

Å ($\sigma(\text{ext}) = 0.023$ Å, $\sigma(\text{aver}) = 0.006$ Å). The order C-(ortho)-C(meta) > C(P bonded)-C(ortho) > C(meta)-C(para) is precisely that found in the C₆F₅ groups (vide supra) and, again, can be explained as a systematic error induced by thermal motion of the phenyl groups. [This result, incidentally, provides excellent evidence that the treatment of phenyl groups as systems having precise *D*_{6h} symmetry is *not* the ideal description for the X-ray diffraction experiment.]

Intermolecular Contacts

There are no extraordinarily short intermolecular contacts, the molecules being separated by normal van der Waals distances. Shortest intermolecular contacts of each type, excluding those involving hydrogen atoms, are F(4A)···F(6E, *n*) = 2.789 (8) Å, F(7A)···C(8E, $\bar{1}$) = 3.017 (10) Å, and C(6D)···C(9S, $\bar{1}$) = 3.208 (22) Å.

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Registry No. RhAg₂(C≡CC₆F₅)₅(PPh₃)₃, 54873-31-3.

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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy of \$2.50 for microfiche, referring to code number AIC503935-11-75.

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Crystal and Molecular Structure of Dibenzotellurophene, C₁₂H₈Te

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The structure of dibenzotellurophene, C₁₂H₈Te, has been determined by use of data collected on an automated diffractometer with monochromatized Mo K α radiation. The compound crystallizes in the orthorhombic space group *P*2₁2₁2₁ with unit cell dimensions *a* = 12.621 (7) Å, *b* = 16.192 (7) Å, *c* = 4.637 (2) Å, and *V* = 947.6 (8) Å³. The density of 1.962 (2) g cm⁻³ calculated on the basis of four molecules per unit cell agrees well with the flotation value of 1.95 (2) g cm⁻³. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to a conventional *R* index of 2.9% based on 1210 observed reflections. The dibenzotellurophene molecule is slightly folded, with dihedral angles of 1.4 (2) and 0.6 (2)° between the five-membered and the six-membered rings. The observed Te-C bond distances are 2.084 (5) and 2.089 (5) Å (average 2.087 Å) and the C-Te-C bond angle is 81.7 (2)°. The intra-ring bond distances and angles in the six-membered rings are close to those observed in dibenzoselenophene, dibenzothiophene, and dibenzofuran. Trends in the geometry of the five-membered rings in the four dibenzochalcophenes are noted.

Introduction

The crystal and molecular structures of dibenzoselenophene,¹ dibenzothiophene,² and dibenzofuran³ have been reported. The present study of the structure of dibenzotellurophene was undertaken primarily as an interesting extension of that series. A second objective was a comparison of the structure of the uncombined dibenzotellurophene molecule with that of the dibenzotellurophene moiety in the diiodide.⁴

Experimental Section

Crystals of dibenzotellurophene were prepared as described earlier.⁵ These were pale yellow needles elongated on the crystallographic *c*

axis with principal faces belonging to the forms {120} and {100}. A preliminary study of two crystals by Weissenberg and precession methods showed orthorhombic symmetry with systematic absences of *h*00 with *h* odd, 0*k*0 with *k* odd, and 00*l* with *l* odd. The space group was thus indicated to be *P*2₁2₁2₁. A crystal fragment bounded prismatically by six faces of the forms indicated above and terminated by fractures approximating faces of the form {001} was selected for data collection. The dimensions were 0.25 mm between (120) and ($\bar{1}\bar{2}$ 0), 0.25 mm between ($\bar{1}\bar{2}$ 0) and (1 $\bar{2}$ 0), 0.30 mm between (100) and ($\bar{1}$ 00), and 0.35 mm between the approximate (001) and (00 $\bar{1}$) surfaces. The crystal was mounted with the normal to (120) 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

Table I. Atomic Positional Parameters in Dibenzotellurophene

Atom	x	y	z
Te	0.31265 (2) ^a	0.90957 (2)	0.51381 (7)
C(1)	0.3979 (4)	0.8131 (3)	0.7025 (11)
C(2)	0.3588 (5)	0.7549 (4)	0.8983 (14)
C(3)	0.4267 (6)	0.6937 (4)	0.9949 (16)
C(4)	0.5303 (6)	0.6894 (4)	0.9039 (15)
C(5)	0.5685 (4)	0.7478 (3)	0.7134 (14)
C(6)	0.5025 (4)	0.8113 (3)	0.6103 (11)
C(7)	0.5358 (4)	0.8753 (3)	0.4083 (10)
C(8)	0.6381 (4)	0.8839 (4)	0.2949 (13)
C(9)	0.6614 (4)	0.9450 (4)	0.1008 (14)
C(10)	0.5840 (4)	1.0014 (4)	0.0150 (15)
C(11)	0.4833 (4)	0.9955 (3)	0.1275 (13)
C(12)	0.4591 (4)	0.9325 (3)	0.3221 (11)
H(2) ^b	0.300 (4)	0.764 (4)	1.000 (15)
H(3)	0.410 (5)	0.666 (4)	1.145 (16)
H(4)	0.583 (4)	0.636 (4)	0.922 (14)
H(5)	0.663 (5)	0.750 (3)	0.680 (16)
H(8)	0.689 (4)	0.859 (4)	0.338 (15)
H(9)	0.738 (5)	0.951 (3)	0.042 (15)
H(10)	0.611 (4)	1.042 (4)	-0.136 (15)
H(11)	0.436 (4)	1.032 (3)	0.066 (14)

^a The numbers given in parentheses here and in succeeding 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.

centering, indexing, and least-squares routines of the instrument were applied to 15 selected reflections in the 2θ range from 15 to 39° to obtain a set of lattice parameters. Based on $\lambda(\text{Mo K}\alpha)$ 0.71073 Å, the results at 25°C are $a = 12.621$ (7) Å, $b = 16.192$ (7) Å, $c = 4.637$ (2) Å, and $V = 947.6$ (8) Å³. The density calculated for four molecules per unit cell is 1.962 (2) g cm⁻³, which compares favorably with the value 1.95 (2) g cm⁻³ measured by flotation in a mixture of ethylene bromide and carbon tetrachloride.

The intensity data were collected with Mo K α radiation, a scan rate of 2° min⁻¹, and a scan range from 1.00° below the K α_1 peak to 1.00° above the K α_2 peak. Background counts were taken for 0.40 of the scan time at each end of the scan range and the pulse height analyzer was set at an 85% window for Mo K α radiation. The intensities of three standard reflections (600), (060), and (002) were measured after every 97 intensity measurements. These showed only statistical variations in a range consistent with the $\sigma(I)$ values involved. Reflection data were measured in the range 2.5° < 2θ < 56°, yielding a total of 1447 measurements. These included 45 periodic checks of standards and 23 space group extinctions. A total of 169 reflections for which $I < 3\sigma(I)$ were considered unobserved and were omitted from the refinement. The number of unique, observed reflections remaining was 1210. The data were all processed as previously described,⁴ with a value of 0.04 for p . In addition to the usual Lorentz and polarization corrections, the values of I and $\sigma(I)$ were also corrected for absorption. The calculated value of μ was 31.8 cm⁻¹ for Mo K α radiation and the transmission factors ranged from 0.375 to 0.500.

Determination and Refinement of the Structure

The approximate position of the tellurium atom was obtained from a three-dimensional Patterson summation. The determination of the

Table II. Atomic Thermal Parameters in Dibenzotellurophene^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te	42.6 (2)	35.9 (1)	483 (2)	4.2 (1)	7.2 (6)	21.2 (5)
C(1)	57 (3)	34 (2)	352 (22)	-2 (2)	-4 (8)	-26 (6)
C(2)	76 (4)	40 (3)	456 (27)	-6 (3)	30 (9)	-25 (7)
C(3)	131 (7)	37 (2)	449 (27)	-19 (3)	12 (16)	-1 (9)
C(4)	99 (5)	35 (2)	523 (31)	8 (3)	-39 (11)	3 (7)
C(5)	74 (4)	38 (2)	434 (27)	6 (3)	-38 (10)	-14 (6)
C(6)	53 (3)	33 (2)	319 (19)	0 (2)	-23 (7)	-23 (5)
C(7)	49 (3)	30 (2)	318 (19)	-2 (2)	-14 (6)	-23 (5)
C(8)	46 (3)	46 (2)	435 (26)	5 (2)	-10 (8)	-12 (7)
C(9)	51 (3)	49 (3)	497 (27)	-3 (3)	10 (8)	-11 (8)
C(10)	68 (4)	43 (2)	460 (27)	-10 (2)	2 (11)	-5 (8)
C(11)	57 (3)	33 (2)	451 (26)	1 (2)	-20 (9)	0 (6)
C(12)	47 (3)	29 (2)	371 (22)	0 (2)	-22 (7)	-22 (5)

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

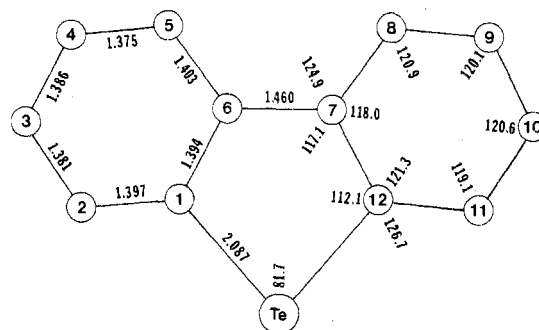


Figure 1. Drawing of the dibenzotellurophene molecule showing average values of the chemically equivalent bonds and angles. Hydrogen atoms are omitted from this and other figures.

carbon atom positions by Fourier and least-squares procedures was straightforward. After the refinement of the positional and anisotropic thermal parameters of the 13 heavier atoms had converged, the eight hydrogen atoms were added at calculated positions with fixed isotropic thermal parameters, $B = 5.0$ Å². At this stage it was also apparent that the strongest (low-order) reflections were showing the effects of secondary extinction. The intensities of all observed reflections were accordingly processed by SECEXT.⁶ Further least-squares refinement then resulted in a final convergence at a conventional R index of 2.9% and a weighted index, R_w , of 3.5%.⁷ In the final least-squares cycle, the largest shift in a positional or thermal parameter was 0.05σ for Te, 0.07σ for C, and 0.3σ for a hydrogen positional parameter. The final "goodness of fit" defined as $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ was 1.39. In this expression $N_o = 1210$, the number of observed reflections used in the refinement, and $N_v = 142$, the number of variable parameters. A final difference Fourier showed maxima of up to $0.5 e/\text{Å}^3$ within 0.7 Å of the tellurium atom but no other maxima or minima of significance.

The final positional and thermal parameters are given in Tables I and II. Table III lists the root-mean-square amplitudes of vibration along the three principal axes of the vibrational ellipsoids together with the corresponding B values for the nonhydrogen atoms. A set of structure factors was calculated on the basis of the tabulated parameters and is available on request.⁸ The atomic scattering factors used for tellurium were obtained by averaging Doyle and Turner's⁹ values for Sb⁰ and I⁰, those for carbon were the neutral atom values given in ref 10, and the hydrogen factors were from Stewart, Davidson, and Simpson.¹¹ The real and imaginary components of anomalous dispersion for Mo K α radiation were applied to the scattering factors for tellurium.¹² An analysis of the values of $||F_o| - |F_c||$ for the 169 unobserved reflections showed 60% to be less than $\sigma(F_o)$, 26% in the range from $\sigma(F_o)$ to $2\sigma(F_o)$, and 10% in the range from $2\sigma(F_o)$ to $3\sigma(F_o)$. Six reflections were beyond this range with a maximum difference of $3.5\sigma(F_o)$.

Description and Discussion of the Structure

The dibenzotellurophene molecule and a view of the crystal structure down the c axis are shown in Figures 1 and 2 respectively. Individual bond distances and angles within the molecule are listed in Table IV and the average values for

Table III. Root-Mean-Square Amplitudes of Vibration and Equivalent B Values^a

Atom	Rms amplitude, Å			Equiv B , Å ²		
	Min	Median	Max	Min	Median	Max
Te	0.179 (1)	0.210 (1)	0.242 (1)	2.53	3.48	4.62
C(1)	0.176 (7)	0.214 (6)	0.229 (7)	2.45	3.62	4.14
C(2)	0.204 (7)	0.226 (7)	0.268 (8)	3.29	4.03	5.67
C(3)	0.208 (7)	0.221 (7)	0.335 (8)	3.42	3.86	8.86
C(4)	0.207 (7)	0.233 (8)	0.294 (8)	3.38	4.29	6.83
C(5)	0.200 (7)	0.219 (7)	0.264 (8)	3.16	3.79	5.50
C(6)	0.165 (7)	0.208 (6)	0.226 (6)	2.15	3.42	4.03
C(7)	0.163 (7)	0.204 (6)	0.215 (6)	2.10	3.29	3.65
C(8)	0.189 (7)	0.215 (7)	0.253 (7)	2.82	3.65	5.05
C(9)	0.201 (7)	0.230 (7)	0.259 (7)	3.19	4.18	5.30
C(10)	0.213 (6)	0.224 (7)	0.256 (6)	3.58	3.95	5.18
C(11)	0.203 (7)	0.211 (6)	0.232 (7)	3.25	3.52	4.25
C(12)	0.168 (7)	0.195 (6)	0.223 (6)	2.23	3.00	3.93

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

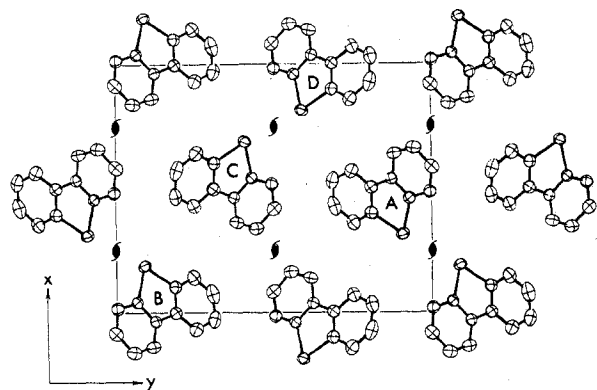


Figure 2. The packing arrangement of dibenzotellurophene molecules as viewed along the z axis, the positive direction of which is into the paper. The coordinates of the symmetry positions, as used in this study: A = x, y, z ; B = $1/2 - x, 1 - y, 1/2 + z$; C = $1 - x, -1/2 + y, 1/2 - z$; D = $1/2 + x, 1/2 - y, 1 - z$.

chemically equivalent bonds and angles are given in Figure 1. Data on a number of least-squares planes of interest are given in Table V which also includes the root-mean-square (rms) displacements of the atoms (shown by asterisks) which were used to define the respective planes. While the dibenzotellurophene molecule as a whole is nearly planar, with an rms deviation of 0.015 Å for the 13 nonhydrogen atoms from their least-squares plane, the five-membered and the two six-membered rings are even more closely planar with rms deviations of 0.005, 0.005, and 0.006 Å, respectively. These latter figures are very close to the esd of the carbon atom positions. The larger deviations of the molecule as a whole from planarity appear to be due primarily to two small distortions: one a bending of ring C with respect to ring B by 0.6 (2)° along the line of C(7)–C(12) and the other a rotation of ring A with respect to ring C by 1.4 (2)° about an axis approximately along the line of C(6)–C(7). This analysis was based on the deviations of individual atoms from least-squares planes B and E in Table V.

The distortions from planarity in the uncombined dibenzotellurophene molecule are significantly smaller than those in the dibenzotellurophene moiety in the diiodide.⁴ In the latter case the rms deviation of the 13 atoms from their least-squares plane is 0.029 Å and the twist along the C(6)–C(7) bond is 3.3°. The larger distortions in the diiodide are probably due to packing constraints caused by the relatively strong intermolecular bonding between tellurium and iodine atoms. As a result, the distances between the least-squares planes through the dibenzotellurophene moieties are only 3.176 and 3.227 Å in the diiodide in contrast to the 3.545-Å separation in un-

Table IV. Bond Distances and Angles in Dibenzotellurophene^a

(a) Distances, Å			
Te–C(1)	2.089 (5)	Te–C(12)	2.084 (5)
C(1)–C(2)	1.398 (8)	C(12)–C(11)	1.395 (7)
C(2)–C(3)	1.384 (9)	C(11)–C(10)	1.377 (7)
C(3)–C(4)	1.376 (9)	C(10)–C(9)	1.396 (8)
C(4)–C(5)	1.381 (9)	C(9)–C(8)	1.369 (8)
C(5)–C(6)	1.406 (7)	C(8)–C(7)	1.400 (7)
C(6)–C(1)	1.389 (7)	C(7)–C(12)	1.399 (6)
C(6)–C(7)	1.460 (7)		
C(2)–H(2)	0.89 (6) ^b	C(11)–H(11)	0.89 (5)
C(3)–H(3)	0.86 (7)	C(10)–H(10)	1.02 (6)
C(4)–H(4)	1.10 (7)	C(9)–H(9)	1.01 (6)
C(5)–H(5)	1.20 (6)	C(8)–H(8)	0.78 (5)

(b) Bond Angles, deg			
C(1)–Te–C(12)	81.7 (2)		
Te–C(1)–C(2)	126.5 (4)	Te–C(12)–C(11)	126.9 (4)
Te–C(1)–C(6)	112.1 (4)	Te–C(12)–C(7)	112.0 (4)
C(1)–C(2)–C(3)	118.3 (6)	C(12)–C(11)–C(10)	119.9 (5)
C(2)–C(3)–C(4)	121.7 (6)	C(11)–C(10)–C(9)	119.5 (6)
C(3)–C(4)–C(5)	119.5 (6)	C(10)–C(9)–C(8)	120.6 (5)
C(4)–C(5)–C(6)	120.7 (6)	C(9)–C(8)–C(7)	121.1 (5)
C(5)–C(6)–C(1)	118.3 (5)	C(8)–C(7)–C(12)	117.7 (5)
C(6)–C(1)–C(2)	121.4 (5)	C(7)–C(12)–C(11)	121.1 (5)
C(5)–C(6)–C(7)	124.5 (5)	C(8)–C(7)–C(6)	125.2 (5)
C(1)–C(6)–C(7)	117.2 (5)	C(12)–C(7)–C(6)	117.0 (4)
H(2)–C(2)–C(1)	121 (4)	H(11)–C(11)–C(12)	123 (4)
H(2)–C(2)–C(3)	118 (4)	H(11)–C(11)–C(10)	117 (4)
H(3)–C(3)–C(2)	119 (4)	H(10)–C(10)–C(11)	128 (3)
H(3)–C(3)–C(4)	117 (4)	H(10)–C(10)–C(9)	112 (3)
H(4)–C(4)–C(3)	126 (3)	H(9)–C(9)–C(10)	122 (3)
H(4)–C(4)–C(5)	112 (3)	H(9)–C(9)–C(8)	117 (3)
H(5)–C(5)–C(4)	117 (3)	H(8)–C(8)–C(9)	111 (5)
H(5)–C(5)–C(6)	122 (3)	H(8)–C(8)–C(7)	128 (5)

^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 0.97 Å suggest a σ value of 0.14 Å.

Table V. Results of Least-Squares Planes Calculations

Atom	Distances of Atoms from Least-Squares Planes, Å ^a				
	Plane A	Plane B	Plane C	Plane D	Plane E
Te	–0.061	–0.004*	–0.024	–0.016*	0.000*
C(1)	–0.008*	0.006*	–0.025	0.010*	0.016
C(2)	0.004*	0.016	–0.031	0.020*	0.031
C(3)	0.003*	–0.015	–0.067	0.000*	0.004
C(4)	–0.005*	–0.051	–0.094	–0.025*	–0.035
C(5)	0.000*	–0.042	–0.071	–0.017*	–0.033
C(6)	0.006*	–0.006*	–0.029	0.008*	0.000*
C(7)	0.008	0.007*	–0.007*	0.013*	0.000*
C(8)	0.037	0.006	0.009*	0.028*	0.001
C(9)	0.004	–0.019	–0.003*	0.000*	–0.031
C(10)	–0.034	–0.026	–0.005*	–0.018*	–0.040
C(11)	–0.037	–0.004	0.007*	–0.006*	–0.014
C(12)	–0.022	0.003*	–0.001*	0.003*	–0.001
Rms dev ^b	0.005	0.005	0.006	0.015	0.000
Interplanar Angles, deg					
[Plane A]–[plane B]				1.4 (2)	
[Plane B]–[plane C]				0.6 (2)	
[Plane A]–[plane C]				1.5 (2)	

^a Atoms used to define the least-squares planes are indicated by asterisks. ^b The root-mean-square deviations (in Å) of the asterisked atoms from their respective least-squares planes.

combined dibenzotellurophene. Also the shortest intermolecular C–C packing distances in the diiodide are 3.267, 3.365, and 3.372 Å, compared to a shortest intermolecular C–C separation of 3.530 Å in dibenzotellurophene. The van der Waals separation between aromatic carbon atoms is given as 3.40 Å.¹³ A listing of packing distances in dibenzotellurophene is given in Table VI and the main features of the packing along

Table VI. Shortest Intermolecular Packing Distances in Dibenzotellurophene^a

1st atom ^b	2nd atom	Symmetry position ^c	Lattice translation	Distance, Å	van der Waals sum, ¹³ Å
Te	Te	B	010	4.056	4.40
Te	Te	B	011	4.056	
Te	C(11)	A	001	3.830	3.90
Te	C(2)	A	001	3.843	
C(7)	C(10)	A	001	3.530	3.40
C(1)	C(12)	A	001	3.549	
C(3)	C(6)	A	001	3.561	
C(5)	C(8)	A	001	3.590	
C(9)	H(9)	B	110	2.94	2.9
H(2)	H(5)	D	101	2.30	2.4
H(9)	H(10)	B	110	2.41	

^a All listed contacts, except those involving hydrogen atoms, are shown on Figure 3. ^b The first atom of each pair is in the molecule in position A of the origin unit cell, 000. ^c See Figures 2 and 3 for further information on symmetry positions and lattice translations.

the 2₁ screw axes parallel to *c* are shown in Figure 3.

A comparison of the tellurium-carbon bond distances in dibenzotellurophene and its diiodide is also of interest. In the present study of dibenzotellurophene, the observed Te-C distances are 2.084 (5) and 2.089 (5) Å with an average of 2.087 Å. In the diiodide, the Te-C distances are 2.111 (4) and 2.113 (4) Å with an average of 2.112 Å. The Te-C distance is thus increased by 0.025 Å, or approximately 5σ, when the covalency of tellurium is increased from two to four in this system. In contrast, the C-Te-C bond angles of 81.7 (2) and 81.8 (2) in the two structures are not significantly different. However, this similarity probably results from geometric requirements of the heterocyclic ring rather than from identical directed valencies.

Table VII presents the average values of chemically equivalent bond distances and bond angles in the series dibenzotellurophene, dibenzoselenophene, dibenzothiophene, and dibenzofuran. In comparing corresponding features of the four compounds, the following points are of interest.

(1) The carbon to heteroatom bond distances, C-X, behave about as expected for bonds between sp² carbon and the heteroatoms involved.

(2) The C-X-C bond angles increase markedly in going from tellurium to oxygen. While these angles normally increase from C-Te-C to C-O-C in unconstrained molecules

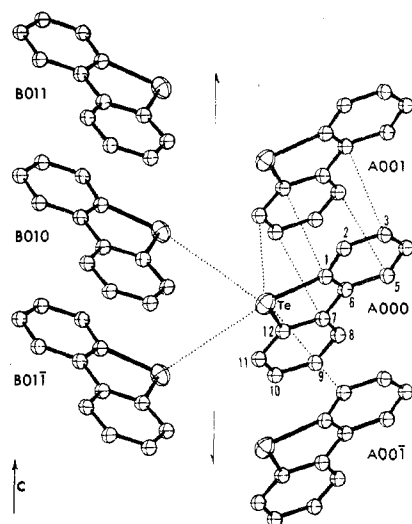


Figure 3. Plot showing the packing of dibenzotellurophene molecules along the twofold screw axes parallel to *c*. The view is perpendicular to the plane which includes the tellurium atoms and the screw axis. The carbon atoms are shown here with small, artificial isotropic thermal parameters. Some of the packing interactions given in Table VI are shown here by means of dotted lines.

such as (CH₃)₂X, etc., the effect observed here is much greater. The reason for this is to be found in the great change in C-X distance within the five-membered ring, while the carbon atoms are resisting too large a shift in their bond angles from the ideal 120° value.

(3) Within the six-membered rings (a) bonds C(1)-C(6) and C(5)-C(6) tend to be long while C(2)-C(3) and C(4)-C(5) tend to be short; (b) the angle at C(2) is less than 120° in all four compounds and decreases as the heteroatom changes from Te to O, and (c) the angle at C(6) is nearly constant at 118.5° ± σ in all four molecules.

(4) Within the five-membered rings the angles at carbon are forced to values less than the ideal 120° value for sp² carbon. While the X-C(1)-C(6) angle remains practically constant at 112.5° ± σ, the C(1)-C(6)-C(7) angle decreases markedly from 117.1 (5) in the tellurium compound to 105.6 (4)° in dibenzofuran.

(5) The angle C(5)-C(6)-C(7) (external to the rings) is greater than 120° in all four molecules and increases from 124.9 (5)° in dibenzotellurophene to 135.5° in dibenzofuran.

Table VII. Comparison of Bond Distances (Å) and Bond Angles (deg) in Dibenzotellurophene, Dibenzoselenophene, Dibenzothiophene, and Dibenzofuran

Distance or angle	Dibenzotellurophene	Dibenzoselenophene ¹	Dibenzothiophene ²	Dibenzofuran ³
X-C(1)	2.087 (5)	1.899 (5)	1.740 (8)	1.418 (6)
C(1)-C(2)	1.397 (7)	1.395 (7)	1.386 (11)	1.401 (8)
C(2)-C(3)	1.381 (7)	1.371 (7)	1.384 (11)	1.383 (8)
C(3)-C(4)	1.386 (8)	1.377 (7)	1.385 (11)	1.377 (8)
C(4)-C(5)	1.375 (8)	1.380 (7)	1.370 (11)	1.386 (8)
C(5)-C(6)	1.403 (7)	1.395 (7)	1.392 (11)	1.387 (7)
C(6)-C(1)	1.394 (6)	1.398 (7)	1.409 (11)	1.382 (7)
C(6)-C(7)	1.460 (7)	1.453 (7)	1.441 (11)	1.480 (6)
C-X-C	81.7 (2)	86.7 (2)	91.5 (4)	104.4 (4)
X-C(1)-C(2)	126.7 (4)	126.1 (4)	126.2 (6)	123.2 (5)
X-C(1)-C(6)	112.1 (4)	112.3 (4)	112.3 (6)	112.9 (4)
C(1)-C(2)-C(3)	119.1 (5)	118.7 (5)	117.8 (7)	115.3 (5)
C(2)-C(3)-C(4)	120.6 (6)	120.9 (5)	121.6 (7)	122.1 (5)
C(3)-C(4)-C(5)	120.1 (5)	120.6 (5)	120.5 (7)	121.4 (5)
C(4)-C(5)-C(6)	120.9 (5)	120.3 (5)	120.0 (7)	118.5 (5)
C(5)-C(6)-C(1)	118.0 (5)	118.1 (5)	118.7 (7)	118.9 (4)
C(6)-C(1)-C(2)	121.3 (5)	121.6 (5)	121.6 (7)	123.9 (5)
C(5)-C(6)-C(7)	124.9 (5)	127.6 (5)	129.4 (7)	135.5 ^a
C(1)-C(6)-C(7)	117.1 (5)	114.3 (5)	111.9 (7)	105.6 (4)

^a This angle was not given in ref 3. The value shown here was calculated from angles C(1)-C(6)-C(7) and C(5)-C(6)-C(1) on the assumption of a planar system.

Table VIII. Comparison of Some Crystallographic Data for $C_{12}H_8X$ Compounds

Compd	Crystal system	Space group	No. of molecules in	
			Unit cell	Asymmetric unit
Dibenzo-tellurophene	Orthorhombic	$P2_12_12_1$	4	1
Dibenzo-selenophene	Orthorhombic	$Pbca$	16	2
Dibenzo-thiophene	Monoclinic	$P2_1/c$	4	1
Dibenzofuran	Orthorhombic	$Pnam$	4	$1/2^a$

^a The dibenzofuran molecule is required crystallographically to have a plane of symmetry perpendicular to the C(6)–C(6') bond at its midpoint.

In general, the four compounds have quite similar molecular structures which differ mainly because of the range of X–C distances involved. However, the crystal structures and packing arrangements differ distinctly from compound to compound. The differences are shown in condensed form in Table VIII. Of particular interest is the number of chemical molecules in the crystallographic asymmetric unit, which ranges from $1/2$ in dibenzofuran to 2 in dibenzoselenophene. The latter compound is unique in the series in forming loosely associated dimers with intermolecular C–C contacts as short as 3.36 Å.

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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 Business Office, Books and Journals Division, 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 AIC50341F-11-75.

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Stereochemistry of Low-Spin Cobalt Porphyrins. VII. (3,5-Dimethylpyridine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II)

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(3,5-Dimethylpyridine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II) crystallizes in the monoclinic system, space group $P2_1/c$. The unit cell has $a = 11.514$ (11) Å, $b = 30.939$ (10) Å, $c = 11.571$ (11) Å, and $\beta = 103.73$ (1)° and contains four molecules. The calculated and experimental densities are 1.292 and 1.29 g/cm³, respectively, at $20 \pm 1^\circ$. Measurement of diffracted intensities employed ω scanning with graphite-monochromated Mo K α radiation on a four-circle diffractometer. All independent reflections for $(\sin \theta)/\lambda \leq 0.602 \text{ \AA}^{-1}$ were measured; 4435 reflections were retained as observed. These data were used for the determination of structure using the heavy-atom technique. The final conventional and weighted discrepancy factors were 0.076 and 0.092, respectively. The square-pyramidal CoN₅ coordination group has an average equatorial bond length of 2.000 Å; the axial Co–N_b bond is 2.161 (5) Å. The cobalt(II) atom is displaced 0.17 Å from the mean porphinato plane and 0.14 Å from the plane of the porphinato nitrogens.

There has been considerable recent interest in structural^{1–5} and solution^{6–10} studies of low-spin cobalt(II) porphyrins. This work has been stimulated by the discovery⁶ that cobalt(II) porphyrins reversibly bind molecular oxygen and that cobaltohemoglobin,¹¹ the product of replacement in hemoglobin of the protohemes by molecules of the corresponding low-spin cobalt(II) protoporphyrin, displays reversible uptake of oxygen that is qualitatively similar in all respects to the uptake of oxygen by hemoglobin. Some controversy has attended the interpretation¹² of the cooperative oxygen binding of cobaltohemoglobin.

Solution studies^{6,8,9} of cobalt(II) porphyrins have shown that alkylamines and -pyridines can add either one or two molecules of base to form five-coordinate or six-coordinate complexes. Imidazoles and substituted imidazoles, however, appear to form *only* five-coordinated complexes. This difference in reactivity between imidazoles and other nitrogenous bases has been suggested¹³ to be the result of electronic effects peculiar to imidazoles.

In the process of attempting to prepare crystals of cobalt(II) porphyrins coordinated by sterically hindered bases, we unexpectedly obtained crystals of (3,5-dimethylpyridine)-