(1)–C(2)	87(1)	I(5)–Te(3)–I(6)	178·3(6)
I(1)–Te(1) ··· I(3)	97(1)	C(5)–Te(3)–C(6)	91(2)
I(1)–Te(1) ··· I(6)	92(1)	C(5)–Te(3) ··· I(1)	75(1)
I(2)–Te(1)–C(1)	90(1)	C(5)–Te(3) ··· I(6)	163(1)
I(2)–Te(1)–C(2)	90(1)	C(4)–Te(3) ··· I(6)	73(1)
I(2)–Te(1) ··· I(3)	86(1)	C(4)–Te(3) ··· I(1)	166(1)
I(2)–Te(1) ··· I(6)	88(1)	I(1) ··· Te(3) ··· I(6)	120(1)
		I(5)–Te(3)–C(5)	91(1)
I(3)–Te(2)–I(4)	178·0(2)	I(5)–Te(3)–C(6)	90(1)
C(3)–Te(2)–C(4)	97(2)	I(5)–Te(3) ··· I(1)	86(1)
C(3)–Te(2) ··· I(4)	73(1)	I(5)–Te(3) ··· I(6)	86(1)
C(3)–Te(2) ··· I(5)	173(1)	I(6)–Te(3)–C(5)	90(1)
C(4)–Te(2) ··· I(5)	79(1)	I(6)–Te(3)–C(6)	89(1)
C(4)–Te(2) ··· I(4)	168(1)	I(6)–Te(3) ··· I(1)	95(1)
I(4) ··· Te(2) ··· I(5)	112(1)	I(6)–Te(2) ··· I(6)	93(1)
I(3)–Te(2)–C(3)	91(1)		

(*c*) Intermolecular I ··· I contacts (<4·35 Å [b])

I(1) ··· I(2^{V})	3·978	I(2) ··· I(5^{VI})	4·250
I(1) ··· I(5^{VI})	4·241	I(3) ··· I(4^{VII})	3·948

(*d*) Some corresponding geometry in Me_2TeCl_2

Te–Cl(1)	2·48(1)	Cl(1)–Te–Cl(2)	173·2(3)
Te–Cl(2)	2·54(1)	C(1)–Te–C(2)	98(1)
Te–Cl(1)	2·08(3)	Cl(1)–Te–C(1)	86(1)
Te–Cl(2)	2·10(3)	Cl(1)–Te–C(2)	88(1)
		Cl(2)–Te–C(1)	87(1)
		Cl(2)–Te–C(2)	88(1)

[a] Thermal motion corrected values, see text. [b] Van der Waal's radii Te = 2·20 and I = 2·15 Å (ref. 18).

Roman numerals as superscripts refer to the following equivalent positions:

I x, y, z
II $\bar{x}, \bar{y}, \bar{z}$
III $\bar{x}, \bar{y} - 1, \bar{z}$
IV $x, y, z + 1$
V $x + 1, y, z$
VI $x, \frac{1}{2} - y, \frac{1}{2} + z$
VII $x - 1, y, z$

thermal motion and extinction parameters might well contain errors due to the approximate absorption correction, the values obtained are physically reasonable. A calculation of the lower- and upper-bound limits[11] of the Te–I distances showed that though the Te–I distances obtained from the final atomic co-ordinates (Table 1) are not significantly different from the lower-bound limits they are invariably all too short. Two methods of correction for thermal motion of bond lengths were considered: a riding model and an independent-atom model. Table 3 summarizes the results of the calculations. Although the motion could be regarded as the iodine atom riding on the tellurium atom, the correction thus obtained is small (*ca.* 3σ different from the uncorrected value). This model is also close to the lower-bound limit situation where the tellurium and iodine atoms possess highly correlated parallel displacements (the upper-bound limit corresponds to highly correlated antiparallel displacements of the two atoms). Since the I–Te–I fragment is linear, correlated parallel displacements merely correspond to rigid body motion (and exclude probable bending modes). For this reason we believe that the riding model probably underestimates the correction. One might expect the true bond length to be intermediate between the upper- and lower-bound limits, a value similar to that given by the independent model; however it has been rejected because it assumes the two

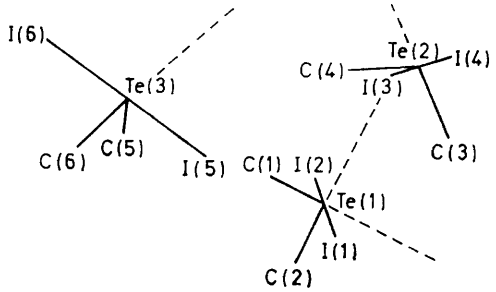

FIGURE 2 A section of the stereo-view showing the labelling within the asymmetric unit

TABLE 3

Thermal corrections * on Te–I bond lengths

	Lower-bound limit	Upper-bound limit	Un-corrected value	Riding model (I on Te)	Independent model
Te(1)–I(1)	2·957	3·026	2·956	2·965	2·991
Te(1)–I(2)	2·875	2·949	2·874	2·885	2·912
Te(2)–I(3)	2·902	2·981	2·899	2·914	2·941
Te(3)–I(4)	2·923	2·998	2·920	2·934	2·961
Te(3)–I(5)	2·846	2·917	2·845	2·854	2·882
Te(3)–I(6)	2·983	3·057	2·982	2·994	3·020

* Calculations based on expressions given in ref. 11.

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bonded atoms to be completely uncorrelated. In any event the error in using uncorrected values is so large that the least-squares estimated standard errors give a misleading impression of the bond length precision. Values from the riding model are used throughout the discussion.

The scattering factors (including full correction for anomalous scattering) were taken from ref. 12. The major programs used were as those in ref. 13 and the NRCC Tangent refinement program. Calculations were carried out at the Simon Fraser University Computer Centre on an IBM 360/50.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20249 (4 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The structure is comprised of three crystallographically independent Me_2TeI_2 molecules in the asymmetric unit. In each molecule the tellurium atom has a distorted octahedral environment formed by two *trans*-Te–I bonds, two *cis*-Te–C bonds and two weak intermolecular Te · · · I contacts. As a result of these intermolecular interactions, the molecules are linked together in corrugated sheets approximately parallel to (010).

In the gaseous state, one might predict[14] a trigonal bipyramidal geometry for Me_2TeI_2 with the lone pair and the methyl groups in a distorted trigonal plane, and the iodine atoms at the axial positions. In the solid state, however, an octahedral environment of varying regularity is found for the tellurium atoms. The weaker intermolecular contacts may be regarded as involving the partial donation and acceptance of electrons of the tellurium atoms with neighbouring iodine atoms. Another example showing that the donor–acceptor role played by a tellurium atom can be critically determined by its environment is found in $[Me_3Te^+][MeI_4Te^-]$ where the tellurium atom acts as a donor in the anion and an acceptor in the cation.[4] In this case, the same tellurium atom is acting both as donor and acceptor, indicating that the factors governing these weak interactions are delicately balanced.

Although α-Me_2TeI_2 and α-Me_2TeCl_2 have somewhat similar molecular structures, the former assumes a more regular octahedral geometry in each of the three molecules than does the latter. This can be attributed to the electronegativity differences between the iodine and chlorine atoms which have two main consequences. Firstly, the chlorine atom does not donate a lone pair of electrons to the tellurium atom readily and secondly, the Te–Cl σ bond polarity leads to a more positive tellurium atom with correspondingly decreased lone-pair donor power. Furthermore, when the methyl groups are replaced by more electron-withdrawing groups the lone-pair donor power of the tellurium atom is correspondingly decreased as in $(p\text{-}ClC_6H_4)_2TeI_2$[15] where all the Te · · · I contacts are $>4{\cdot}10$ Å; (this effect is also found in Ph_2TeBr_2).[16] The lengthening of the bonds may be explained by the polymeric Te · · · I linkages in the structure coupled with unusually high participation of the Te d_{z^2} orbital in the Te–I bonds, or alternatively, they may be regarded as having a covalent bond order of <1. The wide range of the bonds may also be associated with variation in the strength of the intermolecular interactions. For example, Te(3)–I(6) is substantially longer than all the other Te–I bonds. This is consistent with the fact that I(6) forms the shortest [3·659(3) Å] intermolecular contact with Te(1). In addition, I(6) is the only iodine atom that forms more than one intermolecular contact, both to Te(1) and Te(3). As a result of the long Te(3)–I(6), the *trans*-ligand I(5) has an increased orbital overlap with Te(3) to give the shortest Te–I bond, 2·854(3) Å. The considerable lengthening of Te(1)–I(1) [2·965(3) Å] over Te(1)–I(2) [2·885(3) Å] is in accord with the fact that I(2) does not form any intermolecular Te · · · I contact.

The regularity of the 'square' plane formed by the methyl carbon and the weakly bonded iodine atoms also depends on the shortness of the Te · · · I contacts and follows the order Te(3) $<$ Te(2) $\ll$ Te(1). In the case of Te(1), a nearly regular octahedral arrangement of the bond angles is formed. Moreover, the wide range of the I · · · Te · · · I angles and relatively constant, at near 90°, C–Te–C angles are consistent with the idea that more *p* character is associated with the Te–C bonds and high *s* character with the lone pair of electrons of the tellurium atom. This is further supported by the fact that only with the methyl groups occupying *cis*-positions can each Te–C bond obtain the maximum possible *p* character. The small positive ^{125}Te Mössbauer isomer shift[17] $+0{\cdot}55(20)$ mm s^{-1} (with respect to $Cu^{125}I$) is consistent with a bonding scheme involving principally 5*p* and 5*d* orbitals of the Te atom.

The Te–C distances determined are in the range 2·10—2·16(3) Å. The mean value of 2·14 Å is identical to the sum of the covalent radii 2·14 Å.[18] It may be noted that in Me_2TeCl_2 the mean Te–C bond obtained is 2·09(3) Å. While the difference is not significant it is in the direction expected from a bond-shortening effect which one would attribute to the more electronegative tellurium substituents.[19]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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