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The Crystal and Molecular Structure of Allylthiourea

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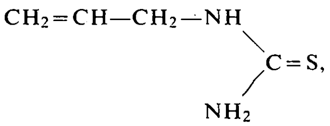
The crystal structure of allylthiourea has been determined by direct phase determination employing the symbolic addition procedure. The space group is $P2_1/c$ with the following cell parameters: $a=8{\cdot}39$ Å, $b=8{\cdot}58$ Å, $c=9{\cdot}77$ Å, $\beta=119°\ 45'$, and $Z=4$. A three-dimensional least-squares refinement with anisotropic temperature factors for the C, N and S atoms was performed. All the hydrogen atoms were located from a difference Fourier map. Hydrogen bonds between the sulfur and nitrogen atoms link the molecules in a continuous chain parallel to the b axis. The $S \cdots H\text{–}N$ bonds are 3·36 Å. The thiourea group is planar and the $C=S$ bond is 1·66 Å, a value somewhat smaller than that found in thiourea and some of its derivatives.

Introduction

The structures of thiourea (Kunchur & Truter, 1958) and a number of its derivatives such as thioacetamide (Truter, 1960), trimethylenethiourea (Dias & Truter, 1964) and ethylenethiourea (Wheatley, 1953) have been carefully determined in a program to study the $C=S$ bond. The investigation of allylthiourea,



$$CH_2{=}CH{-}CH_2{-}NH{\diagdown}C{=}S,\ {\diagup}NH_2$$

was undertaken for the purpose of comparing bond lengths and angles and the mode of possible hydrogen bonding between the sulfur and nitrogen atoms with the structures already determined.

Experimental

Crystals of allylthiourea form white plates elongated parallel to the b axis. Unit-cell parameters were determined from precession photographs with the crystal mounted on the b axis and using copper radiation. They are

$$a=8{\cdot}39\pm0{\cdot}01,\quad b=8{\cdot}58\pm0{\cdot}01,\quad c=9{\cdot}77\pm0{\cdot}01\ \text{Å}$$
$$\beta=119°45'\pm10',\quad Z=4\ .$$

The calculated density is 1·264 g.cm^{-3}; the measured density was found to be 1·247 g.cm^{-3} by the flotation method employing mixed solvents. The present analysis is in agreement with the crystallographic information published previously for allylthiourea (Whitney & Corvin, 1949).

Intensity data were obtained from multiple film, equi-inclination Weissenberg photographs. The rotation axis was parallel to the b axis and layers 0 through 6 were collected. Extinctions indicated that the space group was $P2_1/c$.

Intensities from the Weissenberg photographs were estimated visually by comparison with a calibrated film strip. Corrections for spot size, and Lorentz and polarization factors were computed with a revision by Mr Stephen Brenner of an earlier data reduction program (Norment, 1962) for the IBM 7030 (STRETCH) computer. No absorption corrections were made. The data were adjusted to an absolute scale by the use of a K curve (Karle & Hauptman, 1953). Both the structure factor magnitudes, $|F_{\mathbf{h}}|$, and the normalized structure factor magnitudes, $|E_{\mathbf{h}}|$, were computed. For the monoclinic space group $P2_1/c$, the latter are defined by:

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2/\varepsilon \sum_{j=1}^{N} f_{j\mathbf{h}}^2\,, \tag{1}$$

where $\varepsilon = 2$ when $\mathbf{h}$ is $h0l$ or $0k0$, $\varepsilon = 1$ otherwise, $f_{j\mathbf{h}}$ is the atomic scattering factor for the jth atom, N is the number of atoms in the unit cell and the $F_{\mathbf{h}}^2$ have been corrected by means of the K curve for thermal motion and placed on an absolute scale.

Approximately 760 reflections were determined to have intensities greater than zero. The distribution of the total 910 reflections is shown in Table 1 where the theoretical values are based on a centrosymmetric crystal with randomly distributed atoms. The statistical averages compared in Table 2 correspond to those for a centrosymmetric crystal.

Table 1. *Distribution of normalized structure factor magnitudes*

	$\|E\|>3$	$\|E\|>2$	$\|E\|>1$
Theoretical	0·3 %	5·0 %	32·0 %
Experimental	0·2	4·3	24·4

Table 2. *Statistical averages*

	Experimental	Centro-symmetric	Non-centro-symmetric
$\langle\|E\|\rangle$	0·760	0·798	0·886
$\langle\|E^2-1\|\rangle$	0·940	0·968	0·736
$\langle\|E\|^2\rangle$	0·950	1·000	1·000

Phase determination

The symbolic addition procedure (Karle & Karle, 1963, 1964, 1965; Karle, Britts & Brenner, 1964) was used to determine the allylthiourea phases. The origin was specified by assignment of positive signs to three linearly independent vectors having large $|E|$ magnitudes. Letter phases a, b, and c were assigned in sequence, as required, to three additional vectors also having large $|E|$ values in order to facilitate the Σ_2 procedure. With these six assignments, shown in Table 3, approximately 110 phases for $|E_{\mathbf{h}}| \geq 1·5$ were expressed in terms of a, b, and c employing the Σ_2 relationship,

$$sE_{\mathbf{h}} \sim s \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}\,, \tag{2}$$

where s means 'sign of'. To facilitate the application of the Σ_2 relationship, use was made of a computer program which lists pairs of indices, $\mathbf{k}$ and $\mathbf{h}-\mathbf{k}$, the sum of which is the desired index $\mathbf{h}$. Only those indices were listed for which $|E| \geq 1·5$.

Table 3. *Starting set for the application of* Σ_2

Phase	hkl	$\|E\|$
+	$51\bar{1}$	2·65
+	$63\bar{4}$	2·61
+	$73\bar{2}$	2·56
a	204	2·76
b	$14\bar{1}$	2·37
c	$10\,1\,\bar{9}$	3·10

Equation (2) implies that the sign of a particular $E_{\mathbf{h}}$ is determined by a sum of terms. At the very start of a phase determination, it sometimes is necessary to depend upon a single term rather than a sum. The sign indications from a single term are reliable if the $|E|$'s of the three reflections involved are all very large. The probability that a sign indicated by (2) is correct is given by:

$$P_+(E_{\mathbf{h}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\,(\sigma_3/\sigma_2^{3/2})|E_{\mathbf{h}}| \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \tag{3}$$

where $\sigma_n = \sum_{j=1}^{N} Z_j^n$. As the phase determination progresses, for any particular $E_{\mathbf{h}}$ many terms enter into the sum in (2). Some of these terms may be expressed as functions of letter phases such as in the following example where the phase of $E_{41\bar{3}}$ was being sought. The indices are added and the associated symbols are multiplied.

Index	Phase						
$\bar{6}\,0\,6$	c	$\bar{5}\,3\,6$	$-a$	$\bar{4}\,\bar{1}\,1$	b	$\bar{1}\,4\,3$	$-$
$10\,1\,\bar{9}$	c	$9\,\bar{2}\,\bar{9}$	$-a$	$8\,2\,\bar{4}$	ab	$5\,\bar{3}\,\bar{6}$	$-a$
$4\,1\,\bar{3}$	+	$4\,1\,\bar{3}$	+	$4\,1\,\bar{3}$	a	$4\,1\,\bar{3}$	a

For $E_{41\bar{3}}$, the indications are that the phase is either + or a, or that the symbol a is equivalent to a positive phase. Such indications for the symbol a appeared in many of the individual phase determinations; hence the symbol a was assigned the positive sign.

In another example, some of the terms for the phase of E_{225} were:

$\bar{4}\,1\,4$	$-a$	$\bar{3}\,1\,6$	$-a$	$\bar{2}\,1\,9$	ab	$\bar{1}\,\bar{2}\,2$	+
$6\,1\,1$	+	$5\,1\,\bar{1}$	+	$4\,1\,\bar{4}$	a	$3\,4\,3$	ab
$2\,2\,5$	$-a$	$2\,2\,5$	$-a$	$2\,2\,5$	b	$2\,2\,5$	ab

From this example and from similar relationships for other phase determinations, it was obvious that the symbol b was equivalent to $-a$; or, since $a \equiv +$, then $b \equiv -$. Similarly, there were a few indications that suggested that $c \equiv +$.

These Σ_2 indications for the letter assignments were supported further by application of the Σ_1 phase determining formulae (Hauptman & Karle, 1953). Both the general centrosymmetric expression,

$$sE_{2h2k2l} \sim s(E_{hkl}^2 - 1)\,, \tag{4}$$

and the particular expression for space group $P2_1/c$,

$$sE_{2h02l} \sim s\sum_{k}(-1)^{k+l}(E_{hkl}^2 - 1) \tag{5}$$

were used to obtain the phases shown in Table 4. The probability that a phase be positive was computed using the following expressions:

$$P_+(E_{2\mathbf{h}})=\tfrac{1}{2}+\tfrac{1}{2}\tanh(\sigma_3/2\sigma_2^{3/2})|E_{2\mathbf{h}}|(E_{\mathbf{h}}^2-1) \qquad (6)$$

or

$$P_+(E_{2h02l})=\tfrac{1}{2}+\tfrac{1}{2}\tanh(\sigma_3/2\sigma_2^{3/2})|E_{2h02l}|\sum_{\mathbf{k}}(-1)^{k+l}(E_{hkl}^2-1)\,. \qquad (7)$$

Again the indications were that $a\equiv+$, $b\equiv-$ and that c was probably $+$.

Table 4. *Probabilities from application of Σ_1*

hkl	$\lvert E\rvert$	P_+	Phase from Σ_1	Phase from Σ_2
204	2·76	0·96	+	*a*
$82\bar{6}$	1·97	0·92	+	*a*
002	2·03	0·04	−	*b*
206	2·59	0·08	−	*ab*
$80\bar{2}$	2·06	0·89	+	*a,ac*
$60\bar{6}$	2·11	0·86	+	*c*

Two preliminary E maps (Fourier maps with E rather than F values for coefficients) with 110 terms were computed with the phase assignments $(+-+)$ and $(+--)$ for the letters a, b and c. Both maps revealed the structure, although the first map with $c\equiv+$, the preferred assignment, was much better resolved. It was consequently shown, from the refinement of the structure, that the unknown c should have indeed been positive. The 110 term E maps contained subsidiary diffraction peaks on either side of the sulfur atom. Hence phases for an additional 123 indices were determined for the assignment $(+-+)$ for a, b and c and an E map with 233 terms was computed. Sections from this three-dimensional map are illustrated in Fig. 1

The refinement

The E map of Fig. 1 contains two peaks (at different z values), each approximately half-weight, which could be C(6). At this point it was impossible to determine which of the peaks was correct or if the crystal were disordered. This ambiguity could have been resolved by extending the phase determination by the use of the Σ_2 relationship (2) to many more terms and computing another E map. Instead, the three possibilities were subjected to a least-squares refinement in order to resolve the problem. The function which was minimized was $\Sigma w(F_o-F_c)^2$ with $w=1$ for all observed reflections. Individual scale factors for each layer were refined. The program used was a modification for STRETCH (IBM 7030) of the ORFLS program prepared by Busing, Martin & Levy (1962).

The refinement procedure immediately discarded one of the possible peaks for C(6) and the possibility of disorder. The coordinates of the sulfur, nitrogen and carbon atoms were then refined, first with isotropic and then with anisotropic temperature factors to an R value of 11·6%. A difference electron density map computed at this point revealed all the hydrogen atom positions as illustrated in Fig. 2. Three cycles of refinement were carried out in which the positions of the hydrogen atoms were varied and the remaining parameters were held fixed. All of the hydrogen positions improved with the exception of the two hydrogen atoms on C(6). Excessive thermal motion at the end of a chain of atoms probably prevented a satisfactory refinement; accord-

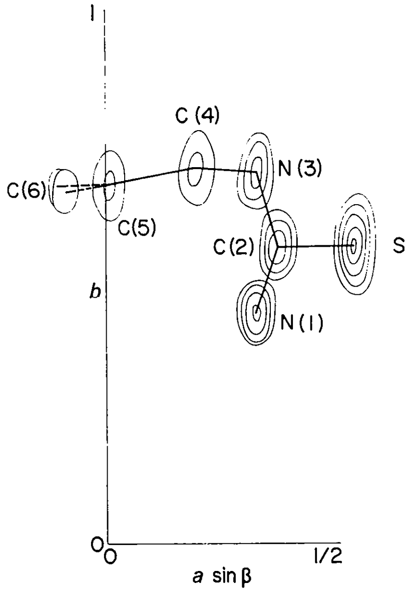


Fig. 1. Sections of a three-dimensional E map, projected on (001), which was computed from 233 phases determined by the symbolic addition procedure. Contours are at equally spaced, arbitrary levels.

Table 5. *Fractional coordinates for allythiourea*

The thermal parameters are of the form $T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$.
Each thermal parameter is multiplied by 10^4.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	0·5510	0·5601	0·2311	203	91	215	11	145	14
N(1)	0·3344	0·4239	0·3162	175	104	152	−4	80	7
C(2)	0·3975	0·5613	0·2912	156	147	94	14	15	19
N(3)	0·3335	0·6978	0·3148	187	118	144	29	83	−13
C(4)	0·2110	0·7064	0·3830	164	222	187	2	99	−27
C(5)	0·0103	0·6674	0·2644	142	240	196	24	77	−3
C(6)	−0·0641	0·6512	0·1160	240	291	169	44	46	−18
Standard deviation									
S	0·0003	0·0004	0·0003	5	4	4	3	4	4
N	0·0009	0·0012	0·0008	13	11	11	14	10	12
C	0·0011	0·0016	0·0011	16	15	16	18	13	18

ingly the positions read from the difference map were retained for H(6) and H(6′). The final R value for the observed data computed with unit weights was 10·1%.*

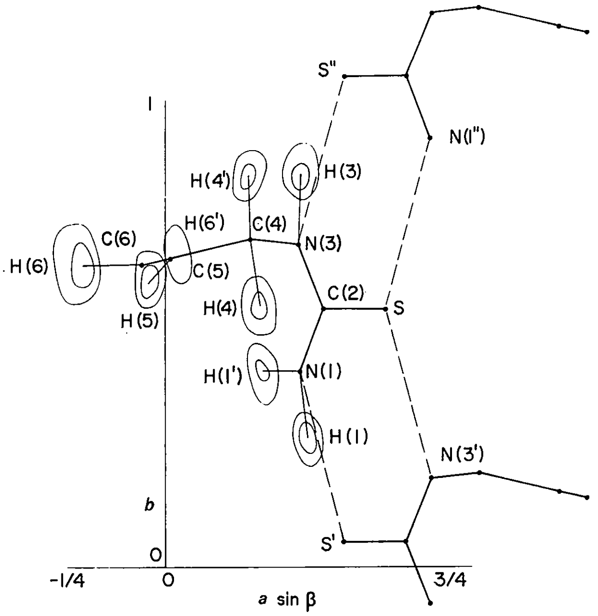


Fig. 2. Sections of a difference electron density map projected on (001). Contours are at 0·25 e.Å^{-3} intervals, beginning with the 0·25 e.Å^{-3} contour. Hydrogen bonds between the S and N atoms are indicated by the dashed lines.

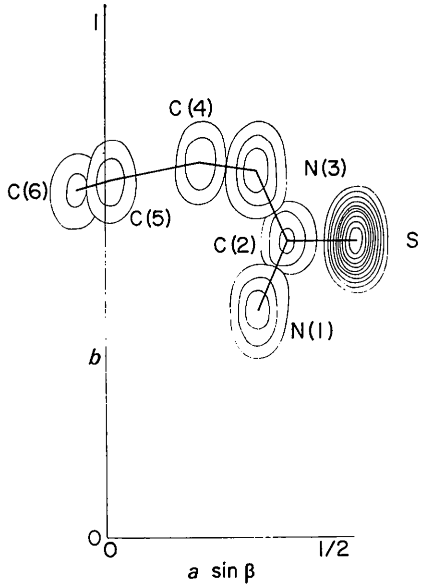


Fig. 3. The final electron density map projected on (001). Contours are at 2 e.Å^{-3} intervals, beginning with the 2 e.Å^{-3} contour.

The atomic form factors used were those listed in *International Tables for X-ray Crystallography.*

The parameters for the heavier atoms are given in Table 5 and the hydrogen coordinates are shown in Table 6. Sections from a final electron density map computed from these parameters are shown in Fig. 3.

Table 6. *The approximate hydrogen coordinates*

Atom	Attached to	x	y	z
H(1)	N(1)	0·353	0·314	0·299
H(1′)	N(1)	0·234	0·437	0·387
H(3)	N(3)	0·351	0·821	0·306
H(4)	C(4)	0·283	0·623	0·513
H(4′)	C(4)	0·250	0·831	0·455
H(5)	C(5)	−0·031	0·643	0·314
H(6)	C(6)	−0·213	0·652	0·033
H(6′)	C(6)	0·030	0·680	0·063

The structure

The thiourea unit of the molecule is planar. The equation of the plane is

$$2{\cdot}5580x+0{\cdot}0410y+6{\cdot}5983z=2{\cdot}9597 \qquad (8)$$

referred to the monoclinic axes, where the value on the right-hand side of the equation is equal to the origin to plane distance in Å (Schomaker, Waser, Marsh & Bergman, 1959). Deviations from the plane are shown in Table 7. The plane determined by the allyl group, C(4), C(5) and C(6),

$$-1{\cdot}5463x+8{\cdot}3724y-0{\cdot}1348z=5{\cdot}5364\,, \qquad (9)$$

forms an angle of 99·6° with the plane of the thiourea group.

Table 7. *Deviation from plane of thiourea group*

Atom	Δ, Å
S	−0·0017
N(1)	−0·0020
C(2)	0·0057
N(3)	−0·0020
r.m.s.	0·0033

Hydrogen atoms H(1) and H(3) lie in the plane of the thiourea but H(1′) lies 0·25 Å out of the plane. Hydrogen atoms H(5), H(6) and H(6′) lie approximately in the plane of the allyl group. The plane of the thiourea group is very close to the (102) and the molecules are packed in parallel planes.

Bond distances and angles for the heavy atoms are shown in Fig. 4 and those involving the hydrogen atoms are listed in Table 8. The terminal C=C and C=S distances are rather short. Significant thermal motion has been found to produce rotational oscillation corrections of 0·01 to 0·02 Å in molecules such as thiourea and thioacetamide where Cruickshank's (1956) calculations were applied. Corrections of the same order of magnitude may be expected for the terminal bonds in this present study.

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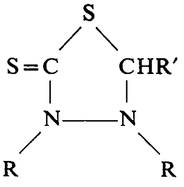
* Observed and calculated structure factors have been deposited as Document number 8351 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $2·50 for photoprints, or $1·24 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 8. *Bond lengths and angles involving the hydrogen atoms*

Bond	Length	Angle	
H(1)–N(1)	0·99 Å	H(1)–N(1)–H(1′)	111°
H(1′)–N(1)	1·33	H(1)–N(1)–C(2)	134
H(3)–N(3)	1·08	H(1′)–N(1)–C(2)	115
H(4)–C(4)	1·32		
H(4′)–C(4)	1·23	H(3)–N(3)–C(2)	139
H(5)–C(5)	0·75	H(3)–N(3)–C(4)	98
H(6)–C(6)	1·16		
H(6′)–C(6)	1·10	H(4)–C(4)–H(4′)	93
		H(4)–C(4)–N(3)	108
		H(4)–C(4)–C(5)	115
		H(4′)–C(4)–N(3)	105
		H(4′)–C(4)–C(5)	120
		H(5)–C(5)–C(4)	105
		H(5)–C(5)–C(6)	126
		H(6)–C(6)–H(6′)	116
		H(6)–C(6)–C(5)	125
		H(6′)–C(6)–C(5)	116

The standard deviation for the bond lengths is 0·15 Å. The deviation for angles involving one hydrogen atom is 8·5°; for angles involving two hydrogen atoms, 17°.

The N(3)–C(4) and C(4)–C(5) bond lengths are typical for single bonds. The two C–N bonds adjacent to the C=S bond have a value of 1·36 Å which is considerably shorter than the single bond value of 1·45–1·48 Å. Table 9 shows a comparison of C–N and C=S bond lengths found in thiourea and some of its derivatives. Each of these determinations was carefully refined with resulting *R* values of 10–12%. In the present study, the C–N bond is somewhat longer and the C=S bond shorter than those in the other four determinations. A similarly low value for C=S (1·65 Å) has been found in a



derivative (Karle & Karle, 1965).

The hydrogen bonding corresponds quite closely to that described for trimethylenethiourea. Each sulfur atom bonds to two nitrogen atoms to form endless double chains approximately parallel to the *b* axis as

Table 10. *Intermolecular distances and angles for hydrogen bonds as illustrated in Fig.* 2

Bond	Length	Angle	
N(1) · · · S′	3·359 Å	N(3′) · · · S · · · N(1″)	136·4°
N(3) · · · S″	3·355	C(2)–S · · · N(3′)	112·0
H(1) · · · S′	2·38	C(2)–S · · · N(1″)	111·5
H(3) · · · S″	2·30	C(2)–N(3) · · · S″	127·9
		C(4)–N(3) · · · S″	104·8
		C(2)–N(1) · · · S′	128·0
		H(3)–N(3) · · · S″	10·9
		H(1)–N(1) · · · S′	8·5

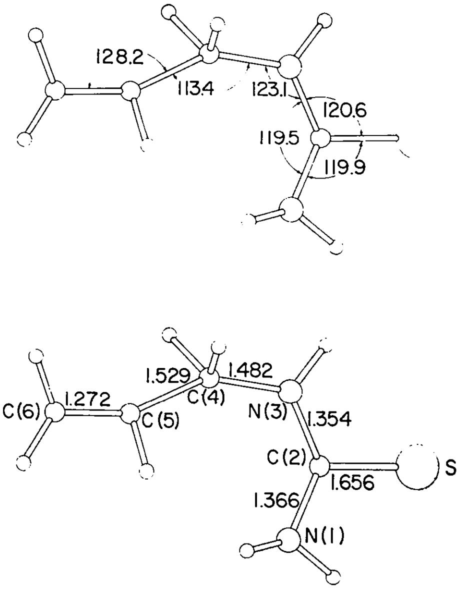
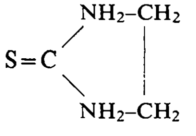
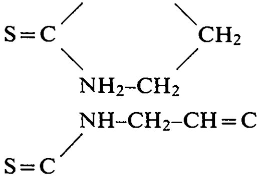
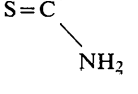


Fig. 4. Bond distances and angles. The standard deviations for the bond distances are between 0·010 and 0·014 Å. The standard deviations for the angles are approximately 1°.

Table 9. *Bond lengths and angles in thiourea and some of its derivatives*

Compound	N–C	C=S	Reference
$S{=}C(NH_2)_2$	1·33	1·72	Kunchur & Truter, 1958
$S{=}C(NH_2)CH_3$	1·32	1·71	Truter, 1960
	1·32	1·71	Wheatley, 1953
	1·33	1·72	Dias & Truter, 1964
 $S{=}C(NH_2)(NH{-}CH_2{-}CH{=}CH_2)$	1·36	1·66	Present study

indicated in Fig. 2. As expected, the hydrogen atoms do not lie directly on the N · · · S line. The bond lengths and angles involved in the hydrogen bonding are listed in Table 10.

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The Crystal Structure of Tetrahydroxy-*p*-benzoquinone

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The crystal structure of tetrahydroxy-*p*-benzoquinone dihydrate has been determined from three-dimensional Weissenberg data and refined by anisotropic differential synthesis and least-squares calculations. The crystals are monoclinic, space group $P2_1/c$, with $a = 5{\cdot}226 \pm 0{\cdot}002$, $b = 5{\cdot}118 \pm 0{\cdot}002$, $c = 15{\cdot}502 \pm 0{\cdot}008$ Å and $\beta = 103{\cdot}89 \pm 0{\cdot}02°$. There are two centrosymmetric quinone molecules with attendant water molecules per unit cell.

The molecules, which possess the quinoid structure with the C=O distance 1·229 Å and the C=C distance 1·342 Å, are remarkably planar, and, through pairs of hydrogen bonds, form chains. The water molecules also are hydrogen bonded to form chains along one set of screw axes. Further hydrogen bonding ties the quinone and water chains together. The anisotropic thermal parameters of the atoms have been interpreted successfully in terms of rigid-body vibrations of the quinone molecule. The quinoid structure and self-complexing charge transfer interactions appear to present a reasonable explanation of the glistening black color of the crystals.

Introduction

Tetrahydroxy-*p*-benzoquinone (THQ), $C_6(OH)_4O_2$, is one of a series of labile oxidation products of inositol which have interested organic and structural chemists for many years. Until recently the standard method for their preparation was to treat inositol with fuming nitric acid, a reaction difficult to control (Gelormini & Artz, 1930; Hoglan & Bartow, 1940; Preisler & Berger, 1942). The reaction leads to a mixture of products difficult to separate, and the individual products in some instances are so reactive toward oxygen that the dissolved oxygen in solvents makes recrystallization difficult or impossible. THQ has also been prepared in 10% yield by the self-condensation of glyoxal in the presence of sodium sulfite, air, and a base (Homolka, 1921; Fatiadi, Isbell & Sager, 1963). The proposed molecular structures and unusual properties of these compounds make structural studies of them highly important. This communication presents the results of a detailed investigation of the molecular and crystal structure of THQ.

The glistening black crystals of THQ are actually the dihydrate, a fact apparently not previously recognized. Elementary microanalysis first disclosed the probable presence of water of hydration. The infrared spectrum of THQ in a Nujol mull had been reported by Fatiadi, Isbell & Sager (1963). Spectra prepared in fluorocarbon mulls* clearly presented the following: (1) OH bands at 3540 and 3370 cm^{-1}, presumably from the H_2O molecules; (2) from 3100–2500 cm^{-1}, absorption from OH strongly hydrogen bonded; (3) a strong band at 1625 cm^{-1} with side peak at 1650 cm^{-1} inter-

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