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The Crystal and Molecular Structure of *o*-Nitrophenol

BY FUJIKO IWASAKI AND YASUOMI KAWANO

Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182, *Japan*

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Crystals of *o*-nitrophenol, $C_6H_5NO_3$, are monoclinic, space group $P2_1/a$ with cell dimensions $a = 6{\cdot}876$ (5), $b = 14{\cdot}389$ (7), $c = 6{\cdot}439$ (3) Å, $\beta = 103{\cdot}79$ (6)° and $Z = 4$. The structure was solved by a direct method and refined by the full-matrix least-squares method to a final R value of 0·071 for 726 diffractometer-collected reflexions. The O···O intramolecular hydrogen-bond distance between the hydroxyl and nitro groups is 2·602 Å. The *o*-quinonoid structure contributes remarkably to the overall resonance state of the molecule.

Introduction

As part of the studies on substituted *o*-nitrophenols, the crystal structure analysis of *o*-nitrophenol was undertaken in order to elucidate the geometry of the intramolecular hydrogen bonding. It has been shown that the phenolic C—O(H) bond lengths are correlated with the acidic strength (pK_a values) (Andersen & Andersen, 1975). The pK_a value (7·23; Brown, McDaniel & Häfliger, 1955) of *o*-nitrophenol is higher than those of the other substituted *o*-nitrophenols for which structures have been determined so far (Iwasaki, Sato & Aihara, 1976; Iwasaki & Kawano, 1977; Kagawa, Kawai, Kashino & Haisa, 1976). It is also interesting to examine the relations between the geometrical structure of the molecule and the acidity of the substance.

Experimental

The crystals were grown from a cyclohexane–benzene solution of commercially available *o*-nitrophenol. They are yellow pillars elongated along the *a* axis. Most of the crystals were twinned on (001). An untwinned crystal was used for the intensity measurements. Since the crystal sublimed rapidly all X-ray data were obtained with the specimen enclosed in a thin glass capillary.

Crystal data

$M_r = 139{\cdot}11$, monoclinic, $P2_1/a$, $a = 6{\cdot}876$ (5), $b = 14{\cdot}389$ (7), $c = 6{\cdot}439$ (3) Å, $\beta = 103{\cdot}79$ (6)°, $U = 618{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}494$, $D_m = 1{\cdot}46$ g cm^{-3}.

Intensity data were collected on a Rigaku automatic four-circle diffractometer, using Mo $K\alpha$ radiation monochromatized with a graphite monochromator. An ω–2θ scan technique was used to obtain intensities, with a scan width of $\Delta\omega = 1{\cdot}0° + 0{\cdot}5° \tan\theta$ and scan speed of 4° min^{-1} in 2θ. Background was counted for 10 s at both ends of the scan range for each reflexion. The intensities of three standard reflexions, measured after every 50 reflexions, decreased over the period of the data collection. Their final intensities were 75% of the original values. The data were corrected for decomposition of the crystal. 726 reflexions in the range $2\theta \leq 60°$ had $|F_o| \geq 3\sigma(F_o)$ and were considered as observed reflexions.

Structure determination

The structure was solved by a direct method. The H atoms were located from a difference Fourier synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and with isotropic temperature factors for H atoms gave a final

Table 1. *Atomic parameters with their estimated standard deviations*

(*a*) Atomic coordinates ($\times 10^4$) of non-hydrogen atoms. The B_{eq} values are the equivalent isotropic temperature factors (Å^2).

	x	y	z	B_{eq}
C(1)	3886 (7)	2668 (4)	9492 (8)	3·8
C(2)	3278 (7)	2969 (3)	7376 (7)	3·1
C(3)	2791 (8)	2331 (3)	5706 (8)	3·8
C(4)	2890 (10)	1401 (4)	6135 (9)	4·5
C(5)	3483 (9)	1110 (4)	8220 (10)	4·9
C(6)	3971 (9)	1719 (4)	9864 (9)	5·0
N	3112 (7)	3953 (3)	6829 (7)	4·4
O(1)	4385 (7)	3231 (3)	11191 (6)	5·8
O(21)	3549 (6)	4519 (2)	8306 (6)	6·0
O(22)	2524 (7)	4171 (2)	4980 (6)	6·5

(*b*) Atomic coordinates ($\times 10^3$) and thermal parameters (Å^2) of hydrogen atoms

	x	y	z	B
H(1)	431 (8)	376 (3)	1079 (8)	4·1 (15)
H(3)	248 (6)	254 (3)	428 (7)	4·1 (11)
H(4)	254 (7)	106 (3)	504 (7)	4·8 (13)
H(5)	350 (7)	47 (3)	851 (6)	5·0 (13)
H(6)	436 (7)	155 (3)	1124 (7)	5·0 (13)

R value of 0·071 for all the observed reflexions. The quantity minimized was $\Sigma\, w(|F_o| - k^{-1}|F_c|)^2$ where $w = 1/\sigma^2(F_o)$, as derived from counting statistics. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All crystallographic computations were performed on the HITAC 8800/8700 computer of the Computer Center of the University of Tokyo, using the local version of the program system *UNICS* (Crystallographic Society of Japan, 1967; Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). The final atomic parameters are listed in Table 1.*

Results and discussion

Molecular packing

The arrangement of the molecules in the crystal is shown in Figs. 1 and 2. Intermolecular contacts less than 3·60 Å are listed in Table 2. The molecules related by the *a*-glide symmetry are stacked to form a column along the *a* axis. The plane of the molecule makes an angle of 86° with the *a* axis. The average interplanar spacing is 3·43 Å. The overlapping of the aromatic rings is considerable. Such an arrangement can be compared with those of weak π–π molecular complexes (Kumakura, Iwasaki & Saito, 1967). The short contacts between adjacent columns are 2·930 Å for O(21)···O(21$^{\mathrm{iii}}$), 3·286 Å for O(22)···C(4$^{\mathrm{ii}}$), and

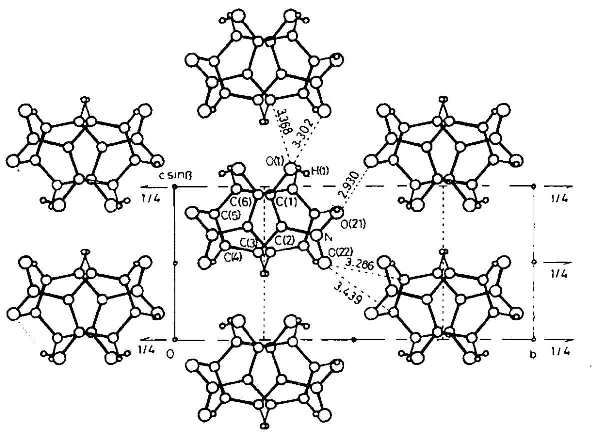

Fig. 1. Projection of the structure along the *a* axis.

Table 2. *Intermolecular contacts* (Å) *less than* 3·6 Å

Symmetry code

Superscript				Superscript			
None	x,	y,	z	(iii)	$1-x$,	$1-y$,	$2-z$
(i)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z	(iv)	x,	y,	$1+z$
(ii)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$1-z$	(v)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1+z$

C(1)···C(1$^{\mathrm{i}}$)	3·472 (8)	N···C(5$^{\mathrm{i}}$)	3·588 (8)
C(1)···C(6$^{\mathrm{i}}$)	3·558 (8)	O(1)···C(6$^{\mathrm{i}}$)	3·459 (8)
C(2)···C(3$^{\mathrm{i}}$)	3·545 (8)	O(21)···C(5$^{\mathrm{i}}$)	3·524 (8)
C(2)···C(4$^{\mathrm{i}}$)	3·568 (8)	O(22)···C(4$^{\mathrm{ii}}$)	3·286 (8)
C(3)···C(3$^{\mathrm{i}}$)	3·472 (8)	O(22)···C(5$^{\mathrm{ii}}$)	3·439 (8)
C(4)···N$^{\mathrm{i}}$	3·547 (8)	O(1)···O(21$^{\mathrm{iii}}$)	3·519 (6)
C(4)···O(22$^{\mathrm{i}}$)	3·537 (8)	O(21)···O(21$^{\mathrm{iii}}$)	2·930 (6)
C(5)···N$^{\mathrm{i}}$	3·507 (8)	O(1)···C(3$^{\mathrm{iv}}$)	3·584 (7)
C(5)···O(21$^{\mathrm{i}}$)	3·586 (8)	O(1)···O(22$^{\mathrm{iv}}$)	3·302 (7)
C(6)···C(1$^{\mathrm{i}}$)	3·556 (8)	O(1)···C(3$^{\mathrm{v}}$)	3·368 (7)
N···C(4$^{\mathrm{i}}$)	3·457 (8)	O(1)···C(4$^{\mathrm{v}}$)	3·544 (8)

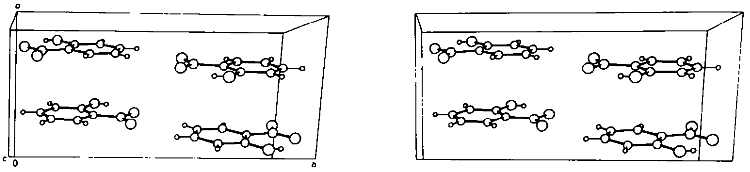

Fig. 2. Stereoscopic drawing of the unit cell viewed down the *c* axis.

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* Lists of the structure factors and the anisotropic temperature factors for non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33202 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

2·73 Å for O(22)···H(4^{ii}), which are close to the normal van der Waals separations. Most of the intercolumn contacts are, however, longer than the sum of the van der Waals radii.

The structure projected on the (100) plane is very similar to the (100) projection of the crystal structure of salicylaldehyde ($a = 7{\cdot}08$, $b = 13{\cdot}90$, $c = 6{\cdot}33$ Å, $\beta = 102°\,56'$, $P2_1/a$; Bourre-Maladière, 1953).* The crystal structure of *o*-nitrophenol bears a close resemblance to that of salicylaldehyde but is not strictly isomorphous. The molecular position of salicylaldehyde is shifted by (0·6, 0, −0·3) Å from that of *o*-nitrophenol. The interplanar distance in *o*-nitrophenol is shorter and the intercolumn packing is somewhat different from that of salicylaldehyde. A molecular-packing analysis (Williams, 1969) was tried for *o*-nitrophenol. By minimizing the lattice energy, the molecular packing obtained was found to be quite close to that of salicylaldehyde: the shift of the molecule from the actual structure of *o*-nitrophenol was (0·6, −0·3, −0·4) Å. From this model the actual structure could not be obtained by the standard least-squares method.

Table 3. *Rigid-body thermal parameters*

Molecular vibration tensors

Translation **T** (×10³) (Å²)

$$\begin{pmatrix} 39\,(2) & 2\,(2) & 1\,(2) \\ & 38\,(2) & 0\,(2) \\ & & 33\,(4) \end{pmatrix}$$

Libration **L** (deg²)

$$\begin{pmatrix} 54\,(5) & -7\,(2) & -7\,(3) \\ & 33\,(3) & -3\,(2) \\ & & 20\,(2) \end{pmatrix}$$

Principal axes of **T** and **L** tensors relative to the crystal axes

R.m.s. amplitude	Direction cosines (×10³)		
0·180 Å	972	−197	−354
0·193	228	684	619
0·200	50	703	−701
4·17°	891	152	−628
5·69	432	8	773
7·53	−141	988	91

R.m.s. $\Delta(U_{ij}) = 0{\cdot}0045$ Å².

Table 4. *Bond distances* (Å) *and angles* (°)

Bond lengths in parentheses are values corrected for the thermal motion.

C(1)–C(2)	1·396 (7) (1·408)	O(1)–H(1)	0·80 (5)
C(1)–C(6)	1·384 (8) (1·389)	C(3)–H(3)	0·94 (5)
C(2)–C(3)	1·393 (8) (1·400)	C(4)–H(4)	0·84 (5)
C(3)–C(4)	1·365 (9) (1·370)	C(5)–H(5)	0·94 (5)
C(4)–C(5)	1·373 (9) (1·380)	C(6)–H(6)	0·90 (5)
C(5)–C(6)	1·354 (9) (1·360)	O(21)···H(1)	1·91 (5)
C(1)–O(1)	1·339 (7) (1·343)		
C(2)–N	1·456 (7) (1·464)		
N–O(21)	1·234 (6) (1·240)		
N–O(22)	1·204 (7) (1·207)		
O(1)···O(21)	2·589 (6) (2·602)		

C(2)C(1)C(6)	117·7 (5)	C(1)O(1)H(1)	109 (4)
C(1)C(2)C(3)	120·7 (5)	C(2)C(3)H(3)	120 (3)
C(2)C(3)C(4)	119·9 (5)	C(4)C(3)H(3)	120 (3)
C(3)C(4)C(5)	119·1 (6)	C(3)C(4)H(4)	114 (4)
C(4)C(5)C(6)	121·8 (6)	C(5)C(4)H(4)	127 (4)
C(1)C(6)C(5)	120·8 (6)	C(4)C(5)H(5)	119 (3)
C(2)C(1)O(1)	124·6 (5)	C(6)C(5)H(5)	119 (3)
C(6)C(1)O(1)	117·6 (5)	C(5)C(6)H(6)	124 (3)
C(1)C(2)N	121·7 (4)	C(1)C(6)H(6)	115 (3)
C(3)C(2)N	117·6 (5)	NO(21)···H(1)	104 (2)
C(2)NO(21)	117·7 (4)	O(1)H(1)···O(21)	143 (5)
C(2)NO(22)	118·8 (5)		
O(21)NO(22)	123·6 (5)		

Molecular structure

The molecular motion has been analysed in terms of rigid-body vibrations (Schomaker & Trueblood, 1968). Some rigid-body thermal parameters of the molecule are given in Table 3. The bond lengths and angles are listed in Table 4. The least-squares plane of the benzene ring is given in Table 5.

The hydroxyl group is linked to O(21) of the *o*-nitro group forming an intramolecular hydrogen bond. O(1)···O(21) is 2·602 Å. It has been observed that the O–H stretching frequency bands, ν_s, occur at about 3250, 3270 and 3095 cm^{-1} (KBr disc) in *o*-nitrophenol, 2,4-dinitrophenol and 2,6-dinitrophenol respectively (Aihara, Hirai & Fukushige, 1977). The observed O···O distances are 2·602, 2·615 and 2·562 Å respectively (Iwasaki & Kawano, 1977; Iwasaki, Sato & Aihara, 1976). The correlation between ν_s and the O···O distances in these compounds, however, deviates significantly from the well-known ν_s *vs* O···O relation as given by Nakamoto, Margoshes & Rundle (1955). This is probably because the H atom is displaced far from the line joining the two O atoms, forming, in the case of the intramolecular hydrogen bond, a six-membered chelate ring. The angle O–H···O is 143, 138 and 152° for *o*-nitrophenol, 2,4-dinitrophenol and 2,6-dinitrophenol respectively.

The benzene ring is planar, deviations being within

Table 5. *Least-squares plane of the benzene ring*

Deviations (Å) of atoms from the least-squares plane expressed in the form $AX + BY + CZ + D = 0$, where X, Y and Z are the coordinates in Å referred to the axes a, b and c^* respectively, are given.

$$-0{\cdot}997X + 0{\cdot}010Y + 0{\cdot}071Z + 0{\cdot}751 = 0$$

C(1)	−0·002	C(5)	0·001	O(21)†	0·024
C(2)	0·003	C(6)	0·000	O(22)†	0·065
C(3)	−0·002	O(1)†	0·000	H(1)†	−0·02
C(4)	0·001	N†	0·023		

† Atoms not used to define the least-squares plane.

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* The original *a* and *c* axes of the crystal of salicylaldehyde have been interchanged here to facilitate comparison with the structure of *o*-nitrophenol.

0·003 Å. The dihedral angles between the benzene ring and the planes of the substituents are 1·72° for the hydroxyl group and 1·58° for the nitro group. The average C—C bond distance in the benzene ring is 1·385 Å. C(1)—C(2) (1·408 Å) is significantly longer and C(3)—C(4) (1·370 Å) and C(5)—C(6) (1·360 Å) are shorter than the normal C—C bond length in benzene. The geometry of the benzene ring and of the intramolecular hydrogen bond is very close to those found in other substituted *o*-nitrophenols (Iwasaki & Kawano, 1977). The short phenolic C—O distance, 1·343 Å, is similar to the corresponding value in 2,4-dinitrophenol, but is shorter than the value expected from a pK_a value of 7·23 (Brown *et al.*, 1955; Andersen & Andersen, 1975; Kagawa *et al.*, 1976). In Fig. 3, the solid line shows the correlation between the phenolic C—O(H) bond lengths of phenols and the pK_a values, as represented by Kagawa *et al.* (1976). It can be seen that the C—O lengths of *o*-substituted phenols, with intramolecular hydrogen bonding, deviate from this line; the change of the C—O lengths *vs* the pK_a values seems to be less than that for other phenols as shown by the broken line.

The *o*-quinonoid structure of the benzene ring contributes remarkably to the overall resonance state of the molecule. Fig. 4 shows the π-bond orders calculated by the CNDO/2 method *vs* the C—C bond lengths of the benzene rings observed in some *o*-nitrophenols. A significant departure from hexagonal symmetry of the benzene ring in the molecule is quite compatible with the difference in the π-bond orders. The calculation by the CNDO/2 method was performed with the program written by T. Kobayashi.

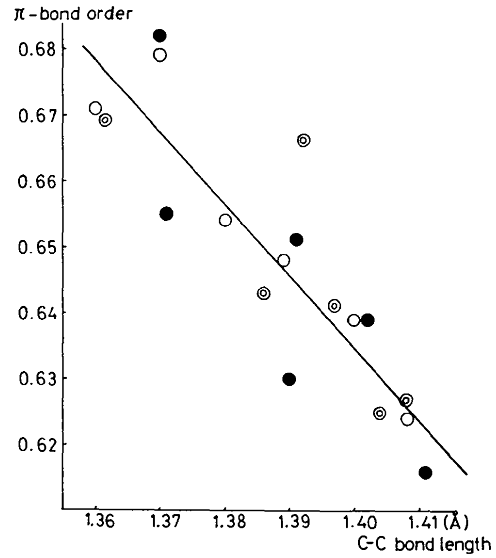

Fig. 4. Relation between the C—C bond lengths (Å) in the benzene ring and the π-bond orders calculated by the CNDO/2 method in some *o*-nitrophenols. ○ *o*-Nitrophenol. ● 2,4-Dinitrophenol. ◎ 2,6-Dinitrophenol.

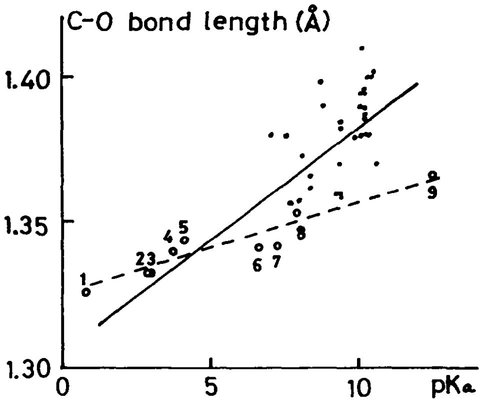

Fig. 3. The phenolic C—O bond lengths *vs* the pK_a values. The solid line and filled circles are based on the diagram by Kagawa *et al.* (1976). The open circles and broken line represent *o*-substituted phenols with intramolecular hydrogen bonding. (1) Picric acid (π-molecular complex with anthracene, Herbstein & Kaftory, 1976). (2) 2-Bromo-4,6-dinitrophenol (Neustadt & Cagle, 1975). (3) 2-Chloro-4,6-dinitrophenol (Andersen & Andersen, 1975). (4) 2,6-Dinitrophenol (Iwasaki, Sato & Aihara, 1976). (5) 2,4-Dinitrophenol (Iwasaki & Kawano, 1977). (6) 2-Nitro-4-chlorophenol (Kawai, Kashino & Haisa, 1976). (7) *o*-Nitrophenol (present study). (8) 2-Hydroxy-3-methoxybenzaldehyde (Iwasaki, Tanaka & Aihara, 1976). (9) Salicylic acid (Bacon & Jude, 1973). The pK_a values were taken from the tables of Brown *et al.* (1955) and *Kagakubinran* (1966).

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Preparation and X-ray Analysis of a 1:2 Adduct of Hexamethylenetetramine and Thiourea

BY THOMAS C. W. MAK AND O. W. LAU

Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong

AND M. F. C. LADD AND D. C. POVEY

Department of Chemical Physics, University of Surrey, Guildford, Surrey, England

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A 1:2 molecular compound of hexamethylenetetramine and thiourea has been prepared and subjected to crystal-structure analysis. The crystals are monoclinic, space group $C2/c$, with $a = 18{\cdot}391\,(6)$, $b = 8{\cdot}380\,(4)$, $c = 9{\cdot}469\,(4)$ Å, $\beta = 109{\cdot}84\,(5)^\circ$ and $Z = 4$. The structure was solved by direct methods and refined by full-matrix least squares with 1193 observed Cu $K\alpha$ diffractometer data to a final R index of 0·079. The hexamethylenetetramine molecule occupies a site of symmetry 2, with all four tertiary N atoms serving as proton acceptors in hydrogen bonding. In the crystal lattice the two types of molecular components are linked by N···H–N and S···H–N hydrogen bonds to form corrugated layers normal to the b axis. Neighboring layers, being related by the c glide, pack with protuberances fitting snugly into recesses.

Introduction

Thiourea forms channel inclusion complexes (Lenné, 1954; Fetterly, 1964) with carbon tetrachloride, branched-chain and alicyclic hydrocarbons, haloparaffins, and other organic molecules with cross-sectional diameters in the range 5·8–6·8 Å (Schiessler & Flitter, 1952). Since hexamethylenetetramine [$(CH_2)_6N_4$, hereafter abbreviated to HMT] appears to meet the spatial requirements for an enclosed guest species, we set out to prepare its thiourea channel complex, but succeeded instead in obtaining a hitherto unreported compound of stoichiometry HMT.-$2(NH_2)_2CS$. To elucidate the nature of molecular association in this 1:2 adduct, we have accordingly undertaken an X-ray analysis. It constitutes part of our current structural investigation on hydrogen-bonded molecular compounds of HMT (Tse, Wong & Mak, 1977; Mak, Tse, Chong & Mok, 1977).

Experimental

Preparation of hexamethylenetetramine–thiourea 1:2 *adduct*

Hexamethylenetetramine (I) and thiourea (II) were recrystallized from ethanol. Compounds (I) (0·6 g, 4 mmol) and (II) (0·6 g, 8 mmol) were dissolved separately in the minimum amount of ethanol. The solutions were mixed, heated to below boiling (~70 °C) for 1 h, and then set aside for crystallization. The reaction mixture, after standing in the dark for several days, deposited colorless, needle-shaped crystals (III)