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References and Notes

(1) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).
(2) A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, **87**, 3272 (1965).
(3) See, for example, ref 1, 4, and 5 for lists of representative references.
(4) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc. A*, 3204 (1970).
(5) H. Alper and A. S. K. Chan, *J. Amer. Chem. Soc.*, **95**, 4905 (1973).
(6) M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).
(7) B. L. Shaw and R. E. Stainbank, *J. Chem. Soc., Dalton Trans.*, 2394 (1973).
(8) M. I. Bruce, R. C. F. Gardner, B. L. Goodall, I. Matsuda, and F. G. A. Stone, Abstracts of Papers, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., 1973, p 121.
(9) H. Alper and A. S. K. Chan, *J. Organometal. Chem.*, **61**, C59, C62 (1973).
(10) H. Alper and A. S. K. Chan, *J. Chem. Soc., Chem. Commun.*, 724 (1973).
(11) R. L. Bennett, M. I. Bruce, I. Matsuda, R. J. Doedens, R. G. Little, and J. T. Veal, *J. Organometal. Chem.*, **67**, C72 (1974).
(12) R. McKinney, G. Firestein, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **95**, 7910 (1973).
(13) S. Trofimenko, *Inorg. Chem.*, **12**, 1215 (1973).
(14) Y. Takahashi, A. Tokuda, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, **35**, 415 (1972).
(15) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 840 (1973).
(16) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 844 (1973).
(17) Performed by use of a local version of Dewar's FAME computer program. Other programs employed in this structure analysis were those previously listed.[16] All computations were carried out on the local PDP-10 computer.
(18) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).
(19) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.
(20) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(21) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(22) Supplementary material.
(23) See ref 16 for further discussion of these parameters and their application to closely related molecules.
(24) D. M. Chipman and R. A. Jacobson, *Inorg. Chim. Acta*, **1**, 393 (1967).
(25) R. J. McKinney, B. T. Huie, C. B. Knobler, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **95**, 633 (1973).
(26) R. F. Bryan, *J. Chem. Soc. A*, 172 (1967).
(27) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967); **7**, 2339 (1968).
(28) M. J. Bennett and R. Mason, *J. Chem. Soc. A*, 75 (1968).
(29) H. Vahrenkamp, *Chem. Ber.*, **104**, 449 (1971).
(30) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).
(31) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, p 224.
(32) See, for example: W. J. Hu and S. J. Lippard, *J. Amer. Chem. Soc.*, **96**, 2366 (1974), and references therein; A. J. Schultz and R. Eisenberg, *Inorg. Chem.*, **12**, 518 (1973), and references therein.
(33) For a recent example of carbonyl insertion into a metal–carbon bond of a metalated sulfur donor ligand complex see H. Alper, W. G. Root and A. S. K. Chan, *J. Organometal. Chem.*, **71**, C14 (1974).

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Crystal and Molecular Structure of Dibenzotellurophene Diiodide, $C_{12}H_8TeI_2$[1]

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The structure of dibenzotellurophene diiodide, $C_{12}H_8TeI_2$, has been determined by the use of three-dimensional X-ray data collected on an automated diffractometer with monochromatized Mo Kα radiation. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 8.807$ (3) Å, $b = 8.182$ (2) Å, $c = 12.001$ (6) Å, $\alpha = 121.16$ (3)°, $\beta = 101.63$ (3)°, $\gamma = 103.05$ (3)°, and $V = 666.2$ (4) Å^3. The density of 2.660 (2) g cm^{-3} calculated on the basis of two molecules per unit cell agrees with the measured density of 2.66 (2) g cm^{-3}. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a conventional R index of 2.6% based on 2376 observed reflections. The dibenzotellurophene moiety is nearly planar but shows a twist of 3.3° between the two six-membered rings. Tellurium forms bonds with two carbon atoms at 2.111 (4) and 2.113 (4) Å with a C–Te–C bond angle of 81.8 (2)°. Approximately normal to the C–Te–C plane, tellurium forms axial bonds with iodine atoms at 2.944 (1) and 2.928 (1) Å. The I–Te–I bond angle is 178.47 (1)°. Tellurium also forms weak bonds with iodine atoms in each of two neighboring molecules with Te···I distances of 3.717 (1) and 3.696 (1) Å. The C–Te···I bond angles are 175.1 (1) and 171.1 (1)° so that the configuration about tellurium is octahedral. The intermolecular Te···I bonds link the molecules into infinite chains along the b axis. The observed C–C bond distances in the six-membered rings range from 1.362 (7) to 1.409 (6) Å (average 1.387 Å) and the C–C bond distance between the rings is 1.469 (6) Å.

Introduction

Crystals of organotellurium diiodides display a range of colors from red-orange through dark violet. Structural studies of five of these compounds have disclosed a variety of intermolecular bonding arrangements and suggest a possible relationship between the types of secondary bonds and the colors of the crystals.[2] Investigations to date indicate that the red crystals involve only Te···I intermolecular bonds and that the dark violet color results when I···I intermolecular bonds are present. Dibenzotellurophene diiodide, $C_{12}H_8TeI_2$, which forms brilliant red crystals, provided another interesting case for structural study. Not only did this present an additional opportunity to observe intermolecular bonding in these compounds, but also of even greater interest was the determination of the structural details of the dibenzotellurophene moiety.

Experimental Section

Dibenzotellurophene diiodide was prepared by grinding the dichloride[3] with a twofold excess of potassium iodide under methyl ethyl ketone. After filtration, the solution deposited deep red prismatic crystals suitable for the X-ray study.

A preliminary investigation of several crystals by means of precession photographs showed them to be triclinic and tentative assignments of the cell dimensions, space group, and number of molecules per unit cell were made. The specimen used for the intensity measurements was 0.13 mm × 0.20 mm × 0.36 mm in directions normal to the $\{10\bar{1}\}$, $\{01\bar{2}\}$, and $\{010\}$ faces, respectively. It was mounted with b^* approximately along the ϕ axis of a four-circle computer-controlled diffractometer (Syntex $P\bar{1}$ autodiffractometer) equipped with a scintillation counter and a graphite monochromator. The automatic centering, indexing, and least-squares routines of the instrument were applied to 15 selected reflections, ten of which were in the 2θ range from 15 to 28°. The lattice parameters at 23° based on Mo Kα = 0.71069 Å are $a = 8.807$ (3) Å, $b = 8.182$ (2) Å, $c = 12.001$ (6) Å, $\alpha = 121.16$ (3)°, $\beta = 101.63$ (3)°, $\gamma = 103.05$ (3)°, and $V = 666.2$ (4) Å^3. The measured density of 2.66 (2) g cm^{-3} compares favorably with the calculated value of 2.660 (2) g cm^{-3} for $Z = 2$. The space group was therefore taken as $P\bar{1}$.

The intensity data were collected with Mo Kα radiation, a scan rate of 2° min^{-1}, and a scan range from 1.00° below the Kα_1 peak to 1.00° above the Kα_2 peak. Background counts were taken for half of the scan time at each end of the scan range and the pulse height analyzer was set at an 85% window for Mo Kα radiation. The intensities of three reference reflections were measured after every 97 intensity measurements. The variations in the recorded values of these standards were random and the deviations from the respective mean values were within ±1.3% for $4\bar{4}0$, ±1.0% for $0\bar{4}3$, and ±0.7% for $20\bar{2}$. In all, 3250 reflections were measured. These included 111 periodic checks of the standards and 197 duplicate $0kl$, $0\bar{k}l$ pairs. The remaining 2942 unique reflections represent all of those accessible within the range $2\theta \leq 54°$ for Mo Kα radiation or all for which $(\sin \theta)/\lambda \leq 0.638$ Å^{-1}. Among these, 566 reflections for which $I \leq 3\sigma(I)$ were considered unobserved and were omitted from the refinement. The number of unique, observed reflections was thus 2376. Among the 197 measured duplicate $0kl$ pairs of reflections, 163 pairs were in the observed category. Of these, 156 pairs (96%) had individual values within $\sigma(I)$ of their respective means and all of the remaining 4% were within $2\sigma(I)$. The calculated value of μ for Mo Kα radiation is 70 cm^{-1}. Absorption corrections[4] were made on the basis of the dimensions and crystal face assignments given earlier. The resulting transmission factors ranged from 0.229 to 0.452. The usual Lorentz and polarization factors were also applied.

The data reduction and processing were carried out by use of PIBAR which makes use of the equations

$$I = N - (t_s/2t_b)(B_1 + B_2)$$

$$\sigma(I) = [N + (t_s/2t_b)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$$

$$|F_o| = k(I/Lp)^{1/2}$$

$$\sigma(F_o) = (k/2)[\sigma(I)/I(Lp)]^{1/2}$$

In these equations, N is the total scan count, B_1 and B_2 are the individual background counts, t_s is the scan time (sec), and t_b is the time (sec) each background is counted. In the present case $t_s = 2t_b$ so that $t_s/2t_b = 1$.

Determination and Refinement of the Structure

For reasons of economy, the structure determination and earlier stages of refinement were performed by use of the 1144 observed reflections in the 2θ range from 5 to 40°. Trial positions for the tellurium and iodine atoms were obtained from a three-dimensional Patterson summation. The solution of the remainder of the structure was straightforward. The carbon atoms were located by means of a difference Fourier and the positional and anisotropic thermal parameters of the 15 nonhydrogen atoms were refined to a conventional R index[5] of 0.035 and weighted index R_w of 0.051. A second difference Fourier showed maxima in the range of 0.5 ± 0.1 e Å^{-3} at positions close to those calculated for the eight hydrogen atoms and these were added to the refinement with variable positional parameters and fixed isotropic thermal parameters, $B = 5.0$ Å^2. The R values were thus decreased to $R = 0.031$ and $R_w = 0.041$. A comparison of $|F_o|$ and $|F_c|$ values at this point indicated that many of the stronger, low-order reflections were being affected by secondary extinction. The intensities of all observed reflections were therefore processed by SECEXT.[6] Further least-squares refinement with the full corrected data set of 2376 reflections resulted in convergence at $R = 0.026$ and $R_w = 0.037$. In the final least-squares cycle, the largest shift in a positional or thermal parameter for Te or I was 0.02σ; for C, 0.06σ; and for a hydrogen positional parameter, 0.2σ. The final "goodness of fit" defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ was 1.43. In this expression, $N_o = 2376$, the number of observed reflections, and $N_v = 160$, the number of variable parameters. A final difference Fourier map showed no maxima above 0.4 e Å^{-3} except in the immediate vicinity of the Te and I atoms where maxima up to 1.1 e Å^{-3} were noted.

The final positional and thermal parameters are listed in Tables I and II. Table III gives the root-mean-square amplitudes of vibration along the three principal axes of the vibrational ellipsoids and the three corresponding B values for each nonhydrogen atom. A set of structure factors was calculated on the basis of the tabulated parameters and is available on request.[7] The atomic scattering factors used for iodine were the I^0 values of Doyle and Turner[8] and their values for Sb^0 and I^0 were averaged to give a set of values for tellurium. The neutral-atom values given in Table 3.3.1 A in Vol. III of ref 9 were used for carbon, and the hydrogen factors were from Stewart, Davidson, and Simpson.[10] The real and imaginary components of anomalous dispersion for Mo Kα radiation were applied to the scattering factors for Te and I.[11]

Table I. Atomic Positional Parameters in $C_{12}H_8TeI_2$

Atom	x	y	z
Te	0.37400 (3)[a]	0.64080 (4)	0.38232 (2)
I(1)	0.20731 (4)	0.93567 (5)	0.46010 (3)
I(2)	0.53597 (4)	0.34367 (5)	0.29713 (3)
C(1)	0.1349 (5)	0.3948 (6)	0.2759 (4)
C(2)	0.0553 (6)	0.3172 (8)	0.3360 (5)
C(3)	−0.1036 (6)	0.1552 (8)	0.2497 (6)
C(4)	−0.1772 (6)	0.0803 (7)	0.1116 (6)
C(5)	−0.0960 (5)	0.1592 (6)	0.0522 (5)
C(6)	0.0644 (5)	0.3196 (6)	0.1338 (4)
C(7)	0.1653 (5)	0.4176 (6)	0.0847 (4)
C(8)	0.1163 (6)	0.3580 (7)	−0.0536 (4)
C(9)	0.2182 (6)	0.4606 (8)	−0.0884 (5)
C(10)	0.3700 (7)	0.6268 (9)	0.0118 (5)
C(11)	0.4227 (6)	0.6930 (8)	0.1511 (5)
C(12)	0.3191 (5)	0.5835 (6)	0.1826 (4)
H(2)[b]	0.100 (6)	0.377 (8)	0.430 (6)
H(3)	−0.166 (6)	0.053 (8)	0.285 (5)
H(4)	−0.300 (6)	−0.049 (8)	0.043 (5)
H(5)	−0.143 (7)	0.121 (8)	−0.040 (6)
H(8)	−0.001 (7)	0.239 (9)	−0.118 (6)
H(9)	0.187 (7)	0.395 (8)	−0.189 (6)
H(10)	0.431 (6)	0.717 (8)	−0.011 (5)
H(11)	0.531 (7)	0.796 (8)	0.223 (6)

[a] The numbers given in parentheses here and in suceeding tables are the estimated standard deviations in the least significant digits.
[b] Hydrogen atoms are numbered to correspond to the carbon atoms to which they are bonded.

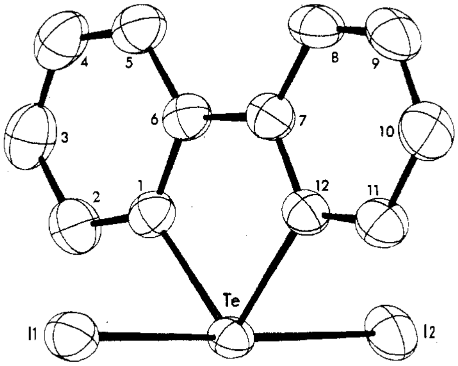

Figure 1. ORTEP plot of the $C_{12}H_8TeI_2$ molecule. The thermal ellipsoids in this and the following figure are drawn at the 50% probability level. Hydrogen atoms are omitted from all figures for purposes of clarity. Carbon atoms are indicated by the numbers 1–12.

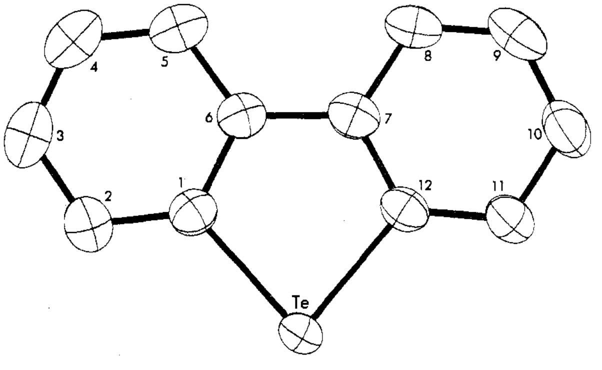

Figure 2. Plot of the dibenzotellurophene moiety.

An analysis of the values of $||F_o| - |F_c||$ for the 566 unobserved reflections showed 82.4% to be less than $\sigma(F_o)$, 14.1% in the range $(1–2)\sigma(F_o)$, and 3.2% in the range $(2–3)\sigma(F_o)$. Two reflections were beyond this range with a maximum deviation of $3.4\sigma(F_o)$.

Description and Discussion of the Structure

The dibenzotellurophene diiodide molecule and the dibenzotellurophene moiety are illustrated in Figures 1 and 2, respectively. Bond distances and angles within the dibenzotellurophene portion of the molecule are given in Table

Table II. Atomic Thermal Parameters in $C_{12}H_8TeI_2$[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te	113.4 (5)	192.9 (8)	63.8 (3)	51.6 (5)	25.0 (3)	70.7 (4)
I(1)	160.2 (6)	226.0 (9)	92.4 (4)	86.6 (6)	34.8 (4)	65.6 (5)
I(2)	201.8 (7)	347.1 (10)	95.0 (4)	168.5 (7)	65.2 (4)	126.9 (5)
C(1)	109(6)	183 (9)	91 (5)	61 (6)	34 (4)	75 (6)
C(2)	173(8)	257 (12)	111 (6)	87 (8)	67 (6)	110 (7)
C(3)	161(9)	265 (14)	175 (8)	70 (9)	87 (7)	143 (9)
C(4)	127(8)	221 (12)	159 (7)	43 (8)	48 (6)	95 (8)
C(5)	130(8)	195 (11)	107 (6)	56 (7)	26 (5)	65 (7)
C(6)	116(6)	171 (9)	89 (4)	63 (6)	31 (4)	71 (6)
C(7)	131(7)	197 (10)	82 (4)	93 (7)	36 (4)	77 (6)
C(8)	147(7)	233 (12)	75 (5)	80 (8)	18 (5)	71 (6)
C(9)	208(8)	341 (15)	85 (5)	156 (9)	57 (6)	120 (8)
C(10)	189(9)	373 (16)	117 (6)	111 (9)	68 (6)	164 (9)
C(11)	156(8)	270 (12)	88 (5)	75 (8)	41 (5)	107 (7)
C(12)	132(7)	203 (10)	75 (4)	87 (7)	37 (4)	78 (6)

[a] All parameters have been multiplied by 10^4. The anisotropic temperature factor expression is of the form $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. The hydrogen atoms were assigned fixed isotropic thermal parameters of 5.0 Å². [b] The root-mean-square amplitudes of vibration derived from the above thermal parameters are given in Table III.

Table III. Root-Mean-Square Amplitudes of Vibration and Equivalent *B* Values[a]

	Rms amplitude, Å			Equivalent *B*, Å²		
Atom	Min	Med	Max	Min	Med	Max
Te	0.161	0.195	0.206	2.04	3.00	3.34
I(1)	0.201	0.213	0.256	3.19	3.58	5.16
I(2)	0.180	0.208	0.289	2.56	3.42	6.59
C(1)	0.181	0.196	0.210	2.59	3.03	3.48
C(2)	0.201	0.230	0.239	3.19	4.17	4.51
C(3)	0.192	0.242	0.284	2.92	4.62	6.36
C(4)	0.193	0.232	0.289	2.94	4.25	6.60
C(5)	0.195	0.210	0.254	3.00	3.48	5.10
C(6)	0.178	0.193	0.215	2.50	2.94	3.64
C(7)	0.164	0.195	0.226	2.12	3.00	4.04
C(8)	0.173	0.215	0.248	2.36	3.64	4.85
C(9)	0.170	0.220	0.287	2.28	3.82	6.50
C(10)	0.176	0.242	0.282	2.45	4.62	6.29
C(11)	0.178	0.224	0.241	2.50	3.97	4.59
C(12)	0.169	0.189	0.220	2.26	2.82	3.82

[a] The equivalent *B* values are related to the root-mean-square amplitudes of vibration, $(\overline{U^2})^{1/2}$, by the expression $B = 8\pi^2(\overline{U^2})$.

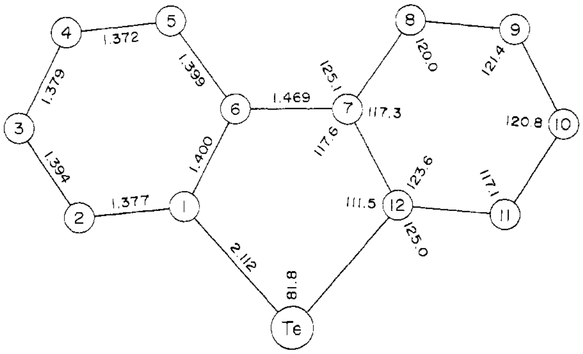

Figure 3. Drawing of the dibenzotellurophene moiety showing average values of the chemically equivalent bonds and angles.

Table IV. Bond Distances and Angles within the Dibenzotellurophene Moiety of $C_{12}H_8TeI_2$[a]

(a) Distances, Å

Te–C(1)	2.111 (4)	Te–C(12)	2.113 (4)
C(1)–C(2)	1.376 (6)	C(12)–C(11)	1.378 (6)
C(2)–C(3)	1.395 (7)	C(11)–C(10)	1.393 (6)
C(3)–C(4)	1.371 (8)	C(10)–C(9)	1.386 (8)
C(4)–C(5)	1.382 (7)	C(9)–C(8)	1.362 (7)
C(5)–C(6)	1.397 (6)	C(8)–C(7)	1.400 (6)
C(6)–C(1)	1.409 (6)	C(7)–C(12)	1.391 (6)
C(6)–C(7)	1.469 (6)		
C(2)–H(2)	0.91 (5)[b]	C(11)–H(11)	0.95 (5)
C(3)–H(3)	1.20 (5)	C(10)–H(10)	1.00 (6)
C(4)–H(4)	1.09 (5)	C(9)–H(9)	0.98 (5)
C(5)–H(5)	0.94 (5)	C(8)–H(8)	1.03 (5)

(b) Bond Angles, Deg

C(1)–Te–C(12)	81.8 (2)		
Te–C(1)–C(2)	125.1 (3)	Te–C(12)–C(11)	124.8 (3)
Te–C(1)–C(6)	111.4 (3)	Te–C(12)–C(7)	111.5 (3)
C(1)–C(2)–C(3)	117.2 (4)	C(12)–C(11)–C(10)	117.0 (4)
C(2)–C(3)–C(4)	120.9 (5)	C(11)–C(10)–C(9)	120.7 (5)
C(3)–C(4)–C(5)	121.5 (4)	C(10)–C(9)–C(8)	121.2 (4)
C(4)–C(5)–C(6)	119.8 (4)	C(9)–C(8)–C(7)	120.1 (4)
C(5)–C(6)–C(1)	117.1 (4)	C(8)–C(7)–C(12)	117.4 (4)
C(6)–C(1)–C(2)	123.5 (4)	C(7)–C(12)–C(11)	123.6 (4)
C(5)–C(6)–C(7)	125.7 (4)	C(8)–C(7)–C(6)	124.6 (4)
C(1)–C(6)–C(7)	117.2 (4)	C(12)–C(7)–C(6)	118.0 (4)
H(2)–C(2)–C(1)	121 (4)	H(11)–C(11)–C(12)	118 (3)
H(2)–C(2)–C(3)	121 (4)	H(11)–C(11)–C(10)	125 (3)
H(3)–C(3)–C(2)	121 (3)	H(10)–C(10)–C(9)	119 (3)
H(3)–C(3)–C(4)	117 (3)	H(10)–C(10)–C(11)	119 (3)
H(4)–C(4)–C(3)	121 (3)	H(9)–C(9)–C(10)	123 (3)
H(4)–C(4)–C(5)	117 (3)	H(9)–C(9)–C(8)	115 (3)
H(5)–C(5)–C(4)	125 (3)	H(8)–C(8)–C(7)	127 (3)
H(5)–C(5)–C(6)	115 (3)	H(8)–C(8)–C(7)	113 (3)

[a] Chemically equivalent bonds and angles are given on the same horizontal line. [b] The esd values for the C–H distances given here and calculated by use of ORFFE appear to be somewhat low. If one assumes that the C–H distances should all be equal, the individual deviations from the mean C–H distance of 1.01 Å suggest a σ value of 0.1 Å.

IV and the average values for chemically equivalent bonds and angles are shown in Figure 3. The dibenzotellurophene moiety is approximately planar but the two six-membered rings of the biphenyl portion are twisted out of plane with each other along the C(6)–C(7) bond by 3.25°. Considered separately, each six-membered ring is planar with all deviations of individual atoms from respective least-squares planes less than 2σ for a carbon position. However, the central five-membered (heterocyclic) ring shows deviations from planarity up to 4σ because of the twist mentioned above. Data for these and other least-squares planes of interest are listed in Table V. The biphenyl axis, defined by atoms C(3), C(6), C(7), and C(10), is also bowed with the concave side toward the tellurium atom. The extent of this bowing is indicated by the angles C(3):C(6)–C(7) and C(6)–C(7):C(10) which have observed values of 175.0 and 175.9°, respectively. The above distortions (twisting and bowing) are apparently the result of the geometric impossibility of a planar central ring with ideal sp² bond angles of 120° at the carbon atoms and an unstrained C–Te–C bond angle in the usual 91–100° range.[2,12,13] The five angles are all forced to smaller values (see Figure 3) and some strain is probably relieved by the twisting. It is interesting to note the large reduction in the C–Te–C bond angle to 81.8° when compared to the value of 91.5° in phenoxatellurin diiodide,[2]

Table V. Results of Least-Squares Planes Calculations

(a) Distances of Atoms from Least-Squares Planes,[a] Å

Atom	Plane A	Plane B	Plane C	Plane D
Te	0.038	−0.009*	−0.093	−0.025*
C(1)	0.003*	0.003*	−0.021	−0.020*
C(2)	0.003*	0.019	−0.009	−0.018*
C(3)	−0.007*	0.039	0.055	−0.001*
C(4)	0.004*	0.064	0.126	0.035*
C(5)	0.002*	0.046	0.111	0.031*
C(6)	−0.005*	0.008*	0.030	−0.004*
C(7)	−0.013	−0.019*	0.001*	−0.017*
C(8)	−0.060	−0.056	0.006*	−0.042*
C(9)	−0.046	−0.063	−0.006*	−0.035*
C(10)	0.035	−0.012	−0.002*	0.016*
C(11)	0.099	0.042	0.009*	0.058*
C(12)	0.054	0.017*	−0.009*	0.021*

(b) Interplanar Angles, Deg

Plane A–plane B	178.7
Plane B–plane C	177.8
Plane A–plane C	176.7

[a] Atoms used to define the least-squares planes are indicated by asterisks.

Table VI. Distances and Angles about Tellurium and Iodine Atoms in $C_{12}H_8TeI_2$[a]

(a) Distances about Tellurium Atom, Å

Te–C(1)	2.111 (4)	Te–C(12)	2.113 (4)
Te–I(1)	2.944 (1)	Te–I(2)	2.928 (1)
Te···I(1)″	3.717 (1)	Te···I(2)′	3.696 (1)

(b) Angles about Tellurium Atom, Deg

C(1)–Te–C(12)	81.8 (2)	I(1)–Te–I(2)	178.47 (1)
C(1)–Te–I(1)	89.0 (1)	C(12)–Te–I(1)	89.5 (1)
C(1)–Te–I(2)	90.5 (1)	C(12)–Te–I(2)	89.0 (1)
C(1)–Te···I(1)″	175.1 (1)	C(12)–Te···I(1)″	93.3 (1)
C(1)–Te···I(2)′	93.6 (1)	C(12)–Te···I(2)′	171.1 (1)
I(1)–Te···I(1)″	91.66 (1)	I(2)–Te···I(1)″	88.75 (1)
I(1)–Te···I(2)′	98.09 (1)	I(2)–Te···I(2)′	83.38 (1)
I(1)″···Te···I(2)′	91.13 (1)		

(c) Distances about Iodine Atoms, Å

I(1)–Te	2.944 (1)	I(2)–Te	2.928 (1)
I(1)···Te″	3.717 (1)	I(2)···Te′	3.696 (1)

(d) Angles about Iodine Atoms, Deg

Te–I(1)···Te′	88.34 (1)	Te–I(2)···Te′	96.62 (1)

[a] Definition of symbols: unprimed atoms are in the $C_{12}H_8$-TeI_2 molecule in symmetry position A of the origin cell, *i.e.*, (A; 000); atoms with a single prime are in molecule (B; 000) and those with a double prime are in molecule (B; 010). The symmetry positions in $P\bar{1}$, as used here, are A = x, y, z and B = $1-x, 1-y, 1-z$. Secondary (intermolecular) bonds are designated thus Te· · ·I(1)″.

The reductions in the angles at carbon atoms C(1) and C(12) average 8.6° while those at carbon atoms C(6) and C(7) average 2.4°. In contrast to these distortions in the angles, the average Te–C distance of 2.112 Å appears to be normal. The tellurium bond radius is 1.37 Å and that for sp^2 carbon is 0.73 Å with a resultant radius sum of 2.10 Å.

Except for the twisting mentioned earlier, the dibenzotellurophene diiodide molecule approximates *mm* symmetry. The extent of the deviations from this symmetry may be noted by examination of the data in Tables IV–VI. The description of the bonding about tellurium is complicated by the presence of three distinctly different types of bonds. The tellurium–carbon bonds already mentioned are normal, single covalent Te–sp^2 C bonds. Perpendicular to the C–Te–C plane, tellurium forms two "axial" bonds with iodine at 2.944 and 2.928 Å. The I–Te–I bond angle is 178.47°. These distances are some 0.23–0.24 Å longer than the sum (2.70 Å) of the normal single-bond radii for tellurium and iodine and the bonds should be considered similar to those in a symmetrical I_3^- ion with bond order $^1/_2$. An octahedral configuration about tellurium is completed by formation of secondary intermolecular bonds with an iodine atom in each of two neighboring molecules. These secondary bonds are at distances of 3.717 and 3.696 Å and form angles of 175.1 and 171.1°, respectively, with the carbon atoms opposite them. For comparison, the sum of the van der Waals radii for tellurium and iodine is 4.35 Å. The remaining 11 bond angles about tellurium range from 83.38 to 98.09° with nine of them within 4° of the ideal 90° value. A complete listing of the distances and angles about tellurium and iodine is given in Table VI and an ORTEP plot of the tellurium coordination is shown in Figure 4.

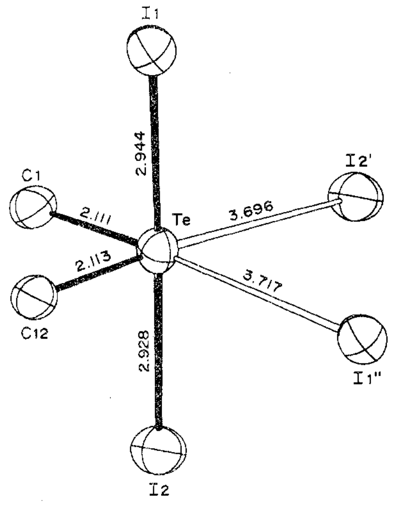

Figure 4. View of the coordination about tellurium. A complete listing of the angles involved is given in Table VI.

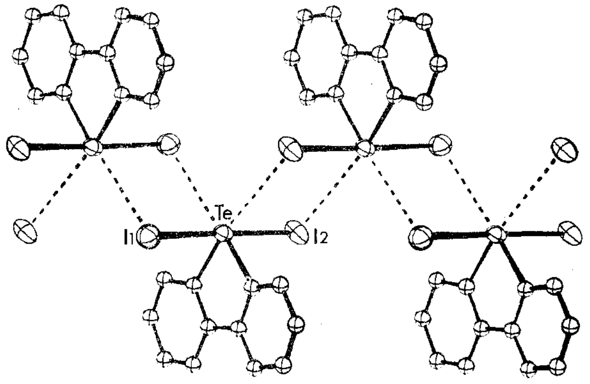

Figure 5. View normal to one of the chains formed by the Te· · ·I intermolecular bonds. The carbon atoms are shown with artificial, small isotropic thermal parameters.

The bonding about iodine is much simpler. Each iodine atom is bonded to two tellurium atoms with bond angles close to 90°. The stronger of these bonds in each case is of order $^1/_2$ and the other is an intermolecular I···Te bond. The iodine atoms are thus held in place by relatively weak forces causing the rather large atomic thermal parameters for these atoms shown in Tables II and III. Individual distances and angles about the iodine atoms are given in Table VI.

The secondary Te···I bonds link the molecules into infinite chains parallel to the crystallographic *b* axis as shown in Figure 5. A view of the structure down the *b* axis is shown in Figure 6. The intermolecular bonding arrangement in the present structure is the same as that in phenoxatellurin diiodide[2] in which the chains are parallel to the *a* axis. The identity distances along the chains are similar in the two crystals: *b* = 8.182 Å in the present case and *a* = 7.991 Å in phenoxatellurin diiodide. In contrast, the four organotellurium diiodides[2] studied prior to the present case all had distinctly different intermolecular bonding patterns. The absence of I···I intermolecular bonds in the red crystals of dibenzotellurophene

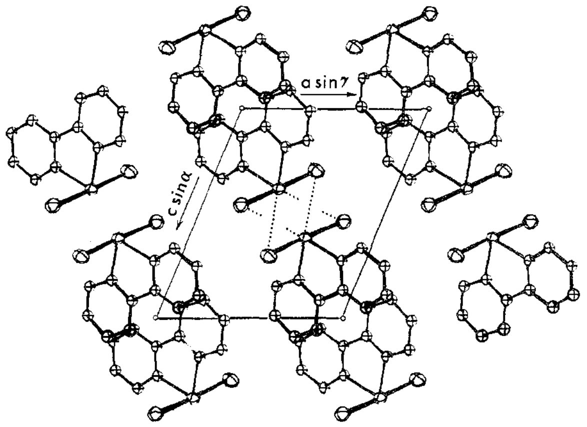

Figure 6. View down the *b* axis, parallel to the direction of the chains.

diiodide gives further support to the color relationship suggested in the Introduction. The intermolecular Te···I bonds in dibenzotellurophene diiodide are the shortest bonds of this kind observed to date. The present values of 3.696 and 3.717 Å are to be compared with the range of values, 3.739–4.30 Å, previously reported.

Symmetry requires the least-squares planes through all of the dibenzotellurophene moieties in the crystal to be parallel. There is some interleaving of the planar groups from neighboring chains as shown in Figure 6. The distances between least-squares planes (measured normal to the planes) are 3.176 Å across the symmetry center at 0, $^1/_2$, 0 and 3.227 Å across the symmetry center at 0, 0, 0. However, the shortest intermolecular packing distances between atoms are somewhat longer: 3.267 Å for C(5)(A; 000)–C(5)(B; $\bar{1}\bar{1}\bar{1}$),[14] 3.365 Å for C(5)(A; 000)–C(9)(B; $\bar{1}0\bar{1}$), and 3.372 Å for C(8)(A; 000)–C(8)(B; $\bar{1}0\bar{1}$). The forces resulting from the C(5)–C(5) and C(8)–C(8) interactions are such as to contribute to the twist of the biphenyl moiety mentioned previously. If the biphenyl moieties were strictly planar (*i.e.*, all atoms in the least-squares planes), the already short C(5)–C(5) and C(8)–C(8) distances would be shorter by ~0.03 and ~0.09 Å, respectively.

The large atomic thermal parameters of the iodine atoms have already been mentioned. Some observations on the vibrations of atoms in the dibenzotellurophene moiety are also of interest. The atoms in the central five-membered ring [Te, C(1), C(6), C(7), C(12)] all have relatively low vibrational amplitudes. In contrast, the outermost or "wing-tip" atoms [C(3), C(4), C(9), C(10)] show the highest amplitudes. This behavior is not surprising, especially since the latter atoms are relatively free of the constraints of short packing contacts with neighboring molecules.

A structural study of uncombined dibenzotellurophene is in progress.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036 Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40686I.

References and Notes

(1) Presented, in part, as Paper No. V-6 at the National Meeting of the American Crystallographic Association, Berkeley, Calif., March 1974.
(2) J. D. McCullough, *Inorg. Chem.*, **12**, 2669 (1973), and references therein.
(3) Dibenzotellurophene dichloride was prepared by a method which will be reported separately: J. D. McCullough, submitted for publication in *Inorg. Chem.*
(4) The computer programs used included the data reduction program PIBAR for the Syntex $P\bar{1}$ diffractometer by Bell and Murphy; ABSN by Coppens for absorption correction; JBPATT, JBFOUR, and PEAKLIST, modified versions of Fourier programs by Blount; a local version of ORFLS (Busing, Martin, and Levy) for structure factor calculations and full-matrix least-squares refinement; SECEXT (Christensen's program modified by Knobler) which makes corrections for the effects of secondary extinction; ORTEP by Johnson for structure plots; MGTL by Gantzel and Trueblood for least-squares planes; a local version of ORFFE (Busing, Martin, and Levy) for distance, angle, and error calculations; and PUBLIST by Hoel for the table of observed and calculated structure amplitudes. All calculations were carried out on the IBM 360-91 at the UCLA Campus Computing Network.
(5) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2]^{1/2}$; $w = [1/\sigma(F_o)]^2$.
(6) In the SECEXT program, secondary extinction corrections are computed by use of the expression $F_{cor} = F_o(1 + C\beta J_o)^{1/2}$ with symbols defined by W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963). In the present case C had the value 3.6×10^{-6}.
(7) Supplementary material.
(8) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 392 (1968).
(9) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.
(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3178 (1965).
(11) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(12) H. Hope, C. B. Knobler, and J. D. McCullough, *Inorg. Chem.*, **12**, 2665 (1973).
(13) C. B. Knobler, J. D. McCullough, and H. Hope, *Inorg. Chem.*, **9**, 797 (1970).
(14) See footnote to Table VI for definition of the symbols used here.