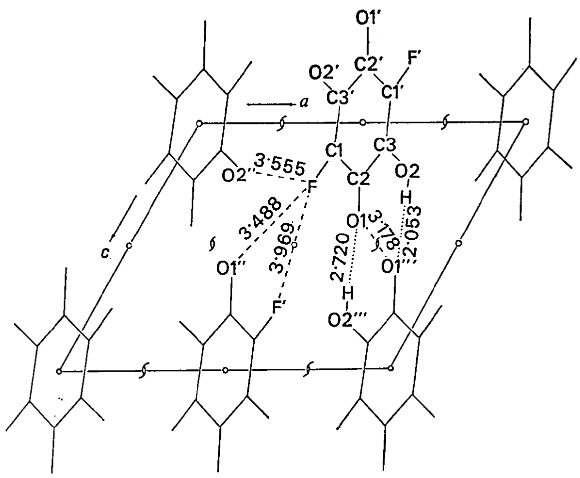

Fig. 2. The crystal structure of fluoranilic acid.

molecules are stacked in columns along the lines $0y0$, $\frac{1}{2}y0$, *etc.* These columns are viewed end-on in Fig. 2. The closest approach of acid molecules belonging to different columns is the hydrogen bond between O(1) and O(2) atoms (2·720 Å).

The fluoranilic acid molecules are linked by these bonds to form ribbons extending throughout the structure. Other short contacts are found between O(1) atoms in molecules related by the screw axis and between fluorine atoms related by a symmetry centre. These and a few more intermolecular contacts are given in Fig. 2.

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References

Andersen, E. K. (1967*a*). *Acta Cryst.* **22**, 188–191.
Andersen, E. K. (1967*b*). *Acta Cryst.* **22**, 191–196.
Andersen, E. K. (1967*c*). *Acta Cryst.* **22**, 204–208.
Bolton, W. (1965). *Acta Cryst.* **19**, 1051–1055.
Chu, S. S. C., Jeffrey, G. A. & Sakurai, T. (1962). *Acta Cryst.* **15**, 661–671.
Cruickshank, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. Pepinsky, J. M. Robertson & J. C. Speakman. Oxford: Pergamon Press.
Dewar, R. K. B. (1968). Dissertation, Univ. of Chicago.
Hvoslef, J. (1968). *Acta Cryst.* **B24**, 23–35.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Klug, H. P. (1965). *Acta Cryst.* **19**, 983–992.
Lawrence, J. L. & MacDonald, S. G. G. (1969). *Acta Cryst.* **B25**, 1247–1251.
MacDonald, S. G. G. & Alleyne, A. B. (1963). *Acta Cryst.* **16**, 520–524.
Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The X-RAY system. Univ. of Maryland, College Park, Maryland.
Trotter, J. (1960). *Acta Cryst.* **13**, 86–95.
Wallenfels, K. & Friedrich, K. (1960). *Chem. Ber.* **93**, 3070–3082.

Acta Cryst. (1975). **B31**, 387

The Crystal and Molecular Structure of 2-Chloro-4,6-dinitrophenol

By E. Krogh Andersen and I. G. Krogh Andersen

Chemical Institute, The University of Odense, 5000 *Odense, Denmark*

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The structure of 2-chloro-4,6-dinitrophenol was determined from three-dimensional diffractometer data collected with Mo radiation (1107 reflexions were observed, *i.e.* 81 % of those in the range covered). The crystals are orthorhombic, space group $P2_12_12_1$, with $a=13{\cdot}518\,(3)$, $b=5{\cdot}933\,(2)$, $c=10{\cdot}315\,(2)$ Å, $Z=4$; $D_m=1{\cdot}746\,(10)$, $D_x=1{\cdot}755$ g cm^{-3}. The carbon ring is planar but the nitro-group oxygen atoms and the hydroxyl group atoms are out of the ring plane (by up to 0·1 Å). The C(1)–C(2) and C(1)–C(6) bonds are significantly longer than the other carbon–carbon bonds. There is an intramolecular hydrogen bond in which the hydroxyl group is donor and an adjacent nitro-group oxygen acceptor. The bond from the latter oxygen atom to the nitrogen atom is significantly longer (0·02 Å) than the other nitrogen–oxygen bonds.

Introduction

The lengths of C–(OH) bonds in various hydroxyl compounds show a marked variation. The shortest C–(OH) bond known to us is 1·29 Å [in trifluoroacetic acid (Nahringbauer & Andersen, 1974)] and the longest is 1·427 Å [in methanol (Venkatesvarlu & Gordy, 1955)]. If the experimentally determined lengths are rounded off to two decimal places all lengths between 1·29–1·43 Å are represented in the determinations published up to 1970. It has been shown (Andersen, 1971) that the C–(OH) bond lengths are linearly correlated with the acidic strength (pK_a values). The short C–(OH) bonds are found in strongly acidic, the long bonds in weakly acidic compounds. This holds for the *ca* 50 hydroxyl compounds for which accurate structure determinations as well as accurate acid dissociation constants have been determined; and it holds whether the acidic hydroxyl group is attached to a trigonally or a tetragonally hybridized carbon atom.

While structure determinations have been made of many weakly acidic phenols only one structure determination of a phenol with pK_a value lower than 7 is known to us [pentachlorophenol (Sakurai, 1962)]. For this reason, and because of an interest in relations between the geometrical structure of molecules and the acidity of the substance, we are studying the structures of phenols with pK_a values lower than 7. In the present paper we report the first result of our studies.

Experimental

The commercially available 2-chloro-4,6-dinitrophenol (Aldrich) was recrystallized from 96% ethanol. Titration, density measurements, lattice constant determinations (by quartz calibrated Guinier–Hägg diagrams) and single-crystal diagrams provided the data recorded in Table 1. The substance is piezoelectric (Hettich & Steinmetz, 1932). The intensity data were collected on an automatic diffractometer (scintillation counter and pulse-height discriminator). Zirconium-filtered Mo $K\alpha$ radiation was used and the intensities were recorded in the ω scanning mode (scan angle 1·4°, scanning speed 1·25° min^{-1}). Background measurements were made for half the scan time at each end of the scanning interval. The 600 reflexion was measured every ten reflexions. These measurements provided material for establishing corrections for a linear (with time) fall-off of intensities, which amounted to 10% during the entire data collection. All independent reflexions within the range $2\cdot5 \le \theta \le 30°$ were measured. The 1107 reflexions (81% of the total) had intensities greater than twice the standard deviation of the measurement. They were corrected for Lorentz- and polarization factors and converted into structure factors.

Table 1. *Crystal and chemical data for* 2-*chloro*-4,6-*dinitrophenol*

Values in parentheses are standard deviations.

$C_6H_3ClN_2O_5$	F.W.(obs by titration) 219·3
$Z=4$	F.W.(calc) 218·6
Orthorhombic	Systematic absences
$a=13\cdot518$ (3) Å	$h00$ $h=2n+1$
$b=$ 5·933 (2)	$0k0$ $k=2n+1$
$c=10\cdot315$ (3)	$00l$ $l=2n+1$
	Space group $P2_12_12_1$
μ(Mo $K\alpha$)$=4\cdot67$ cm^{-1}	
$D_m=1\cdot746$ (10) g cm^{-3}	$D_x=1\cdot755$ g cm^{-3}

Dimensions of crystal used in data collection:
0·15 × 0·30 × 0·60 mm

Determination and refinement of the structure

Structure determination

The structure was determined by direct methods with the programs *NORMSF*, *SINGEN* and *TANGEN* of the X-RAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The origin and enantiomorph were defined by assigning the phases 90°, 0°, 90°, 90° to 013, 908, 930 and 701 respectively. The phase determinations were carried out in five cycles with decreasing minimum limit for inclusion of the normalized structure factors. The five cycles yielded phases for 141 structure factors, and an E map based on these phases showed all the non-hydrogen atoms. Structure factors calculated from positional parameters from the E map and an overall isotropic temperature factor of 2·7 resulted in an R value of 0·33.

Table 2. *Final positional and thermal parameters and estimated standard deviations for* 2-*chloro*-4,6-*dinitrophenol*

For the numbering of atoms see Fig. 1. Quantities given are positional coordinates (× 10^4) and U_{ij}(× 10^4 Å^2), where T.F. = $\exp\,[-2\pi^2 \sum \sum U_{ij}a_i^*a_j^*h_ih_j]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	8552 (1)	−1996 (3)	5300 (2)	696 (8)	641 (9)	663 (8)	186 (8)	118 (7)	−89 (8)
O(1)	6464 (3)	−1363 (7)	5101 (4)	701 (23)	570 (22)	666 (22)	−92 (21)	−50 (20)	−176 (20)
O(41)	9224 (3)	4963 (9)	8262 (5)	657 (25)	909 (35)	985 (35)	−267 (27)	−270 (25)	6 (34)
O(42)	7863 (4)	6787 (9)	8466 (5)	1042 (36)	711 (32)	766 (30)	−134 (30)	−54 (26)	−271 (28)
O(61)	4886 (3)	926 (8)	5476 (4)	502 (19)	827 (29)	822 (28)	−152 (22)	−219 (20)	−89 (27)
O(62)	4869 (3)	3736 (9)	6779 (5)	420 (19)	971 (33)	1194 (40)	212 (24)	−112 (24)	−282 (37)
N(4)	8350 (4)	5212 (9)	8055 (4)	677 (28)	646 (30)	493 (23)	−201 (26)	−149 (22)	−25 (23)
N(6)	5300 (3)	2283 (9)	6204 (5)	403 (18)	693 (31)	596 (24)	−31 (22)	−47 (18)	18 (25)
C(1)	6884 (4)	271 (9)	5796 (4)	559 (25)	446 (26)	359 (19)	−49 (22)	29 (18)	−5 (19)
C(2)	7908 (4)	187 (9)	6003 (4)	524 (24)	431 (26)	418 (23)	92 (22)	111 (19)	26 (20)
C(3)	8390 (3)	1768 (9)	6737 (4)	397 (20)	534 (28)	464 (22)	5 (20)	6 (18)	82 (23)
C(4)	7839 (3)	3499 (9)	7269 (4)	463 (21)	482 (27)	366 (22)	−101 (20)	−42 (17)	40 (19)
C(5)	6833 (3)	3692 (8)	7101 (4)	452 (21)	406 (24)	405 (20)	2 (20)	8 (18)	22 (19)
C(6)	6371 (3)	2072 (9)	6374 (4)	354 (17)	492 (24)	354 (17)	−10 (21)	−1 (15)	53 (18)
H(1)	5730	−830	4880	380					
H(3)	9150	1660	6920	380					
H(5)	6460	4720	7500	380					

Refinement

The structure was refined by the full-matrix least-squares method. The calculations were performed with the program *CRYLSQ* of the X-RAY 72 system.

The quantity minimized was $\sum w(F_o-F_c)^2$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). No contributions from unobserved reflexions were included. Three cycles of least-squares calculations resulted in an R value of 0·13. In these cycles unit weights were used and the positional and individual isotropic temperature factors were allowed to vary. Difference electron-density maps calculated at this stage showed the hydrogen atom peaks. In the final cycles of least-squares calculations the positional parameters and anisotropic temperature parameters were varied. Hydrogen atoms were included with fixed parameters. The weights were now calculated from $w=(a+F_o+bF_o^2)^{-1}$. These weights produced $w(F_o-F_c)^2$ values almost independent of $\sin\theta$ and magnitudes of F_o. In the last cycle the average ratio parameter shift/standard deviation was 0·02 (maximum value 0·07). R was 0·057 (unobserved reflexions excluded). The parameters from this calculation are given in Table 2.*

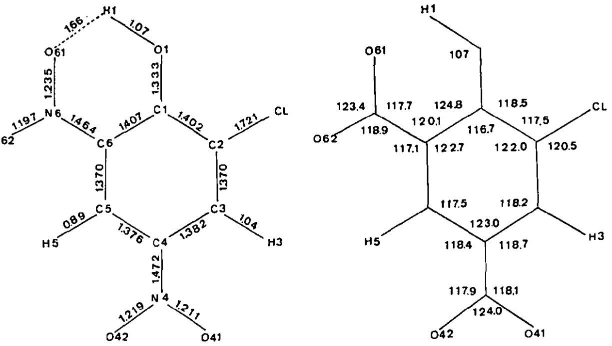

Fig. 1. The molecular structure of 2-chloro-4,6-dinitrophenol. (*a*) Bond lengths in Å. (*b*) Angles in degrees. The standard deviation of the Cl–C(2) bond is 0·004 Å. The standard deviations of bonds between carbon, nitrogen and oxygen atoms are 0·007 Å. The standard deviations of the angles are 0·4°.

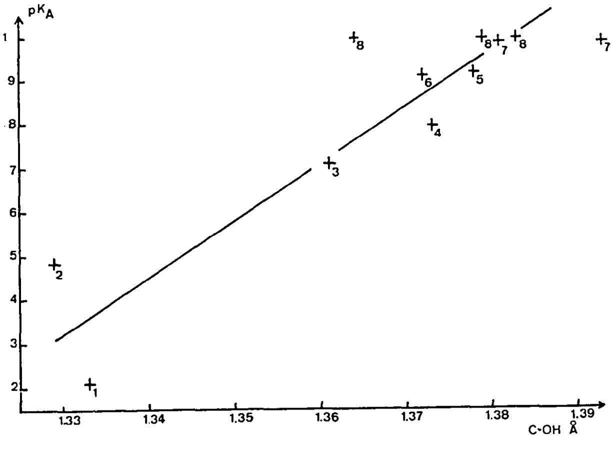

Fig. 2. pK_a values of phenols *vs*. C–(OH) bond lengths. References in square brackets refer to the pK_a values, the others to the C–(OH) bonds. (1) 2-Chloro-4,6-dinitrophenol: [Robinson (1967)]; this determination. (2) Pentachlorophenol: [Robinson & Bates (1966)]; Sakurai (1962). (3) *p*-Nitrophenol: [*Stability Constants* (1964)]; Coppens & Schmidt (1965). (4) Phloroglucinol: [Sunkel & Staude (1968)]; Maartmann-Moe (1965). (5) Resorcinol: [Sunkel & Staude (1968)]; Ito, Minobe & Sakurai (1970). (6) Pyrocatechol: [Sunkel & Staude (1968)]; Brown (1966). (7) Hydroquinone: [Sunkel & Staude (1968)]; Sakurai (1968); Maartmann-Moe (1966). (8) Phenol: [*Stability Constants* (1964)]; Sakurai (1968); Pedersen, Larsen & Nygaard (1969); Forest & Dailey (1966).

Description and discussion of the structure

The molecular structure

Details of the molecular structure of the phenol are given in Fig. 1. The mean C–C distance is 1·384 Å with a standard deviation of 0·017 Å. This is more than twice the standard deviation of the individual C–C bond lengths and a classification of the C–C bonds into long [C(1)–C(6) and C(1)–C(2)] and short bonds seems justified. We postpone comments on this point until more structures of strongly acidic phenols have been determined. The C(6)–C(1)–O(1) angle (125°) is much larger than the C(2)–C(1)–O(1) angle (119°). This might be interpreted as repulsion between the phenol group O(1)–H(1) atoms and the adjacent nitro group oxygen atom O(61) to which the hydroxyl group is hydrogen bonded. Non-radial C–(OH) bonds are, however, always found in phenols (also in cases where overcrowding cannot be inferred). The large angle is found, in all determined phenol structures, to be to the side where the hydrogen atom of the hydroxyl group is pointing.

It has for a long time been postulated that *o*-nitrophenols have internal hydrogen bonds. Such bonds account for the lack of change in the infrared spectra of *o*-nitrophenol solutions on dilution and for the low melting points of *o*-nitrophenols as compared with *e.g.* *p*-nitrophenols. The structure determination reported here is, to our knowledge, the first direct evidence for such bonds.

From Table 3 it is concluded that the carbon ring is planar. All exocyclic atoms [except N(4)] deviate significantly from the ring plane, but the nitrogen atoms lie in the planes defined by the adjacent oxygen and carbon atoms. This may be seen from Table 3, where the dihedral angles between the nitro group planes and the carbon ring plane are also listed.

The C–(OH) distances in phenols and their acid dissociation constants are related as previously mentioned and as shown in Fig. 2 where C–(OH) bond

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30633 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Deviations of atoms* (Å) *from planes through the* 2-*chloro*-4,6-*dinitrophenol molecule*

Plane I $-2{\cdot}015x-3{\cdot}270y+8{\cdot}468z=3{\cdot}432$
Plane II $-2{\cdot}857x-3{\cdot}086y+8{\cdot}536z=2{\cdot}885$
Plane III $-1{\cdot}950x-3{\cdot}692y+7{\cdot}934z=3{\cdot}049$

(*a*) Deviations of atoms included in the plane calculation

I		II		III	
C(1)	0·000	C(4)	0·0	C(6)	0·0
C(2)	−0·004	O(41)	0·0	O(61)	0·0
C(3)	0·004	O(42)	0·0	O(62)	0·0
C(4)	−0·001				
C(5)	−0·003				
C(6)	0·004				

(*b*) Deviations of atoms not included in the plane calculation

I		II		III	
Cl	−0·015	N(4)	0·004	N(6)	−0·004
O(1)	0·030				
O(41)	0·082				
O(42)	−0·067				
N(4)	0·002				
O(61)	−0·083				
O(62)	0·106				
N(6)	0·006				

Angle between planes I and II: 4·00°
Angle between planes I and III: 5·06°

lengths for eight phenols have been plotted against their pK_a values. The figure stresses the need for further investigation of the structures of strongly acidic phenols.

The crystal structure

Fig. 3 shows the content of the unit cell viewed along the [010] direction. Two intermolecular contact distances between non-hydrogen atoms are shorter than 3·000 Å: the 2·968 Å distance between O(62) and N(6) and the 2·990 Å distance between O(42) and C(1). A short contact distance of 3·054 Å is found between chlorine atoms and the O(61) atoms. Other contact distances between oxygen atoms belonging to neighbouring molecules are shown in Fig. 3.

This investigation was supported by the Carlsberg Foundation.

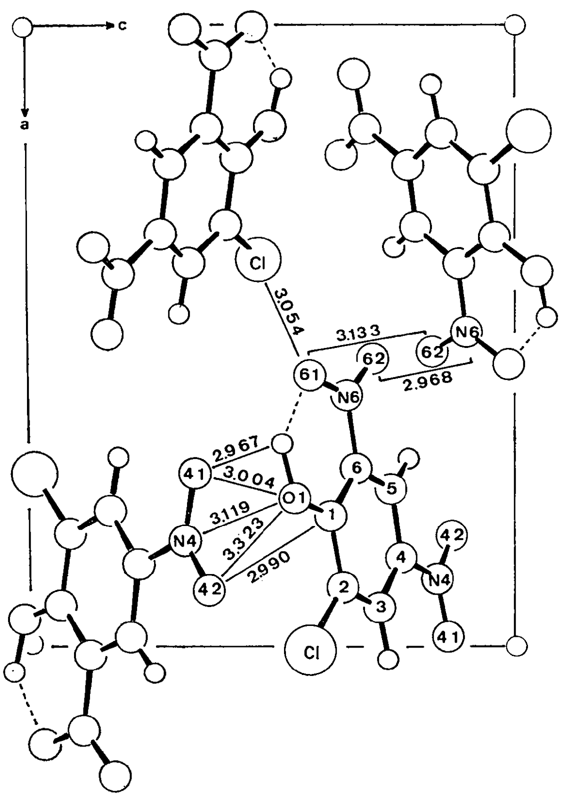

Fig. 3. Intermolecular distances in the crystal structure of 2-chloro-4,6-dinitrophenol.

References

Andersen, E. K. (1971). *Experimentelle studier over strukturen af hydroxyquinoner og deres salte.* Dissertation, Odense Universitetsforlag.

Brown, C. J. (1966). *Acta Cryst.* **21**, 170–174.

Coppens, P. & Schmidt, G. M. J. (1965). *Acta Cryst.* **18**, 654–663.

Forest, H. & Dailey, B. P. (1966). *J. Chem. Phys.* **45**, 1736–1746.

Hettich, A. & Steinmetz, H. (1932). *Z. Phys.* **76**, 688–706.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

Ito, T., Minobe, M. & Sakurai, T. (1970). *Acta Cryst.* **B26**, 1145–1151.

Maartmann-Moe, K. (1965). *Acta Cryst.* **19**, 155–157.

Maartmann-Moe, K. (1966). *Acta Cryst.* **21**, 979–982.

Nahringbauer, I. & Andersen, E. K. (1974). In preparation.

Pedersen, T., Larsen, N. W. & Nygaard, L. (1969). *J. Mol. Struct.* **4**, 59–77.

Robinson, R. A. (1967). *J. Res. Natl. Bur. Stand.* **71** A, 385–389.

Robinson, R. A. & Bates, R. G. (1966). *J. Res. Natl. Bur. Stand.* **70** A, 553–556.

Sakurai, T. (1962). *Acta Cryst.* **15**, 1164–1173.

Sakurai, T. (1968). *Acta Cryst.* **B24**, 403–412.

Stability Constants (1964). Special Publication No. 17. London: The Chemical Society.

Stewart, J. M., Kruger, G., Ammon, H., Dickinson, C. H. & Hall, S. R. (1972). Univ. of Maryland Comput. Sci. Tech. Rep. TR-192.

Sunkel, J. & Staude, H. (1968). *Ber. Bunsen Ges.* **72**, 567–573.

Venkatesvarlu, P. & Gordy, W. (1955). *J. Chem. Phys.* **23**, 1200–1202.