

ORGANOTELLURIUM DIODIDES. THE MOLECULAR STRUCTURE OF THE
 α MODIFICATION OF 1,1-DIODO-3,4-BENZO-1-TELLURACYCLOPENTANE,
 α -C₈H₈TeI₂

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Summary

The crystal and molecular structure of the thermochromic molecule, α -1,1-diiodo-3,4-benzo-1-telluracyclopentane, α -C₈H₈TeI₂, has been determined from three-dimensional X-ray data collected by counter techniques with monochromatized MoK α radiation. α -C₈H₈TeI₂ is molecular. The configuration about tellurium is distorted octahedral with the two iodine atoms in axial positions. The benzylic carbon atoms and two iodine atoms from neighboring molecules occupy the equatorial positions. The intramolecular Te-C (2.139(12), 2.145(12)Å) and Te-I (2.900(1), 2.928(1)Å) distances are normal. Two intermolecular Te...I interactions involving only one of the iodine atoms (I(2)) have distances of 3.653(1) and 3.878(1)Å. The shorter distance links the molecules into chains parallel to \underline{c} and the longer distance into chains along the 2₁ screw axis. The secondary bonding in yellow-orange α -C₈H₈TeI₂ is relatively weak, and there are no short I...I distances. The compound is the lightest in color of the organo-tellurium iodides whose structures have been determined. The refinement, carried out using 1321 nonzero reflections for which $I \geq 3\sigma(I)$, and assuming anisotropic thermal motion for all nonhydrogen atoms, led to a final value of the conventional R factor (on F) of 0.040. Crystal data (28°C) are as follows: space group P2₁/c, $\underline{a} = 12.599(3)$, $\underline{b} = 9.899(2)$, $\underline{c} = 9.268(1)$ Å, $\beta = 104.89(1)^\circ$ and $V = 1117$ Å³. The observed and calculated densities are 2.89(2)g/cm³ and 2.887(1)g/cm³, respectively.

Introduction

During structural studies of a series of organotellurium diiodides of the types R₂TeI₂ (R = p-ClC₆H₄) and RTeI₂ (R = C₄H₈S, C₄H₈O, C₁₂H₈O, and C₁₂H₈), McCullough has pointed out a relationship between the intermolecular bonding and the colors of the compounds which range from orange to dark violet [1-5]. It appears that the orange-red crystals involve only Te...I intermolecular bonds, and that the dark violet color results when I...I intermolecular bonds are present. Despite the importance of understanding the nature of these interactions, particularly in a broader context, an electronic spectroscopic characterization of these compounds has not been reported. Although differences in color appear to result from differences in the type and extent of heavy atom (Te, I) interactions, a

comparative spectroscopic study of the compounds would necessitate consideration of the electronic influence of the organic group, R, as well. One approach to circumvent the added complexity of the different organic groups in a comparative study is to consider polymorphic systems of a given compound. Such an approach would allow direct comparison of the heavy atom interactions between compounds without regard for the organic group.

To date, only two organotellurium iodide polymorphs have been structurally described [6,7]. These polymorphs are of the triiodide, 2-biphenyltellurium triiodide, and as such appear more complex than the simpler diiodide systems. Recently, Günther and Ziolo prepared two modifications of the cyclic organotellurium diiodide, 1,1-diiodo-3,4-benzo-1-telluracyclopentane, which were subsequently shown to be polymorphs [8]. Details of the intermolecular interactions were not available. As part of our effort to structurally and spectroscopically characterize these solids, we have determined, and report here, the structure of the yellow-orange polymorph, α -C₈H₈TeI₂.

Experimental Section

Suitable crystals of α -C₈H₈TeI₂ were kindly provided by Dr. W.H.H. Günther. These were prepared by the method previously described [8].

Crystallographic data

A preliminary investigation of several of the crystals by means of oscillation and Weissenberg photographs showed them to have monoclinic symmetry and systematic absences $h0l$, $l = 2n + 1$, consistent with earlier data [8]. A crystal bounded by $\{001\}$, $\{100\}$, $\{010\}$, and $\{2\bar{1}0\}$ with crystal dimensions normal to these faces of 0.01, 0.005, 0.0084, and 0.01 mm was mounted with \bar{c} approximately along the Φ axis of a Syntex P $\bar{1}$ diffractometer equipped with a scintillation counter and a graphite monochromator. Scans of $0k0$ reflections showed $0k0$, $k = 2n + 1$, to be absent. The automatic centering, indexing and least-squares routines of the instrument were applied to 15 selected reflections in the 2θ range from 31° to 43° to obtain lattice parameters. Based on λ (MoK α) 0.71073\AA , the results at 28°C are $a = 12.599(3)\text{\AA}$, $b = 9.899(2)\text{\AA}$, $c = 9.268(1)\text{\AA}$, $\beta = 104.89(1)^\circ$, $V = 1117.1(4)\text{\AA}^3$. Previously reported cell constants were determined at 23°C and gave a slightly smaller volume (0.4%) [8]. The density calculated on the basis of four molecules per unit cell is $2.887(1)\text{g/cm}^3$ while that measured by flotation in bromoform is $2.89(2)\text{g/cm}^3$. The space group is $P2_1/c$.

The intensity data were collected with MoK α radiation, a scan rate of $3.0^\circ \text{min}^{-1}$, and a scan range from 1.7° below the $K\alpha_1$ peak to 1.5° above the $K\alpha_2$ peak. Background counts were taken for one-half the scan time at each end of the scan range. Intensities of three standard reflections ($1\bar{3}\bar{2}$), $(31\bar{2})$, and (112) were recorded after every 97 intensity measurements. The standards showed only random variations in a range consistent with the

respective values of $\sigma(I)$. With 2θ maximum = 55° , 2838 reflections were measured, including 93 checks of standard reflections. The remaining 2745 unique reflections included 163 space group absences and 1261 reflections for which $I \leq 3\sigma(I)$. The latter were considered unobserved and were omitted from the refinement. The data were corrected for Lorentz and polarization effects and processed as previously described [5], with a value of 0.04 for p. Absorption corrections ($\mu = 83.3 \text{ cm}^{-1}$ for $\text{MoK}\alpha$ radiation) were made based on the dimensions and crystal face assignments given above.† The resulting transmission factors ranged from 0.738 to 0.848.

Determination and refinement of the structure

Positions for the tellurium and iodine atoms were obtained from a three-dimensional Patterson summation. The eight carbon atoms were located on a Fourier map and their positional and isotropic thermal parameters were refined with the positional and anisotropic thermal parameters of the tellurium and iodine atoms. This refinement converged to a conventional R index of 0.05 and a weighted index of 0.053. A difference Fourier showed maxima in the range $0.7 \pm 0.2 \text{ e}^{-\text{\AA}^{-3}}$ at positions close to those calculated for the eight hydrogen atoms based on C-H distances of 0.95 \AA . In the subsequent refinement, the hydrogen atoms were included in the structure factor calculations with positional parameters fixed at the calculated values and with assigned isotropic thermal parameters of 5.0 \AA^2 . The least-squares refinement converged at $R = 0.040$ and $R_w = 0.042$. In the final least-squares cycle, the largest shifts in a positional and thermal parameter for tellurium or iodine was 0.01σ and for carbon 0.03σ . The final "goodness of fit" defined as $[\sum w(|F_o| - |F_c|)^2 / (\text{No} - \text{Nv})]^{1/2}$ was 1.11. In this expression $\text{No} = 1321$, the number of observed reflections, and $\text{Nv} = 100$, the number of variable parameters. In the final difference Fourier, no peaks above $0.7 \text{ e}^{-\text{\AA}^{-3}}$ were noted.

Final atomic positional and thermal parameters are listed in Tables I and II. The root-mean-square amplitudes of vibration of non-hydrogen atoms along the three principal axes of the vibrational ellipsoids, together with the corresponding B values, are given in Table III.* The structure factors, calculated on the basis of the tabulated parameters, are listed in Table IV.* The atomic scattering factors were those given in Table 2.2A of reference 9. The real and imaginary components of anomalous dispersion from Table 2.3.1 of reference 9 were applied to the scattering factors for Te and I. An analysis of the values of $||F_o| - |F_c|| / \sigma(F_o)$ for the 1261 unobserved reflections showed 78% to be less than 1, 16% in the range from 1 to 2, 4.3% in the range from 2 to 3, and 1.2% in the range from 3 to 4. Three reflections had values greater than 4, with a maximum value of 5.2.

*Tables III, IV and VII have been deposited as NAPS Document No. 03485 (8 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P. O. Box 3513, Grand Central Station, New York, NY 10017. A copy can be secured by citing the document number, remitting \$5.00 for photocopies or \$3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the United States and Canada, postage is \$3.00 for a photocopy or \$1.00 for a fiche.

TABLE I

Atomic positional parameters in α -C₈H₈TeI₂^a

Atom	x	y	z
I(1)	0.24625(8)	0.43457(10)	0.01169(11)
I(2)	0.00247(8)	0.70414(9)	0.38428(11)
Te	0.11882(7)	0.56499(8)	0.19178(9)
C(1)	0.2022(10)	0.4474(11)	0.3815(13)
C(2)	0.2987(11)	0.5303(12)	0.4652(14)
C(3)	0.3663(12)	0.4811(14)	0.5982(17)
C(4)	0.4565(13)	0.5555(17)	0.6676(16)
C(5)	0.4803(10)	0.6762(19)	0.6170(17)
C(6)	0.4139(12)	0.7267(15)	0.4822(16)
C(7)	0.3223(10)	0.6551(12)	0.4079(13)
C(8)	0.2477(10)	0.7094(12)	0.2649(14)
H(1) ^b	0.228	0.360	0.348
H(2)	0.152	0.427	0.446
H(3)	0.352	0.397	0.642
H(4)	0.507	0.525	0.760
H(5)	0.545	0.728	0.671
H(6)	0.432	0.814	0.440
H(7)	0.287	0.727	0.185
H(8)	0.214	0.801	0.285

^aEstimated standard deviations in the least significant digits are given in parentheses in this and in following tables.

^bThe assigned parameters of the hydrogen atoms were not included in the least-squares refinement.

TABLE II

Atomic thermal parameters in α -C₈H₈TeI₂^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	76(1)	93(1)	140(2)	-7(1)	41(1)	-30(1)
I(2)	63(1)	95(1)	120(1)	5(1)	31(1)	-10(1)
Te	46(1)	65(1)	79(1)	-4(1)	9(1)	-2(1)
C(1)	62(10)	60(13)	100(18)	20(10)	29(11)	22(13)
C(2)	60(10)	84(15)	74(17)	12(10)	24(11)	3(13)
C(3)	62(12)	91(16)	157(26)	16(11)	17(14)	-13(17)
C(4)	84(14)	142(22)	103(21)	37(15)	7(14)	-14(19)
C(5)	28(9)	218(27)	127(23)	12(14)	0(12)	-82(22)
C(6)	59(12)	133(19)	108(21)	3(12)	5(13)	-38(16)
C(7)	46(9)	77(13)	82(17)	-4(9)	20(11)	-8(12)
C(8)	63(11)	73(14)	88(18)	-20(10)	12(11)	4(13)

^aAll parameters have been multiplied by 10⁴. The anisotropic temperature factor expression is of the form $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. Isotropic thermal parameters for all hydrogen atoms were assigned to be 5.0Å².

Description and Discussion of the Structure

The crystal structure of α -(1,1-diiodo-3,4-benzo-1-telluraclopentane) consists of $C_8H_8TeI_2$ molecules linked by intermolecular $Te \cdots I$ contacts. The molecule and a view of the unit cell are shown in Figures 1 and 2, respectively. Bond distances and angles within the molecule are listed in Table V, and important intermolecular distances and angles are given in Table VI.

The configuration about tellurium is distorted octahedral, as has been found for previous structures [3-5], with I(1) and I(2) in the axial positions normal to the benzo-1-tellurocyclopentane ring. The I(1)-Te-I(2) angle is $176.53(4)^\circ$. Carbon atoms 1 and 8 of the ring system and two iodine atoms I(2)', $[x, 1/2-y, -1/2+z]$; I(2)", $[\bar{x}, -1/2+y, 1/2-z]$ from two neighboring molecules occupy the equatorial positions. The primary source of the distortion from ideal geometry is the location of the I(2)" atom. The X-Te-X (X = C, I) angles involving I(2)" show distortions from the ideal value of between 15 and 20° while those not involving I(2)" show distortions of between 1 and 7° .

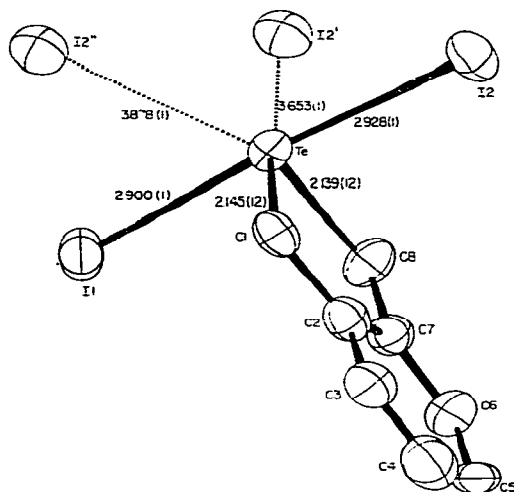


Figure 1. ORTEP plot of the α - $C_8H_8TeI_2$ molecule with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted and secondary bonds are indicated by dotted lines.

The Te-C distances of $2.145(12)$ and $2.139(12)\text{\AA}$ are identical to the sum of the single covalent bond radii, 2.14\AA [10]. The C(1)-Te-C(8) angle is $86.0(5)^\circ$ and is greater than the corresponding angles in dibenzotellurophene ($81.7(2)^\circ$) [11] and dibenzotellurophene diiodide ($81.8(2)^\circ$) [5], presumably due to the longer C-C bond length. Carbon-tellurium-carbon angles in other cyclic systems range from 91 to 100° [5], and are at the high end of this range

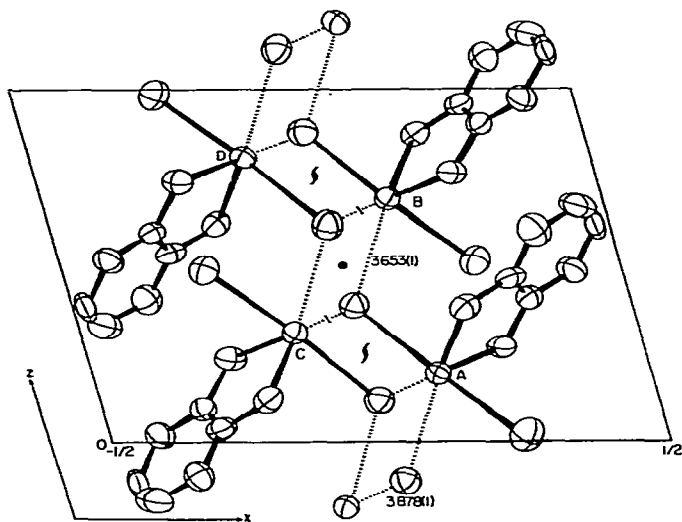


Figure 2. Projection, down the b axis, of a selected portion of the structure of α - $C_8H_8TeI_2$ centered about $0,0,1/2$. The symbols, A(000), and so on, used to designate individual molecules are given in Footnote a, Table VI.

TABLE V

Bond distances and angles in α - $C_8H_8TeI_2$

<u>Distances, Å</u>			
Te-I(1)	2.900(1)	C(3)-C(4)	1.367(20)
Te-I(2)	2.928(1)	C(4)-C(5)	1.345(21)
Te-C(1)	2.145(12)	C(5)-C(6)	1.405(20)
Te-C(8)	2.139(12)	C(6)-C(7)	1.379(17)
C(1)-C(2)	1.507(18)	C(7)-C(8)	1.513(17)
C(2)-C(3)	1.394(18)	C(2)-C(7)	1.406(16)
<u>Bond Angles, Deg</u>			
I(1)-Te-I(2)	176.53(4)	C(2)-C(3)-C(4)	118.2(14)
I(1)-Te-C(1)	90.2(3)	C(3)-C(4)-C(5)	123.2(14)
I(1)-Te-C(8)	89.6(3)	C(4)-C(5)-C(6)	119.4(14)
I(2)-Te-C(1)	88.4(3)	C(5)-C(6)-C(7)	119.5(14)
I(2)-Te-C(8)	87.2(3)	C(6)-C(7)-C(2)	119.6(12)
Te-C(1)-C(2)	106.7(8)	C(6)-C(7)-C(8)	120.4(12)
C(1)-C(2)-C(3)	119.6(11)	C(2)-C(7)-C(8)	120.0(11)
C(1)-C(2)-C(7)	120.3(11)	C(7)-C(8)-Te	106.9(8)
C(3)-C(2)-C(7)	120.0(12)	C(1)-Te-C(8)	86.0(5)

TABLE VI

Intermolecular distances and angles about iodine and tellurium in α -C₈H₈TeI₂^a

<u>Distances about Te, Å</u>		<u>Angles about I(2), Deg</u>	
Te...I(2)'	3.653(1)	Te'-I(2)'...Te	127.32(4)
Te...I(2)''	3.878(1)	Te''-I(2)''...Te	123.93(3)
		Te'''...I(2)''...Te	68.04(3)
<u>Angles about Te, Deg</u>			
I(1)-Te...I(2)'	90.00(4)	C(1)-Te...I(2)'	173.1(3)
I(1)-Te...I(2)''	74.68(3)	C(1)-Te...I(2)''	74.7(3)
I(2)-Te...I(2)'	91.01(3)	C(8)-Te...I(2)'	87.1(3)
I(2)-Te...I(2)''	107.97(3)	C(8)-Te...I(2)''	154.8(3)
I(2)''...Te...I(2)''	111.96(3)		

^aIntermolecular bonds are indicated here and in Figure 2 by means of dotted lines. Unprimed atoms are in symmetry position A of the origin cell, (000); single primed atoms are in position B of cell (011); doubly primed atoms are in position C of cell (010) and triply primed atoms are in position D of cell (010). Position A: x, y, z; B: x, 1/2-y, 1/2+z; C: \bar{x} , 1/2+y, 1/2-z; D: \bar{x} , \bar{y} , \bar{z} .

in noncyclic systems [12]. The Te-C-C angles are 106.7(8) and 106.9(8)° and are slightly smaller than the corresponding angles in C₄H₈OTeI₂ [3], C₁₂H₈TeI₂ [5], and C₁₂H₈Te [11]. The intramolecular Te-I distances of 2.900(1) and 2.928(1)Å are longer than the sum of the respective single covalent bond radii (2.70Å) [10], and are near the usual value of 2.94Å observed for axial Te-I distances in other R≡TeI₂ structures [2-5].

As in other organotellurium diiodides [2-5], and in the triiodides [6,7], intermolecular bonding plays an important role in α -C₈H₈TeI₂. Secondary bonds are all of the Te...I type and involve only one of the iodine atoms, I(2). As a result, the Te-I(2) distance is significantly longer (28 σ) than the Te-I(1) distance. Additionally, the C(1,8)-Te-I(2) angles are slightly smaller than the C(1,8)-Te-I(1) angles which are 90°, resulting in a slight bending of the I-Te-I axis toward the planar ring away from the other iodine atoms. There are no short I...I distances. Two different Te...I(2) contacts occur, and are indicated by dotted lines in Figure 2: Te...I(2)' at 3.653(1)Å and Te...I(2)'' at 3.878(1)Å. Both are much shorter than the sum of the van der Waals radii, 4.35Å [11]. The shorter Te...I distance links the molecules into chains parallel to the c axis while the longer type links the molecules into chains along the 2₁ screw axis. The closest intermolecular contacts are H(3)''...H(5) [1-x, y-1/2, 1.5-z], 2.52Å and C(6)''...H(7) (x, 1.5-y, 1/2+z) at 2.80Å.

The I...Te...I angle apparently can have a wide range of values and does not correlate with

the C-Te-C angle. In the present structure the angle is $111.96(3)^\circ$ and is larger than the corresponding I-Te-I angle in the three known octahedral diiodides. The values of the angle in these molecules is $72.72(2)^\circ$ for C_4H_8OTeI [3], $77.71(4)^\circ$ for $C_{12}H_8OTeI_2$ [4], and $91.13(1)^\circ$ for $C_{12}H_8TeI_2$ [5].

Seven planes in the α - $C_8H_8TeI_2$ molecule with atom deviations are described in Table VII.* The nine-member hetero ring is planar with the maximum atom deviation being -0.04\AA (C(1)) and the minimum 0.000\AA (C(8)). The tellurium atom is 0.03\AA from the plane. The six C-C distances in the benzene portion of the nine-membered ring have a mean value** of $1.383(10)\text{\AA}$. The two nonaromatic C-C distances have values of $1.507(18)$ and $1.513(17)\text{\AA}$. The mean C-C-C angle for all C-C-C angles in the molecule is $120.0(4)^\circ$.

Secondary bonding in the light orange α - $C_8H_8TeI_2$ is all of the Te...I type with only one iodine atom involved, and the bonds are of two types. Compared with other organotellurium iodine compounds, the secondary bonding in the present compound is weak. The bond order [10] of the two Te...I interactions in α - $C_8H_8TeI_2$ is 0.02 and 0.04. In the bright red $C_{12}H_8TeI_2$, for example, two Te...I interactions occur, both of bond order 0.04 [5]. Not unexpectedly, α - $C_8H_8TeI_2$ is the lightest in color of all the organotellurium diiodides whose structures have been determined [2-5]. Our observations thus support the high degree of correlation noted by McCullough between the color and the type and degree of secondary bonding. Presumably, the origin of the color is an iodine to tellurium charge transfer transition in the ultra violet region. A comparison of the available intermolecular distances for all of the organotellurium iodides will be presented upon the completion of the structure of the other modification of α - $C_8H_8TeI_2$, the red polymorph, β - $C_8H_8TeI_2$. In this molecule the Te...I interaction is expected to be greater.

Acknowledgements

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†The computer programs used in the present work are listed in footnote 4 of ref. 5. The function $\sum w||F_o| - |F_c||^2$ was minimized in the least-squares refinement and the discrepancy indices were defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ where $w = [1/\sigma(F_o)]^2$.

**Standard deviations for the mean values of equivalent distances or angles were calculated as $[\sum(x-\bar{x})^2 / (n(n-1))]^{1/2}$.

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