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Crystal and Molecular Structure of the β Modification of 1,1-Diiodo-3,4-benzo-1-telluracyclopentane, β-$C_8H_8TeI_2$. Comparative Study of Secondary Bonding Systems and Colors in Organotellurium Iodides

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The crystal structure of the β polymorph of 1,1-diiodo-3,4-benzo-1-telluracyclopentane, β-$C_8H_8TeI_2$, has been determined from three-dimensional X-ray data collected by counter techniques. The compound crystallizes in the orthorhombic space group *Fdd*2 with unit cell parameters (23 ± 1 °C) $a = 12.328$ (3) Å, $b = 14.974$ (2) Å, and $c = 12.291$ (4) Å, with $Z = 8$. The structure was solved by direct methods and was refined by full-matrix least-squares methods based on 1245 reflections ($h + k \pm l$) with $F_o^2 > 3\sigma(F_o^2)$. Refinement, assuming anisotropic thermal motion for the six unique non-hydrogen atoms, converged at $R(F) = 0.030$. The Te atom lies on a 2-fold axis. Although no such symmetry is found in α-$C_8H_8TeI_2$, the molecular structure is similar. The configuration about tellurium is distorted octahedral, and iodine occupies axial positions with respect to two benzylic carbon atoms and two iodine atoms from neighboring molecules in equatorial positions. The Te–C, Te–I, and Te···I distances are 2.136 (8), 2.905 (1), and 3.668 (1) Å, respectively. The crystal structure differs from that of the α form in the intermolecular bonding arrangements of the heavy atoms and in the polar arrangement of the molecules. The two equivalent intermolecular Te···I interactions lie intermediate in length between those found in the α polymorph; the latter are found in an arrangement Te···I···Te. An I···I contact is observed at 4.042 (1) Å. The stronger intermolecular interaction in the β polymorph is consistent with its darker (red) color. The equatorial I···Te···I angle is 66.87 (2)°, nearly the supplement of the comparable angle in α-$C_8H_8TeI_2$. Discussion of the heavy-atom interactions in these polymorphs and in other organotellurium iodide compounds is provided.

Introduction

To date, the structures of some 11 organotellurium iodides have been reported.[2-6] These range in color from the yellow-orange α polymorph of 1,1-diiodo-3,4-benzo-1-telluracyclopentane[2] through reds and purples to the black α polymorph of 2-biphenyltellurium triiodide.[6] Since the colors of various organotellurium diiodides in nonoxygenated organic solvents (chloroform, cyclohexane, etc.) are in the yellow range,[7-10] it has been suggested[10,11] that the darker colors of these compounds in the solid state result from two types of intermolecular bonding. Secondary Te···I bonds appear to produce red colors while I···I bonds cause purple to black colors that are usually accompanied by a metallic luster. While these compounds appear to provide an opportunity for the study of the nature of charge-transfer interactions, no comparative electronic spectroscopic investigation of the compounds has been reported.

Recently, in a report on the structure of the α modification of 1,1-diiodo-3,4-benzo-1-telluracyclopentane,[2] the advantage of using polymorphs in the study of secondary bonding effects was pointed out. Specifically, it was noted that comparative spectra of polymorphs would eliminate the influence of differing organic groups. To date, however, only one polymorphic organotellurium iodide system has been structurally described, that of 2-biphenylyltellurium triiodide.[6,11] To complete the investigation of the first (and simpler) diiodide system, we report here on the structure of the β modification of 1,1-diiodo-3,4-benzo-1-telluracyclopentane. A comparative study of the intermolecular interactions in the structurally studied organotellurium iodides is also provided.

Experimental Section

Suitable crystals of β-$C_8H_8TeI_2$ were kindly provided by Dr. W. H. H. Günther. These were prepared by the method previously described.[9]

Unit cell parameters obtained by refinement of the setting angles obtained by computer-controlled centering of 25 reflections are as follows: $a = 12.328$ (3), $b = 14.974$ (2), $c = 12.291$ (4) Å; $V = 2268.9$ Å^3 (23 ± 1 °C). Systematic absences for hkl ($h + k$, $k + l$ ($l + h$) $\neq 2n$), $0kl$ ($k + l \neq 4n$), and $h0l$ ($l + h \neq 4n$) completely determine space group *Fdd*2. Agreement of the observed (2.85 (2) g/cm^3) and calculated (2.84 g/cm^3) densities was obtained for $Z = 8$.

Intensity data were collected at Molecular Structure Corp. on an Enraf-Nonius CAD4 automatic diffractometer using graphite-monochromatized Mo Kα radiation. A red octahedral crystal measuring 0.12 × 0.20 × 0.20 mm was mounted in a random orientation. The width at half-height from ω scans was 0.2°.

A total of 1840 reflections ($h + k \pm l$) were collected by the ω–θ scan technique in the range $0 < 2\theta$(Mo Kα) $< 60°$. Data were collected at 23 ± 1 °C. The scan rate varied from 2 to 20°/min in ω. The scan range (in degrees) was determined as a function of θ to correct for the separation of the Kα doublet. The scan width was calculated as θ scan width $= 0.7 + 0.350 \tan \theta$. Moving-crystal–moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 2.6 mm; the vertical aperture was set at 2.0 mm. The diameter of the incident beam collimator was 0.7 mm, and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 20.7.

Intensities and their standard deviations were calculated as described previously.[12] The factor p was set to 0.05. No significant change was observed in the intensities of three check reflections measured every 41 min. Lorentz and polarization corrections were applied, and corrections for absorption were made with use of an empirical ψ-scan correction.[13] Relative transmission coefficients ranged from 0.805 to 0.966 with an average value of 0.887. The calculated linear absorption coefficient (Mo Kα), μ, is 81.6 cm^{-1}. A secondary extinction correction was applied. The final coefficient, refined in least-squares, was 1.8×10^{-6}.

The structure was solved with use of the atomic coordinates from a previous structure solution obtained by direct methods.[14] Of the 1650 unique and not systematically absent reflections, 1245 having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement, which was carried out by full-matrix least-squares methods. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. All calculations were performed on a PDP 11/60 based TEXRAY system. Atomic scattering factors for all atoms were taken from the compilation of Cromer and Waber.[15] Anomalous dispersion effects were included in F_c.[16] The values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] Hydrogen atom contributions were omitted.

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(1) (a) University of California. (b) Deceased, Jan 28, 1985. (c) Xerox Corp.

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Table I. Atomic Positional and Thermal Parameters (Å^2) for Atoms in β-$C_8H_8TeI_2$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Te	0.0	0.0	0.0	3.52 (2)	3.42 (2)	2.14 (1)	−0.06 (2)	0	0
I	1214.3 (4)	−1662.8 (4)	−9.7 (7)	4.96 (2)	4.57 (2)	3.98 (2)	1.12 (2)	0.80 (3)	0.31 (2)
C1	1013 (6)	503 (6)	−1270 (7)	4.0 (3)	3.8 (3)	2.9 (2)	−1.3 (3)	0.1 (3)	0.3 (2)
C2	489 (6)	249 (4)	−2313 (5)	4.5 (3)	2.6 (2)	2.2 (2)	0.4 (2)	0.4 (2)	−0.0 (2)
C3	965 (9)	513 (6)	−3313 (6)	7.9 (5)	5.4 (4)	2.1 (2)	3.3 (3)	1.1 (3)	0.5 (3)
C4	449 (10)	248 (7)	−4335 (6)	8.7 (6)	5.4 (4)	3.6 (3)	3.7 (4)	2.3 (3)	1.4 (3)

[a] The positional parameters have been multiplyed by 10^4. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hkabB_{12} + 2hlacB_{13} + 2klbcB_{23})]$, where a, b, and c are reciprocal lattice constants.

After the final complete cycles of refinement, no parameter shifted by more than 0.01 of its estimated standard deviation. The esd of an observation of unit weight was 1.14. The highest peak in the final difference Fourier map was 0.86 e/Å^3. No significant trends appeared in plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F|$, $\lambda^{-1} \sin\theta$, reflection order in data collection, and various classes of indices. The final agreement factors are $R_1 = 0.030$ and $R_2 = 0.042$.

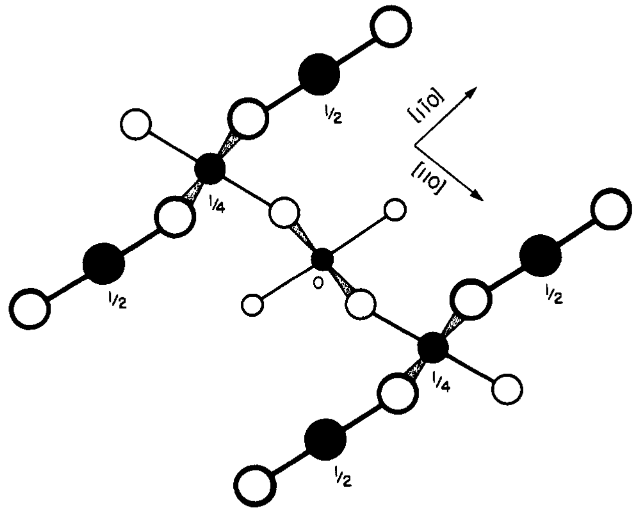
A check on the polarity sense of the crystal was made by carrying out a second refinement with the signs of the f'' terms changed. The check showed no significant difference in the refinement, the final R values, or the bond distances from those of the present sense, suggesting that the data are of insufficient quality to permit a distinction to be made.

The positional and thermal parameters for the atoms are given in table I. The observed and calculated structure factors are available as supplementary material.

Description and Discussion of the Structure

The molecular structure of 1,1-diiodo-3,4-benzo-1-telluracyclopentane in the β polymorph is similar to that in the α modification as shown by a comparison of bond distances and angles. The structure of the molecule and the extended configuration about the tellurium atom are illustrated in Figure 1. While no molecular symmetry is required in the α crystals, the molecules lie on 2-fold axes in the β polymorph and in both cases the molecular symmetry approximates *mm*2. The molecular geometries of the two forms are not significantly different. The nine-membered hetero ring is planar with the maximum atom deviation being 0.025 Å (C(1)) and the minimum 0.000 Å (Te). Bond distances and angles involving iodine atoms are an exception, however, since the positions of these atoms are considerably influenced by the differing intermolecular bonding systems in the two polymorphs.

The greatest interest in the structure of the β polymorph is in the intermolecular bonding, especially in its relationship to secondary bonding systems in the α form and in other organotellurium iodides. One may think of the secondary bonding in the β polymorph as forming zigzag chains, the general directions of which parallel the two diagonals of the c face of the unit cell. Within a given unit cell, the eight tellurium atoms are distributed two each at the levels $z = 0$ (or 1), $^1/_4$, $^1/_2$ and $^3/_4$. A given chain contains Te atoms at two adjoining levels, and the chains alternate in direction so that one set is parallel to [110] while those above and below are parallel to [1$\bar{1}$0], and so on:



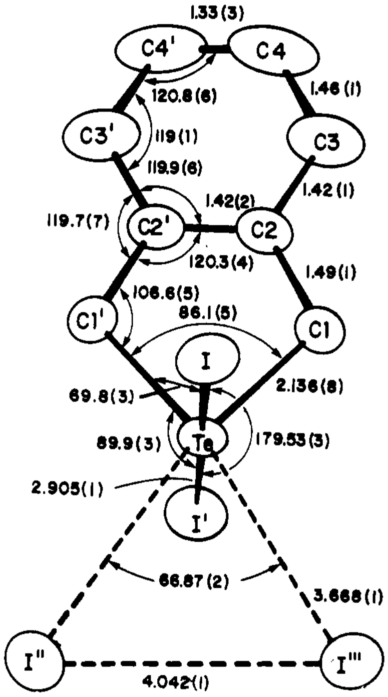


Figure 1. Atom-labeling scheme, bond distances (Å), and angles (deg) in β-$C_8H_8TeI_2$.

The chains are cross-linked at each tellurium atom to give an infinite three-dimensional network as shown in Figure 2. A stereoscopic packing diagram of the compound is given in Figure 3 along with a comparative view of the α modification. An interesting feature of the intermolecular bonding in the β polymorph is the formation of three-membered rings consisting of two equivalent Te···I bonds with a length of 3.668 (1) Å and a bond order[18] of 0.04 and one I···I bond with a length of 4.042 (1) Å and a bond order of 0.01. The Te···I bonds are at the short (strong) end of the range of values for these bonds listed in Table II while the I···I bond is at the long (weak) end for this type.[19]

The secondary bonding systems in the organotellurium iodides studied structurally to date are discussed in ref 2–11, 21–24, and 29. From the information given in these publications and in Table II, some inferences may be drawn regarding the relationships between crystal color and structure in these compounds. First, it should be remembered that solutions of organotellurium *diiodides* in chlorinated hydrocarbons and cyclohexane are yellow.[7–10] On crystallization, all of the diiodides studied form Te···I bonds.[20]

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(18) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960. The relationship used here is eq 7–5, p 239, $D(n') = D(1) - 0.71 \log n'$, in which n' is the bond order, $D(1)$ is the bond length of a single bond, and $D(n')$ is the bond length of a bond of order n'. $D(1)$ is taken here as 2.70 Å for Te–I and 2.66 Å for I–I.

(19) One might consider the upper limit of the length of a secondary bond as being the sum of the van der Waals radii for the atoms involved. However, the present authors have arbitrarily set the upper limit at 4.10 Å for both Te···I and I···I bonds, which corresponds to a bond order n' of 0.01. The van der Waals radius sums are 4.35 and 4.30 Å, respectively.

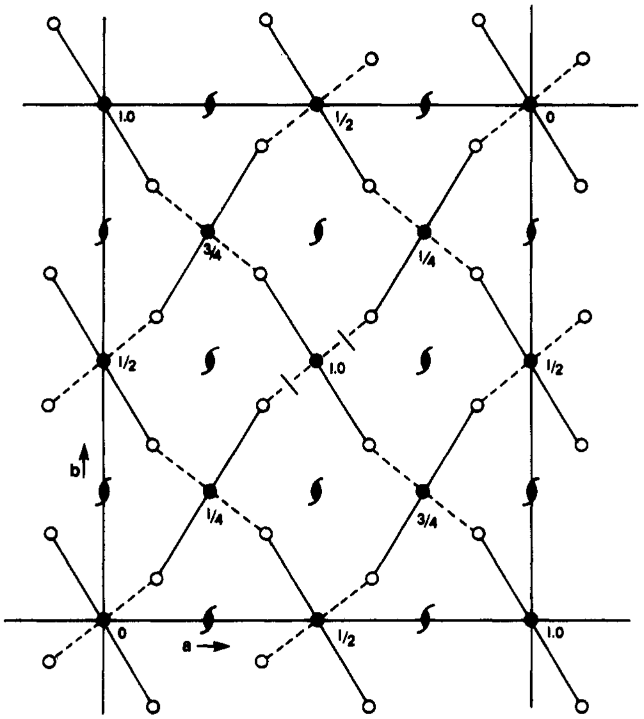

Figure 2. Projection down the *c* axis of the tellurium–iodine network in β-$C_8H_8TeI_2$. The shaded and open circles represent tellurium and iodine atoms, respectively.

Table II. Some Inter- and Intramolecular Te–I and I–I Distances (Å) in Organotellurium Diiodides

compd	Te–I[c]	Te···I[d]	I···I[d]
α-$(C_6H_5)_2TeI_2$[29]	2.928 (1)	3.995 [0.01]	
(deep carmine red)[a]	2.928 (1)[e]		
β-$(C_6H_5)_2TeI_2$[29,b]	2.959 (1)	3.926 [0.02]	
(deep orange-red)	2.893 (1)	3.924 [0.02]	
		3.850 [0.03]	
	2.942 (1)		
	2.883 (1)		
(*p*-$ClC_6H_4)_2TeI_2$[23]	2.947 (2)	4.13 [0.01]	4.14 [0.01]
(garnet red)	2.922 (2)		3.85 [0.02]
$C_4H_8OTeI_2$[21]	2.886 (1)	3.814 [0.03]	
(bright red)	2.938 (1)	3.692 [0.04]	
$C_4H_8STeI_2$[22,b]	2.884 (2)	3.76 [0.03]	3.66 [0.04]
(purple-black)	2.939 (2)	3.95 [0.02]	3.90 [0.02]
		4.13 [0.01]	
	2.851 (2)	4.16 [0.01]	
	2.985 (2)		
$C_{12}H_8TeI_2$[24]	2.944 (1)	3.717 [0.04]	
(bright red)	2.928 (1)	3.696 [0.04]	
$C_{12}H_8OTeI_2$[10]	2.945 (2)	3.739 [0.03]	
(bright red)	2.941 (2)	3.788 [0.03]	
α-$C_8H_8TeI_2$[2]	2.900 (1)	3.653 [0.04]	
(orange)	2.928 (1)	3.878 [0.02]	
β-$C_8H_8TeI_2$	2.905 (1)	3.668 [0.04]	4.042 [0.01]
(red)	2.905 (1)[e]	3.668 [0.04]	

[a] Color of the crystals. [b] The crystallographic asymmetric unit contains two chemical molecules. [c] By axial pairs. [d] Bond orders[18] in brackets. [e] Molecular symmetry requires equality of axial pairs.

If these are the only secondary bonds of significant strength present, the solids are orange or red. Introduction of secondary I···I bonds brings about a darkening of the color, and as these bonds become stronger, the color becomes purple or black, often with a metallic luster. The α and β polymorphs of $C_8H_8TeI_2$ and of $(C_6H_5)_2TeI_2$ illustrate the effects of I···I secondary bonds on the color of the crystals. The α (yellow-orange) polymorph of $C_8H_8TeI_2$ contains secondary bonds only of the Te···I type, and these involve only one of the two iodine atoms.[2] In the β (orange-red) polymorph, both iodine atoms (equivalent in this case) are involved in Te···I bonds, and there is a weak I···I bond with a bond order of 0.01, which is apparently enough to darken the color from that of the α form. In the polymorphs of $(C_6H_5)_2TeI_2$, the α form is carmine red and the β form is orange-red. Neither form is dark colored, a fact consistent with the lack of significant I···I bonding in either crystal. In the 2-biphenylyltellurium triiodide polymorphs, the dark red β modification involves one Te···I bond, and there is a fairly strong I···I bond of length 3.337 Å and bond order 0.13.[11] While the black α form involves no Te···I bonds, there are two I···I bonds, one at 3.239 Å with a bond order of 0.17 and one at 3.772 Å with a bond order of 0.03.[6]

While not involving polymorphs, two other sets of comparisons are of interest. The first of these involves the 4,4-diiodides of two very similar cyclic tellurides: 1-oxa-4-telluracyclohexane[21] and 1-thia-4-telluracyclohexane.[22] Crystals of the oxa diiodide are bright red and, although the two Te···I secondary bonds are strong, there are no I···I interactions strong enough to be classified as secondary bonds. In contrast, crystals of the diiodide of the thia compound contain Te···I bonds that are mainly at the weaker end of the range, but there are two I···I intermolecular bonds, one of length 3.66 Å with a bond order of 0.04 and one of length 3.90 Å with a bond order of 0.02. As a result of these I···I bonds, the crystals are dark purple with a metallic luster.

The other set of compounds to be compared are the diiodides of bis(*p*-chlorophenyl)tellurium (DCDPTe),[23] phenoxatellurine (POTe),[10] and dibenzotellurophene (DBTe).[24] In all three of these compounds tellurium forms two Te–C(sp^2) bonds to benzene rings. The intermolecular bonding systems in the diiodides of these tellurides are closely related in atomic arrangement, but the secondary bond lengths in $DCDPTeI_2$ are quite different from those in $POTeI_2$ and $DBTeI_2$. Referring to Table II, we see that the bright red crystals of $POTeI_2$ and $DBTeI_2$ involve strong Te···I bonds but no secondary I···I bonds. In $DCDPTeI_2$, all Te···I separations are over 4.10 (with bond orders less than 0.01) and I···I interactions take their place, one with a length of 3.85 Å and a bond order of 0.03. As a result, these crystals are deepened in color to a garnet red with beginnings of a metallic luster.

The effect of increasing the number of I···I bonds in a system by adding *molecular* iodine to the crystals is observed in the comparison of the deep red crystals of α-$(CH_3)_2TeI_2$ with those of its black iodine adduct, $(CH_3)_2TeI_2 \cdot I_2$.[5] With the molecular structure of $(CH_3)_2TeI_2$ essentially the same in the two crystals, the former has *two* weak I···I bonds (3.948 and 3.978 Å with bond orders ~0.02) per *three* $(CH_3)_2TeI_2$ units. In comparison, the black adduct has two I···I bonds per $(CH_3)_2TeI_2$ unit with lengths of 3.404 and 3.456 Å and bond orders of 0.09 and 0.08, respectively. One might raise the issue of the I–I bonds (one per $(CH_3)_2TeI_2$ unit) that are also present in the adduct. However, it should be remembered that the color of a free uncomplexed I_2 molecule is violet (as in the gas, CCl_4 solution, etc.), not black. The familiar dark purple to black metallic color of crystalline iodine is probably due to the two strong I···I secondary bonds per I_2 molecule that are present. These are 3.56 Å long with a bond order of 0.05.[25]

In $[(CH_3)_3Te^+][CH_3TeI_4^-]$,[2,26] which was formerly considered to be an isomer of α-$(CH_3)_2TeI_2$,[27] there are no interionic I···I secondary bonds in the crystals shorter than 4.43 Å.[3] Hence, it is unlikely that the dark green color of the solid could come from this source. The chromophore in the ionic compound is probably the nearly planar TeI_4 group in the anion. The four iodine atoms are approximately at the corners of a square about tellurium, and they alternate above and below their mean plane with displace-

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(20) The diiodide of bis(*p*-chlorodiphenyl)tellurium[23] may be considered an exception, although there is one Te···I "bond" at 4.13 Å, just slightly beyond our arbitrary upper limit of 4.10 Å in ref 19.

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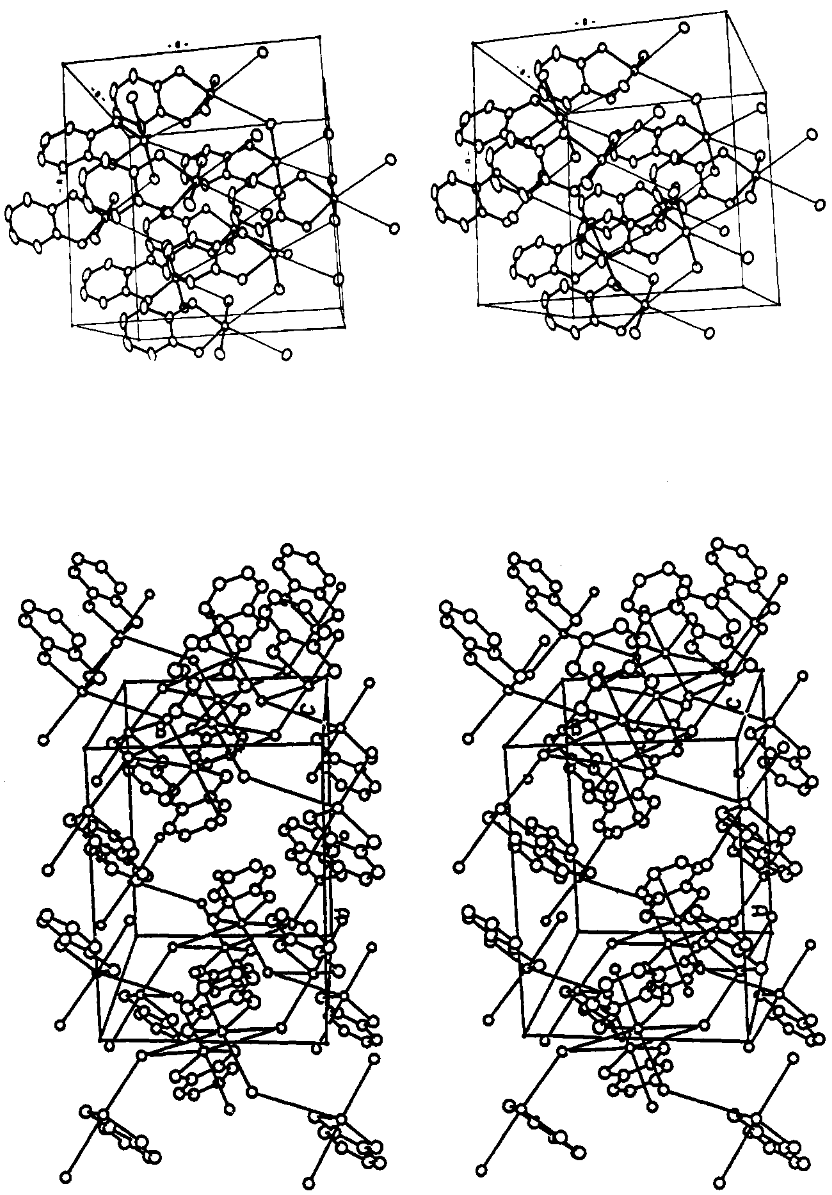

Figure 3. Stereoscopic packing diagrams of (upper) β- and (lower) α-$C_8H_8TeI_2$.

ments of ~0.1 Å. The Te–I distances range from 2.84 to 2.98 Å, consistent with those in the true diiodides. As a result of this configuration, the iodine atoms are crowded together so that the four separations along the edges of the square average 4.13 Å.

Crowding of iodine atoms about a central atom can be a source of color. For example, CH_3I and CH_2I_2 are colorless but CHI_3 is a yellow solid and CI_4 is a dark red solid. Also $(CH_3)_2SnI_2$ is a white solid while CH_3SnI_3 and SnI_4 are yellow and red solids, respectively.

In all of the organotellurium diiodide structures reported thus far, the I–Te–I systems are nearly linear with each of the opposed Te–I bonds of order approximately $^1/_2$. The bonding in the I–Te–I system may be described as "three-center-four-electron" similar to that in the triiodide ion and related groups. There is a definite reverse relationship between the lengths of the two bonds in a pair. Lengthening one through secondary bonding of the iodine atom to an atom in another molecule shortens the other bond of the pair. Thus, while the individual Te–I bonds (some 11 pairs in the 9 diiodides in Table II) vary from 2.851 to 2.985 Å (a variation of 4.9% of the mean value), the sums of the bond lengths in the I–Te–I groups vary from 5.820 to 5.886 Å, or only 1.1% of the mean value. An examination of the five axial I–Te–I systems in the four triiodides in Table III shows a variation of 2.775 to 3.285 Å in the individual Te–I distances, or 17% of the mean value. In contrast, the sums of the bond lengths by pairs range from 5.856 to 6.065 Å, for a variation of 3.5% of the mean.

Table III. Some Inter- and Intramolecular Te–I and I–I Distances (Å) in Organotellurium Triiodides

compd	Te–I[c]	Te···I[d]	I···I[d]
cis-$(C_6H_5TeI_3)_2$[29]	3.152 (2)		3.848 [0.03]
(red-black)[a]	2.792 (2)		
	3.179 (2)		
	2.775 (2)		
trans-$(C_6H_5TeI_3)_2$[29]	3.285 (2)		3.886 [0.02]
(deep red)	2.780 (2)		
α-$C_{12}H_9TeI_3$[b]	2.833 (1)		3.772 [0.03]
(black)	3.099 (1)		3.239 [0.15]
	2.769 (1)		
β-$C_{12}H_9TeI_3$[11]	2.828 (1)	3.703 [0.04]	3.337 [0.11]
(red)	3.028 (1)		
	2.748 (1)		

[a] Color of the crystals. [b] Each of the nondimerized 2-biphenylyltellurium triiodides contains, in addition to the axial Te–I bonds, a strong Te–I bond of order 0.75–0.80. [c] By axial pairs. [d] Bond orders in brackets.

The intermolecular bonding differences in α- and β-$C_8H_8TeI_2$ manifest themselves in the different crystal morphologies of the compounds. The β form exists as nearly isometric crystals while the α form exists as plates or short needles.[9] This difference may be rationalized in terms of the periodic bond chain model[28] and relates to the three-dimensional bonding network in the β polymorph vs. the two-dimensional layered structure of the α form.[2] Molecular packing in the two forms also differs with the β polymorph being polar. In this form, the orientation of the molecules is such as to give rise to a net dipole moment of the moieties in the *c* direction of the crystals. Optical second-harmonic generation has been observed in β-$C_8H_8TeI_2$ with Kurtz powder measurements indicating a bulk susceptibility about an order of magnitude greater than that for *m*-nitroaniline.[29] The slightly denser α form is centrosymmetric.[2]

Alcock and Harrison[30] note that "the chlorine substituents in the para positions in $(p\text{-}ClC_6H_4)_2TeI_2$ produce a very significant change in structure as compared to the unsubstituted compound...". Their suggestion of an inductive effect has considerable merit, as has been demonstrated in these laboratories in the case of ring substituents in the $(C_6H_5)_2SeBr_2$ system.[31-34]

The earliest studies in this area were started in 1941 when the structure of $(C_6H_5)_2SeBr_2$[31] was determined. The unexpectedly long observed Se–Br bonds of 2.52 (1) Å were noted and recognized as a possible weakness in these bonds. A series of determinations of the dissociation constants for equilibria of the type

$$(XC_6H_4)_2SeBr_2 = (XC_6H_4)_2Se + Br_2$$

in carbon tetrachloride solution was undertaken. The results not only demonstrated the weakness of the Se–Br bonds but also showed the substantial and predictable inductive effects of the ring substituents on *K*(diss).[32-34] Some observed values for *K*(diss), where $K(\text{diss}) = [R_2Se][Br_2]/[R_2SeBr_2]$, were, at 25 °C

substituent	*K*(diss) (25 °C), M L^{-1}
p-CH_3	3.6×10^{-5}
H	4.8×10^{-4}
p-Cl	2.1×10^{-3}

Thus a *p*-Cl substituent weakens the Se–Br bonds relative to those in diphenylselenium dibromide, while a *p*-CH_3 substitution strengthens these bonds. The effects of substituents on the Se–Br bond distance was not clear in the early studies. For one thing, the esd of the determination of the length of a Se–Br bond in those days of two-dimensional photographic methods was 0.01–0.02 Å, and the effect we were looking for was probably a little larger than this. Secondly, the effects of secondary bonding, while little studied at that time, caused significant changes in the Se–Br distances. For example, while the Se–Br distance was observed to be 2.52 (1) Å in $(C_6H_5)_2SeBr_2$,[31] it was observed to be 2.55 (2) Å in $(p\text{-}CH_3C_6H_4)_2SeBr_2$,[35] a shift (though of doubtful significance) in the direction opposite to that expected from inductive effects. More significantly, the tolyl compound has an intermolecular Br···Br bond of 3.58 (2) Å ($n' = 0.02$), which accounts not only for the lengthening of the Se–Br bonds but also for the fact that crystals of the tolyl compounds are deep red while those of the phenyl compound are yellow-orange.

Returning to the I–Te–I systems, we suggest that while individual Te–I bond lengths (and strengths) are greatly affected by secondary bonding, the average values of the Te–I bonds in a given axial system are not. We further suggest that the average Te–I bond distance in a given organotellurium diiodide is a measure of the inductive effects brought to the Te atom by the organic part of the molecule. The customary reference point in diaryl systems is the diphenyl compound, for which we now have[30] three average values: 2.928, 2.926, and 2.913 Å. The average of these is 2.923 Å, which value we will use as a reference in comparing I–Te–I systems.

Now in $(p\text{-}ClC_6H_4)_2TeI_2$ the average Te–I distance is 2.935 Å, a shift of 0.012 Å in the expected direction. Since the difference is some 12σ, it is probably significant. Further work along these lines (i.e., $(p\text{-tol})_2TeI_2$, tol = tolyl) should prove interesting.

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Supplementary Material Available: Listings of the observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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