

The Crystal Structure of Phenoxatellurine, $C_{12}H_8OTe$

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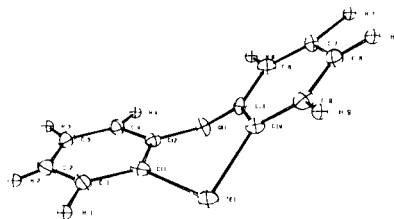
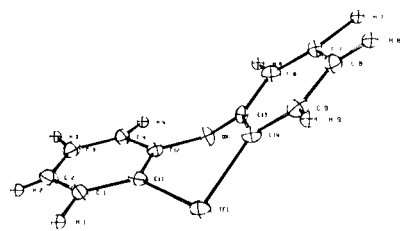
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The crystal structure of phenoxatellurine, $C_{12}H_8OTe$, was determined by X-ray diffractometer methods. The crystals are orthorhombic, $P2_12_12_1$, $a = 6.036(1)$, $b = 8.160(1)$, $c = 20.717(5)$ Å at $t = 22^\circ$. The positions of all atoms, including hydrogen, were found. The central ring is folded along the Te-O axis (138°). Average bond distances are Te-C = 2.098, C-O = 1.397, C-C = 1.382 Å. The phenyl rings are planar with a dihedral angle of 145° ; C-Te-C = $89.4(3)^\circ$, C-O-C = $121.2(5)^\circ$. The structure is compared to those of phenoxathionine and phenothiazine.

Introduction.

The chemistry of organic tellurium compounds has been a relatively neglected field, and a recent survey (2) has indicated some of the numerous gaps in our knowledge of it. One of many remarkable organic tellurium molecules is a heterocyclic anthracene analogue, phenoxatellurine, pt, $C_{12}H_8OTe$. The compound is remarkable for its thermal stability, the relative ease with which it may be transformed into a variety of materials in which tellurium exhibits higher oxidation numbers (3), especially IV, and the variety of complexes that it and its derivatives appear to form with one another (4). The molecule is similar to phenoxthionine, the structure of which was determined in 1966 (5). A preliminary study of pt was reported by Wood, McCale, and Williams (6). They suggested that the molecule is folded about the Te-O axis, and the angle of fold is in the range $130-150^\circ$. According to Hosoya (5), crystals of phenoxathionine, phenoxaselenine, and phenoxatellurine are isomorphous. The present study of pt has been carried out with X-ray diffractometer methods so as to provide a firm basis for comparison with other phenoxatellurine derivatives in which the oxidation number of Te is varied, and thus to examine how changes in oxidation number affect the structures of a series of closely related organic tellurium compounds.



EXPERIMENTAL

Pale yellow needles of pt were crystallized from acetone. A crystal, $0.4 \times 0.5 \times 0.4$ (mm)³, was mounted on a pyrex fiber and examined on a Buerger precession camera with $CuK\alpha$ radiation. From systematic extinctions, the space group was identified as $P2_12_12_1$. The crystal was aligned on a Syntex autodiffractometer. Values of 2θ for 20 general reflections were measured, and least-squares refinement gave lattice constants $a = 6.036(1)$, $b = 8.160(1)$, $c = 20.717(5)$ Å at $t = 22^\circ$. Intensities were collected by scanning in 2θ (scan rate = $4^\circ/\text{min.}$, scan range = 3° , 2θ max. = 65°), using $MoK\alpha$ radiation ($\lambda = 0.7107$ Å) monochromatized by reflection from the (002) plane of an oriented graphite crystal (2θ mon = $12^\circ 15'$). Lorentz, polarization and absorption corrections were applied to 1215 independent reflections for which $I > 3\sigma(I)$ where $\sigma(I)$ was estimated from counting statistics. The polarization factor was taken to be $(P_1 + P_2)/2$, where (7)

$$P_1 = \frac{\cos^2 2\theta + |\cos 2\theta \text{ mon}|}{1 + |\cos 2\theta \text{ mon}|} \text{ and}$$

$$P_2 = \frac{\cos^2 2\theta + \cos^2 2\theta}{1 + \cos^2 2\theta \text{ mon}}$$

The absorption correction was obtained from ϕ -scan data.

Structure Determination.

The coordinates of Te were obtained from a three-dimensional Patterson synthesis. A combination of least-squares refinements and difference Fourier syntheses led to the location of all atoms, including hydrogen. Block-

TABLE I

Atomic Coordinates and Standard Deviations ($\times 10^4$) for (a) Phenoxatellurine and (b) Phenoxathionine

	(a)			(b)			
	x/a(σ)	y/b(σ)	z/c(σ)	x/a(σ)	y/b(σ)	z/c(σ)	
Te	-732.0(9)	984.9(7)	3663.2(3)	S	-440(15)	1436(11)	3614(4)
O5	3751(7)	3171(8)	3656(3)		3957(33)	3402(24)	3656(9)
Cl	819(16)	1354(10)	2264(4)		561(61)	1454(43)	2278(13)
C2	2254(20)	1774(12)	1776(5)		1972(62)	1918(41)	1778(15)
C3	4101(19)	2688(11)	1907(4)		4104(60)	2809(39)	1873(14)
C4	4565(14)	3145(10)	2539(4)		4625(57)	3350(37)	2522(14)
C6	2874(14)	5148(11)	4430(5)		2978(56)	5286(36)	4496(13)
C7	1508(16)	5746(11)	4901(4)		1512(49)	5757(34)	5002(13)
C8	-546(17)	5043(11)	5024(4)		-552(57)	4903(33)	5074(12)
C9	-1237(14)	3758(11)	4645(5)		-1238(49)	3637(38)	4622(12)
C11	1277(13)	1784(9)	2904(5)		1186(48)	2015(32)	2941(12)
C12	3151(13)	2692(9)	3023(4)		3247(53)	2960(35)	3035(12)
C13	2216(11)	3802(10)	4079(3)		2383(49)	3952(33)	4086(11)
C14	147(12)	3089(9)	4190(4)		315(50)	3130(31)	4112(11)
H1	-440(148)	554(94)	2133(41)				
H2	2045(249)	1332(143)	1400(59)				
H3	5186(131)	3224(94)	1601(37)				
H4	5622(170)	3685(119)	2805(47)				
H6	4257(179)	5609(115)	4275(48)				
H7	2029(221)	6961(140)	5471(61)				
H8	-1956(186)	5466(119)	5193(50)				
H9	-3041(164)	3355(112)	4694(44)				

diagonal least-squares refinement (8) with unit weights, anisotropic temperature factors for Te, O and C, and isotropic temperature factors for H gave a final value for the R_1 factor, $R_1 = \sum | |F_o| - |F_c| | / \sum |F_o| = 0.040$. For the final least-squares refinements the data were weighted by the empirical function $\omega = 1/\sigma^2$; $\sigma = -0.50 + 0.032 |F_o|$, $|F_o| > 40.0$; $\sigma = 0.96 - 0.004 |F_o|$, $|F_o| < 40.0$. Corrections for anomalous dispersion were included (9) and the B's for hydrogen were fixed at the values obtained in the previous refinement since they were very slow to converge. Since the space group, $P2_1 2_1 2_1$, is non-centrosymmetric, two enantiomeric forms of the crystals are produced, which may be considered to differ only with regard to the choice of coordinates (x,y,z) or $(\bar{x},\bar{y},\bar{z})$. Both coordinate possibilities were tested, and the best values of the agreement indices obtained were $R_1 = 0.039$, $R_2 = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2} = 0.045$; the error in an observation of unit weight, Σ , was $\Sigma = 1.22$. Refine-

ment was continued until all parameter shifts were less than 10% of their estimated standard deviations.

In order to compare the structure of pt with that of phenoxathionine, the 353 values of $|F_o|$ given by Hosoya squares refinement of non-hydrogen atom coordinates and temperature factors. Because there were relatively few data, only S was refined anisotropically. Both coordinate possibilities, $\pm (x,y,x)$ were tested, on the assumption that $\text{CuK}\alpha$ radiation was used by Hosoya. (Although the radiation employed was not specified, the maximum value of $\sin\theta$ reported by him corresponds to $\text{CuK}\alpha$). No significant differences in the final structures were obtained with either choice of coordinates, nor were any hydrogen atoms visible in difference Fourier syntheses. The final results gave $R_1 = 0.128$, $R_2 = 0.139$, which are reasonable values for photographic data. The coordinates of Table I were obtained with the scattering factor, f , for sulfur, taken as $f = \sqrt{(f_o + \Delta f')^2 + (\Delta f'')^2}$.

TABLE II

Temperature Factors and Standard Deviations for
(a) Phenoxatellurine and (b) Phenoxathionine.

(a) Phenoxatellurine. (β -values are multiplied by 10^4).

	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Te	259.7(11)	154.2(6)	30.5(1)	-51.9(20)	-4.9(10)	-1.9(7)
O5	179(12)	232(10)	22(1)	0(18)	-5(8)	-18(7)
C1	368(26)	162(13)	24(2)	31(37)	-20(15)	-17(8)
C2	476(36)	155(14)	33(3)	42(42)	-22(19)	-18(11)
C3	414(32)	181(14)	25(2)	62(42)	28(17)	8(9)
C4	300(27)	167(13)	23(2)	-28(33)	-1(14)	-4(9)
C6	253(22)	153(13)	32(3)	-42(30)	-2(14)	2(10)
C7	407(28)	163(14)	16(2)	3(33)	6(12)	-5(8)
C8	337(26)	180(14)	22(2)	43(38)	16(16)	3(9)
C9	267(23)	173(14)	30(2)	18(30)	8(12)	13(10)
C11	245(21)	109(10)	33(2)	11(25)	-21(12)	-7(8)
C12	229(20)	129(11)	24(2)	22(26)	7(11)	1(8)
C13	211(17)	176(13)	15(2)	-9(28)	-12(9)	3(8)
C14	211(18)	128(10)	28(2)	1(24)	-4(10)	1(8)

The temperature factors for hydrogen were isotropic and held constant at the following values:

B(\AA^2)		B		B	
H1	4.2	H4	5.9	H8	6.2
H2	8.7	H6	6.2	H9	5.0
H3	3.2	H7	7.8		

(b) Phenoxathionine. (β -values are multiplied by 10^4 and temperature factors for all atoms except S are isotropic).

	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
S	231(25)	173(13)	25(2)	20(57)	7(18)	-5(11)

	B(σ) \AA^2		B(σ)		B(σ)
O5	4.1 (4)	C6	3.3 (6)	C11	2.9 (6)
C1	4.8 (7)	C7	3.1 (6)	C12	3.2 (6)
C2	5.0 (8)	C8	3.4 (6)	C13	2.6 (5)
C3	4.6 (7)	C9	3.2 (6)	C14	2.8 (5)
C4	3.9 (6)				

Results and Discussion.

The coordinates and temperature factors from the final weighted least-squares refinements are given in Tables I and II. Bond distances and angles calculated for pt and phenoxathionine are listed in Table III, and stereo views of pt are presented in Figure 1 (10).

The structure of pt is isomorphous with that of phenoxathionine, as stated by Hosoya (5) and as suggested by Wood, McCale and Williams (6). As may be seen from Table III, the geometry of the two molecules is very similar. The bond distances and angles in the phenyl rings of pt are quite regular. The maximum angular variation

TABLE III

Bond Angles, Bond Distances and Their Standard Deviations for (a) Phenoxatellurine and (b) Phenoxathionine.

(a) Phenoxatellurine					(b) Phenoxathionine				
Bond Distances (Å)					Bond Distances (Å)				
Cl1-Te	2.093 (9)	C2-C3	1.373(16)	C1-H1	1.04(8)	Cl1-S	1.75 (3)	C2-C3	1.46 (5)
Cl4-Te	2.104 (8)	C3-C4	1.390(13)	C2-H2	0.87(12)	Cl4-S	1.73 (3)	C3-C4	1.43 (4)
Cl2-O5	1.415 (10)	C4-C12	1.370(11)	C3-H3	1.01(8)	Cl2-O5	1.39 (3)	C4-C12	1.37 (4)
Cl3-O5	1.379 (9)	C6-C13	1.376(12)	C4-H4	0.95(10)	Cl3-O5	1.36 (3)	C6-C13	1.38 (4)
Cl1-C12	1.379 (11)	C6-C7	1.370(13)	C6-H6	0.97(11)	Cl1-C12	1.44 (4)	C6-C7	1.41 (4)
Cl3-C14	1.402 (10)	C7-C8	1.394(14)	C7-H7	1.57(12)	Cl3-C14	1.39 (4)	C7-C8	1.40 (4)
Cl-C11	1.400 (12)	C8-C9	1.375(14)	C8-H8	0.99(11)	Cl-C11	1.48 (4)	C8-C9	1.41 (4)
Cl-C2	1.377 (16)	C9-C14	1.374(12)	C9-H9	1.15(10)	Cl-C2	1.37 (4)	C9-C14	1.45 (4)
Bond Angles (°)					Bond Angles (°)				
Cl1-Te-Cl4	89.4 (3)	Te-Cl1-C1	121.3 (6)	Cl1-S-Cl4	97 (1)	S-Cl1-C1	121 (2)		
Te-Cl1-C12	120.8 (6)	Cl-C11-C12	117.8 (8)	S-Cl1-C12	120 (2)	Cl-C11-C12	119 (2)		
Cl1-C1-C2	120.5 (9)	Cl-C2-C3	120.3 (9)	Cl1-C1-C2	117 (3)	Cl-C2-C3	124 (3)		
C2-C3-C4	119.9 (9)	C3-C4-C12	119.3 (8)	C2-C3-C4	117 (3)	C3-C4-C12	121 (3)		
C4-C12-C11	122.0 (8)	C4-C12-O5	116.2 (7)	C4-C12-C11	121 (2)	C4-C12-O5	118 (3)		
Cl1-C12-O5	121.7 (7)	C12-O5-C13	121.2 (5)	Cl1-C12-O5	121 (2)	C12-O5-C13	118 (2)		
O5-C13-C14	123.6 (7)	O5-C13-C6	116.0 (7)	O5-C13-C14	119 (2)	O5-C13-C6	117 (3)		
C6-C13-C14	120.3 (7)	C7-C6-C13	119.0 (8)	C6-C13-C14	123 (3)	C7-C6-C13	119 (3)		
C6-C7-C8	121.5 (8)	C7-C8-C9	118.8 (8)	C6-C7-C8	120 (2)	C7-C8-C9	121 (3)		
C8-C9-C14	120.5 (8)	C9-C14-Te	121.7 (6)	C8-C9-C14	119 (3)	C9-C14-S	118 (2)		
C9-C14-C13	119.6 (7)	Te-Cl4-C13	118.7 (6)	C9-C14-C13	118 (2)	S-Cl4-C13	124 (2)		
Cl1-C1-H1	123 (5)	C2-C1-H1	115 (5)						
Cl-C2-H2	118 (9)	C3-C2-H2	122 (10)						
C2-C3-H3	130 (4)	C4-C3-H3	110 (4)						
C3-C4-H4	144 (6)	Cl2-C4-H4	97 (6)						
C7-C6-H6	128 (6)	Cl3-C6-H6	113 (6)						
C6-C7-H7	130 (5)	C8-C7-H7	108 (5)						
C7-C8-H8	134 (6)	C9-C8-H8	102 (6)						
C8-C9-H9	117 (5)	Cl4-C9-H9	122 (5)						

occurs for two adjacent angles, Cl-C11-C12 = 117.8 (8)° and Cl1-C12-C4 = 122.0(8)°. The differences seem to us unlikely to be significant, since if a slight underestimation of errors has occurred, these values would not differ from 120° by more than 2.5 σ . Similar caution should be applied to the difference in bond distances between Cl2-O5 = 1.415(10) and Cl3-O5 = 1.379(9) Å. The angle Cl1-Te-Cl4 = 89.4 (3)° is significantly different from the corresponding angle Cl1-S-Cl4 = 97 (1)°, and the trend is consistent with that generally observed in the chalcogenides (11). The corresponding angles, with oxygen at the vertex, are 121.2 (5)° and 118 (2)°.

Both molecules are folded along the chalcogen-oxygen axis, with the central ring in the boat conformation. The two phenyl rings of pt are planar, with a maximum deviation from least-squares planes (12) of 0.03 Å, and with a dihedral angle between planes of 145°. The angle of fold of the central ring is 138°, so that it appears that the molecule is bent back along the Cl1-C12 and Cl3-C14 axes as well as folded along the Te-O axis. Similar results, 151° and 141°, respectively, were obtained for phenoxthionine. These observations are in agreement with those of Bell, *et al.* (13), for phenothiazine, C₁₂H₈SNH.

The existence of pt in a folded rather than a planar

configuration may be qualitatively interpreted by means of MO arguments in the same way as has been done for phenothiazine (14). Planar pt would have symmetry C_{2v} and its MO's would resemble those of a perturbed acridine (15). However, the introduction of O and Te in the central ring would increase from 14 to 16 the number of electrons to be accommodated in the π -MO's, and two electrons would occupy the lowest antibonding MO. This occupied MO (B1-SZ in acridine-like systems) has large contributions from the ao's of the atoms that correspond to O and Te. In the folded structure, O and Te are at least partially removed from the π -system and the net effect is presumably a decrease in the total energy of the system. The reason for the additional folding that occurs along the C11-C12 and C13-C14 bonds is not apparent to us. However, since the molecule is already folded along the Te-O axis, the requirement of extensive π -overlap between C11, Te and C14 and between C12, O and C13 need not be met, and the folding which takes place along C11-C12 and C13-C14 would not be expected to affect the total energy greatly.

In keeping with these ideas regarding the, at least partial, removal of the heteroatoms from the π -system, the average bond distances, found in pt, Te-C = 2.098 Å and C-O = 1.397 Å, are fairly close to the sum of the appropriate covalent single bond radii (16), 2.14 Å and 1.43 Å, respectively, and are much larger than those reported for double bonds, 1.904 Å in SCTe, and 1.22 Å for the average C-O distance in aldehydes and ketones (17).

There are no abnormally short non-bonded contact distances between different molecules in the structure of pt. Excluding hydrogen, the shortest of these contacts are Te ... C3' = 3.58 Å and C9 ... O5' = 3.70 Å.

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