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The Crystal and Molecular Structure of Phenoxthionine, C_6H_4–O–S–C_6H_4

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The crystal structure of phenoxthionine has been determined by X-ray diffraction methods. Three-dimensional intensity data recorded by a Weissenberg camera and visually estimated were used in the final least-squares refinement with an individual isotropic temperature factor for each atom. All H atoms were entirely neglected. The molecule is folded about the line joining the heterocyclic atoms, S and O. The best planes for two benzene rings were determined and the angle of fold between these planes was found to be about 138°. The carbon atoms satisfy the coplanarity fairly well, while the two atoms S and O lie slightly outside of the dihedral angle made by these two best planes. The S–C and O–C bond lengths were found to be about 1·75 and 1·39–1·40 Å respectively. The bond angles C–S–C and C–O–C were found to be about 98° and 118° respectively.

Introduction

Wood, McCale & Williams (1941) investigated morphological and optical properties of crystals of the three compounds, phenoxtellurine, phenoxselenine, and phenoxthionine C_6H_4–O–S–C_6H_4 (Fig. 1), and also obtained their crystal data by the X-ray method. Mostly from chemical considerations, they concluded that the molecules of these compounds should be folded about the line joining the heterocyclic atoms. The angle of fold in the case of phenoxthionine was suggested to be 150–160°.

Thomas (1956) attempted the X-ray structure analysis of these compounds and solved the structures of phenoxtellurine and phenoxselenine, but, as for phenoxthionine, he did not proceed further than the (100) Patterson synthesis because of his doubt about the isomorphism.

As has already been reported (Hosoya, 1958 and 1963), it is interesting to compare the molecular structure of phenoxthionine with those of thianthrene, its dioxides and tetraoxide with special regard to the angle of fold and some of bond lengths. In the present work, details of the crystal and molecular structure of phenoxthionine are described.

Crystal data

The crystals are orthorhombic with

$a = 5{\cdot}95 \pm 0{\cdot}03$, $b = 7{\cdot}78 \pm 0{\cdot}04$, $c = 20{\cdot}54 \pm 0{\cdot}10$ Å;
$Z = 4$; $d_{calc} = 1{\cdot}41$, $d_{obs} = 1{\cdot}38$ g.cm^{-3}.

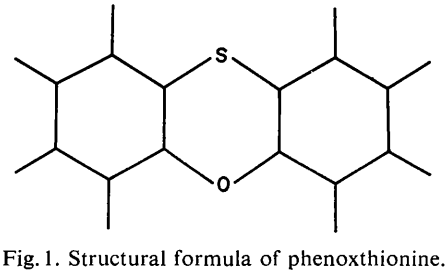


Fig. 1. Structural formula of phenoxthionine.

The space group is $P2_12_12_1$, as Wood *et al.* (1941) determined by the systematic absences. The crystal data needed no modification from the value already reported, although the unit was converted from kX to Å.

Intensity measurements

The crystals were thin prismatic needles in shape when crystallized from alcoholic solution. Since it was difficult to make a cylindrical or a spherical crystal, a small sample cut out from a needle crystal was used for taking photographs. This sample was about 0·1 mm in linear dimension. Because the crystals volatilize on exposure to air, it was necessary to cover the surface of a specimen with a suitable substance before photographs were taken. The error caused by this treatment as well as that due to the absorption by the prismatic specimen was estimated to be less than 10% in relative intensity and was not corrected.

Equi-inclination Weissenberg photographs without integration were taken with the multiple-film method and intensities of the spots were visually estimated with a calibration wedge.

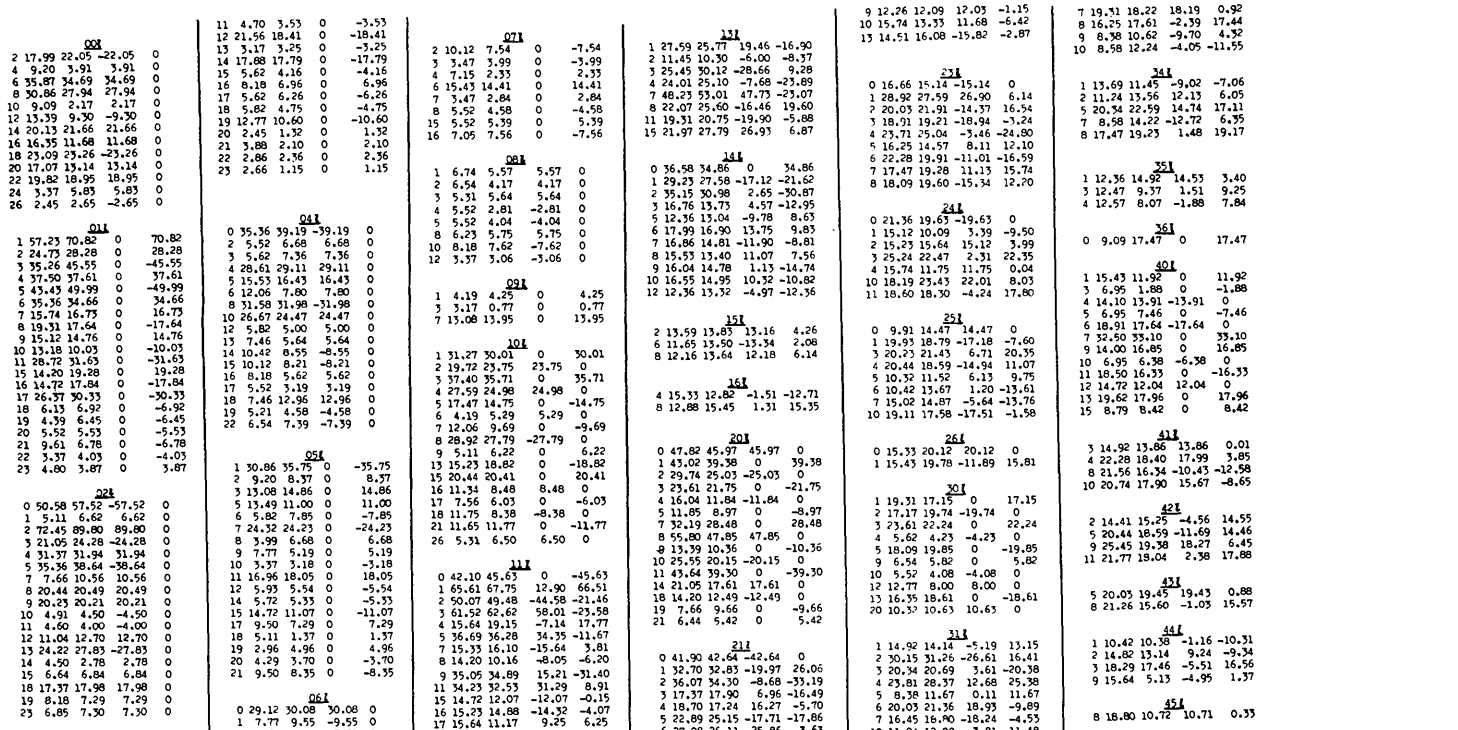
Structure determination

The more or less similar unit-cell dimensions and the identical space group found in phenoxthionine, phenoxselenine and phenoxtellurine had already suggested isomorphism in the structures of these three compounds (Wood, McCale & Williams, 1941). This was more strongly confirmed by the fact that the intensities of $0kl$ reflexions of phenoxthionine observed by Thomas (1956) showed a similar feature to those of the corresponding reflexions of the other two compounds. The analysis, therefore, was carried out assuming isomorphism, and the assumption later proved to be correct.

In the (100) Patterson map for phenoxthionine, a sulphur–sulphur field peak and Harker peaks accompanying it could be located, although not so clearly as in the case of phenoxselenine or phenoxtellurine. The first Fourier map on this projection, which has a center

Table 1. *The observed and calculated structure factors*

Within each group the columns, reading from left to right, contain the values of l, $|F_o|$, $|F_c|$, A_c and B_c.



of symmetry, was found to be fairly good. It is apparent that the signs of many terms were rightly assigned by use of the atomic parameters of the isomorphous phenoxselenine solved by Thomas. Several cycles of refinement with a fixed over-all temperature factor were carried out on an Elliott 402 computer, and the reliability index of the observed $0kl$ reflexions came down to 23·8%. The same procedures were done on the (010) projection and the R value of the observed $h0l$ reflexions decreased to 9·9%.

Three-dimensional data were obtained by rotating the crystal around the a axis, and F_o values obtained were brought into a common scale with the use of $h0l$ reflexions. Three-dimensional refinement was carried out on an IBM 7090 computer, using the ERBR1 program originally devised by Van den Hende (1961). In this program, an isotropic temperature factor is assumed for each atom. An equal weight was given to every $|F_o|$ value. After nine cycles of refinement, the R value for 352 observed terms came down to 13·4% and then remained practically constant. The final values of $|F_c|$, A_c and B_c as well as the scaled $|F_o|$ are listed in Table 1. All refined parameters for atoms are shown in Table 2. The projected shapes of molecules are shown in Fig. 2, together with the bond length and the bond angle values. Throughout the above computations, hydrogen atoms were entirely neglected, because they are not important concerning the main features of the molecular structures.

Table 2. *Fractional coordinates of the atomic positions and isotropic temperature factors*

	x/a	σ*	y/b	σ	z/c	σ	B
C(1)	0·0564	34	0·8575	29	0·2287	26	5·01 Å^2
C(2)	0·1951	38	0·8101	33	0·1786	31	6·00
C(3)	0·4131	34	0·7209	29	0·1879	27	5·07
C(4)	0·4646	31	0·6633	26	0·2520	24	4·29
O(5)	0·3964	21	0·6609	18	0·3652	17	4·69
C(6)	0·2987	29	0·4703	24	0·4509	22	3·71
C(7)	0·1506	28	0·4229	23	0·5008	20	3·41
C(8)	−0·0568	29	0·5119	24	0·5075	21	3·67
C(9)	−0·1271	28	0·6382	23	0·4632	20	3·29
S(10)	−0·0446	9	0·8568	7	0·3614	6	4·24
C(11)	0·1169	28	0·7975	23	0·2934	20	3·33
C(12)	0·3215	29	0·7021	24	0·3023	21	3·63
C(13)	0·2382	28	0·6017	23	0·4096	20	3·32
C(14)	0·0297	28	0·6844	23	0·4121	20	3·34

* σ is the standard deviation expressed in $10^{-3} \times$ Å.

Size and shape of the molecule

Bond lengths and bond angles among atoms in a molecule were obtained as shown in Table 3. According to the data reviewed by Abrahams (1956), a sulphur–carbon distance is about 1·82 Å in the single-bond case and about 1·61 Å in the double-bond case. The distance, 1·75 Å, found in phenoxthionine, means that this bond has double-bond character of about 60%.

Table 3. *Bond lengths and angles*

Bonds		Standard deviation
S(10)–C(11)	1·753 Å	43×10^{-3} Å
S(10)–C(14)	1·751	43
O(5)–C(12)	1·401	54
O(5)–C(13)	1·386	52
C(12)–C(11)	1·434	59
C(13)–C(14)	1·396	58
C(1)–C(11)	1·451	66
C(4)–C(12)	1·371	64
C(9)–C(14)	1·447	58
C(6)–C(13)	1·374	60
C(1)–C(2)	1·367	79
C(4)–C(3)	1·422	70
C(9)–C(8)	1·399	59
C(6)–C(7)	1·399	60
C(2)–C(3)	1·481	79
C(8)–C(7)	1·419	60

Angles		Standard deviation
C(11)–S(10)–C(14)	97·68°	0·03°
C(12)–O(5)–C(13)	117·63	0·05
S(10)–C(11)–C(12)	119·83	0·04
S(10)–C(14)–C(13)	123·54	0·04
O(5)–C(12)–C(11)	120·31	0·05
O(5)–C(13)–C(14)	118·29	0·05
S(10)–C(11)–C(1)	120·47	0·04
S(10)–C(14)–C(9)	117·23	0·04
O(5)–C(12)–C(4)	116·42	0·05
O(5)–C(13)–C(6)	118·23	0·05
C(12)–C(11)–C(1)	119·46	0·05
C(13)–C(14)–C(9)	118·94	0·05
C(11)–C(12)–C(4)	122·89	0·06
C(14)–C(13)–C(6)	123·40	0·05
C(11)–C(1)–C(2)	116·84	0·06
C(14)–C(9)–C(8)	116·83	0·05
C(12)–C(4)–C(3)	119·53	0·06
C(13)–C(6)–C(7)	118·80	0·06
C(1)–C(2)–C(3)	123·77	0·07
C(9)–C(8)–C(7)	122·51	0·06
C(4)–C(3)–C(2)	117·04	0·07
C(6)–C(7)–C(8)	119·26	0·06

It should be noticed that the C–S–C angle (97·7°) is much smaller than the C–O–C angle (117·6°), which has already been discussed elsewhere (Hosoya, 1963) from a more general point of view: the difference of these angles indicates the participation of *d* orbitals in the bonding of S. The valence orbitals in O are limited to 2*s* and 2*p* or hybrids of these two, while sulphur can be converted to the excited configuration $(3s)^2(3p)^3(3d)$.

The least-squares planes or the best planes for two benzene rings were given by the following equations:

$$0{\cdot}36951X + 0{\cdot}84324Y + 0{\cdot}39040Z = 1{\cdot}19996$$

for C(1, 2, 3, 4, 11, 12),

$$0{\cdot}18038X + 0{\cdot}39016Y + 0{\cdot}90291Z = 0{\cdot}82590$$

for C(6, 7, 8, 9, 13, 14).

These planes are relevant to the molecule accompanied by the bond length and bond angle values shown

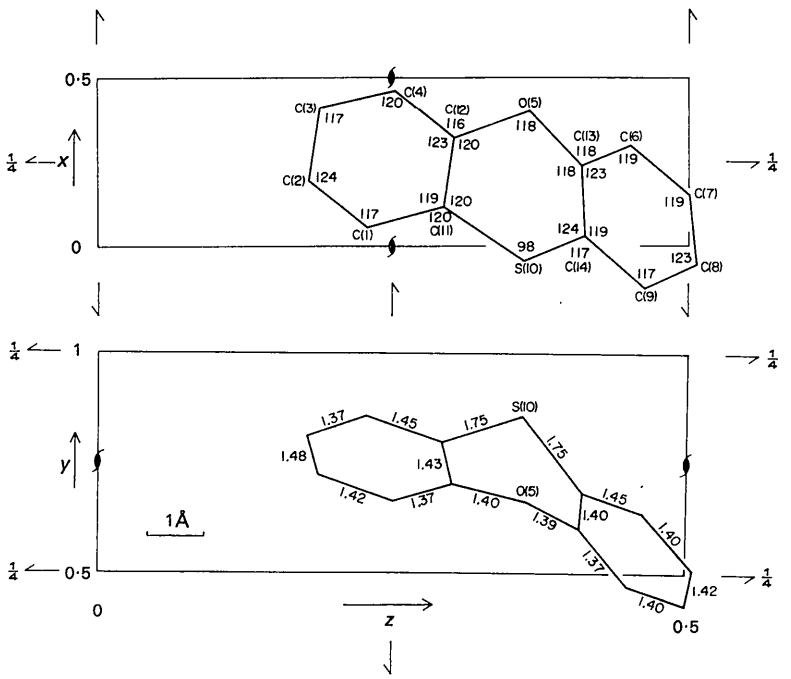


Fig. 2. Structure of phenoxthionine projected on (100) and (010).

in Fig. 2. The dihedral angle between these two best planes was found to be 138°25′. The folded shape of the molecule is also due to the presence of a sulphur atom as has already been shown (Hosoya, 1963). The distances of atoms from the best planes are listed in Table 4. Coplanarity of carbon atoms making a benzene ring is fairly good, while both sulphur and oxygen atoms lie slightly outside the dihedral angle made by two benzene rings.

Two-dimensional work was done at University College, Cardiff, Great Britain. The author is indebted to Prof. A. J. C. Wilson for the use of equipment purchased with a Royal Society Grant. A set of Weissenberg photographs of the (100) projection used at a very early stage of this work was kindly supplied by Mr Thomas, to whom the author expresses his thanks. He is also indebted to British Nylon Spinners Ltd for financial assistance with the cost of computations on Elliott 402, and he also thanks the British Council for the award of a scholarship in 1956–8 when the two-dimensional work was done. The three-dimensional work was done in Tokyo. The author is indebted to Japan IBM Co. Ltd, which offered IBM 7090 machine time under the University Contribution System.

Table 4. *Distances to the best planes for the two benzene rings*

C(1)	0·024 Å	C(6)	−0·014 Å
C(2)	−0·042	C(7)	−0·016
C(3)	0·029	C(8)	0·029
C(4)	−0·006	C(9)	−0·016
C(11)	0·000	C(13)	0·027
C(12)	−0·010	C(14)	−0·014
O(5)	0·128	O(5)	0·185
S(10)	0·134	S(10)	0·096

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'Gel' et 'Coagel'. I. Identification. Localisation dans un Diagramme de Phases et Détermination de la Structure du 'Gel' dans le Cas du Stéarate de Potassium

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The potassium stearate–water system has been studied by means of X-ray diffraction and polarized light microscopy. The 'gel' and 'coagel' phases have been clearly identified and their stability domain localized in a phase diagram. The structure of the 'gel' has been determined and its parameters discussed.

Il est actuellement bien établi que les propriétés singulières des savons, et des amphiphiles en général, trouvent leur explication dans la constitution chimique très particulière de ces substances. On distingue, en effet, dans une molécule de savon, deux parties, un groupe polaire et une chaîne hydrocarbonée, suffisamment éloignées l'une de l'autre pour se comporter de manière quasiment indépendante. De plus, ces deux parties sont douées de solubilités notablement différentes: le groupe polaire manifeste une affinité marquée à l'égard des solvants polaires, alors que la chaîne hydrocarbonée, elle, est soluble presqu'uniquement dans les solvants non polaires. Le comportement remarquable des savons, en présence d'eau notamment, résulte de la nécessité pour ces deux tendances contraires à se concilier.

Pour analyser les principales propriétés d'un tel système, on convient généralement de se reporter à son diagramme de phases. Dans celui-ci, on définit essentiellement trois domaines. Dans le premier, qui couvre à température suffisamment élevée toutes les proportions de savon et d'eau, on rencontre la solution micellaire, phase peu visqueuse et optiquement isotrope. Dans le deuxième, qui se situe à des températures moyennes, on trouve les phases mésomorphes, médiane et lisse en particulier, présentant une biréfringence optique spontanée. Aux températures inférieures à celles définies par la courbe T_c, s'étend le domaine d'existence du 'gel' et du 'coagel'; il est d'usage de différencier

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