

The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones. VIII. Fluoranilic Acid

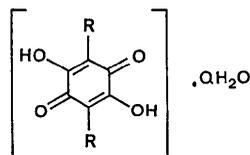
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The structure of fluoranilic acid has been determined from three-dimensional diffractometer data. The space group is $P2_1/a$, with $a=8.690$, $b=5.717$, $c=7.356$ Å, $\beta=120.54^\circ$. The ring system is similar to that of *p*-benzoquinone. There are, however, carbon-carbon single bonds of two lengths (1.456 and 1.496 Å), and there are two kinds of carbon-oxygen distance (1.215 and 1.334 Å) corresponding to C=O and C-OH bonds. The carbon ring is planar, but the exocyclic atoms are out of this plane (up to 0.04 Å).

Introduction

The structure determination of fluoranilic acid (R=F, Q=0 in formula I) was made to provide further information on the molecular structure of organic hydroxyl compounds in which the hydroxyl groups show stronger acidity than the usual.



(I)

In previous papers of this series we have reported the structure of chloranilic acid (R=Cl, Q=0), the structure of chloranilic acid dihydrate (R=Cl, Q=2) and the structure of a compound with the composition R=NO₂, Q=6. This substance called nitranilic acid proved to be a hydronium salt (Andersen, 1967*a, b, c*).

Experimental

Fluoranilic acid is prepared by a method described by Wallenfels & Friedrich (1960). The material used for this study was supplied by Dr K. Wallenfels (University of Freiburg). The fluoranilic acid was dried over phosphorous pentoxide and recrystallized from dry petroleum spirit. The crystals are red. Accurate lattice

constants were determined as described by Andersen (1967*a*). The lattice constants are given in Table 1. The density of the crystals was determined by flotation in bromoform/benzene mixtures.

Equi-inclination Weissenberg diagrams were taken from a crystal of dimensions 0.3 × 0.2 × 0.2 mm enclosed in a Lindemann capillary. These showed the systematic absences in Table 1.

Complete intensity data were collected on an automatic diffractometer equipped with scintillation counter and pulse-height discriminator. Zirconium-filtered Mo *K*α radiation was used. The intensity was recorded during an ω scan of 1.4°, at a scan speed of 1.25° min⁻¹, and for half the scan time at each end of the scanning interval. The $\bar{6}00$ reflexion was remeasured after every 15 reflexions. These measurements provided material for the calculations of scale factors for each group of 15 reflexions. The factors were in the range 0.96–1.00.

All reflexions (617) within the range $0.062 \leq \sin \theta/\lambda \leq 0.59$ were measured. 81 had intensities less than twice the standard deviation of the measurement (calculated from counting statistics alone) and were discarded. The remaining 536 were corrected for Lorentz and polarization effects and converted into structure factors. No correction for absorption was applied.

Structure determination

The structure was determined by a symbolic addition procedure. This was performed with a program written by Dewar (1968). The program was used in its automatic mode. This resulted in an *E* map based on 102 normalized structure factors and a set of signs which had a much higher probability than any other set suggested by the Dewar program. The four largest peaks in the *E* map could be identified as two of the carbon atoms, one oxygen atom and the fluorine atom. The remaining two atoms in the asymmetric unit, one oxygen and one carbon atom, could not be found. A Fourier synthesis was now calculated with signs from structure-factor calculations based on position param-

Table 1. Crystal data for fluoranilic acid

C ₆ H ₂ O ₄ F ₂	F.W. 176.08
Z=2	F(000) 176
Monoclinic	Systematic absences
<i>a</i> =8.690 (3) Å	<i>hkl</i> : no absences
<i>b</i> =5.717 (1)	<i>h0l</i> : <i>h</i> odd
<i>c</i> =7.356 (2)	<i>0k0</i> : <i>k</i> odd
$\beta=120.54$ (2)°	$P2_1/a$ assumed
Data collection: Mo <i>K</i> α radiation	
μ Mo <i>K</i> α=2.09 cm ⁻¹	
$D_o=1.871$ (8) g cm ⁻³	$D_c=1.857$ g cm ⁻³

eters for the four atoms in the *E* map. The remaining carbon and oxygen atoms could be located in the synthesis.

Structure refinement

The structure was initially refined by Fourier methods. This resulted in an *R* index of 0.33. The refinement was then continued by full-matrix least-squares calculations. These were performed by use of the *ORFLS* program included in the X-RAY 1970 structure-calculating system (Stewart, Kundell & Baldwin, 1970). The quantity minimized was $\sum w(F_o - F_c)^2$. The weighting scheme was that suggested by Cruickshank (1961), where $w = (a + F_o + bF_o^2)^{-1}$. With $a = 10.0$ and $b = 0.01$ the mean values of $w(F_o - F_c)^2$ were almost independent of $\sin \theta$ and the magnitudes of F_o . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Two cycles of least-squares refinement led to an *R* index of 0.18. Two subsequent cycles including anisotropic temperature factors gave *R* = 0.070. Until now only the fluorine, oxygen and carbon atoms had been included in the calculations. At this stage a three-dimensional difference synthesis was calculated. In this the hydrogen atom could easily be located.

The refinement was terminated with two cycles of least-squares calculations in which 58 parameters were varied. The thermal parameters for hydrogen in this calculation were given fixed values (the *B* factor for hydrogen was arbitrarily set to 3.4 \AA^2 , the mean B_{11} , B_{22} and B_{33} for the O(2) atom to which it is bound). The average ratio parameter shift/standard deviation was 0.02 (maximum value 0.13). The parameters (and standard deviations) given in Table 2 are from the final cycle. The *R* index was 0.043, the R_w 0.059. In all

Table 2. *Final atomic parameters and standard deviations*

For the numbering of atoms see Figs 1 and 2.
(a) Positional parameters ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
F(1)	4414 (2)	1734 (3)	2388 (3)
C(1)	4674 (4)	3268 (5)	1156 (4)
C(2)	5865 (3)	5222 (5)	2248 (4)
C(3)	6146 (3)	6976 (4)	932 (4)
O(1)	6632 (3)	5509 (4)	4146 (3)
O(2)	7284 (3)	8714 (4)	1962 (3)
H(1)	7509 (56)	8699 (73)	3093 (72)

Table 2 (cont.)

(b) Thermal parameters (\AA^2) (in the form $-\frac{1}{4} \sum \sum B_{ij} h_i h_j a_i^* a_j^*$)

	B_{12}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
F(1)	4.53 (9)	3.86 (8)	2.81 (7)	-0.66 (6)	1.86 (6)	0.24 (6)
C(1)	3.27 (11)	2.70 (11)	2.61 (10)	0.22 (9)	1.71 (9)	0.57 (9)
C(2)	2.56 (10)	3.02 (11)	1.82 (9)	0.25 (8)	0.93 (8)	0.05 (9)
C(3)	2.81 (11)	2.61 (11)	2.60 (10)	-0.05 (9)	1.32 (9)	-0.18 (9)
O(1)	4.14 (10)	3.78 (9)	2.45 (8)	-0.13 (8)	1.35 (7)	0.13 (7)
O(2)	4.80 (11)	3.78 (9)	2.72 (8)	-1.39 (8)	1.90 (8)	-0.54 (7)
H(1)	3.45	3.45	3.45		1.75	

calculations (also *R* index calculations) contributions from unobserved reflexions were omitted.*

The molecular structure

The perpendicular distances from the atoms in the molecule to planes through the carbon atoms are given in Table 3. From this table it is evident that the carbon ring is planar within our limits of accuracy. The fluorine and O(2) atoms are significantly out of the ring plane, the O(2) atom by as much as 0.04 Å. In the two determinations of the structure of chloranilic acid the carbon ring was also found to be planar, but the maximum deviations of the exocyclic atoms from planarity occur differently in the two structures. In the anhydrous acid it is the O(1) and O(2) atoms, in the dihydrate the chlorine and the O(1) atoms that show significant deviations from the ring plane. Therefore the various deviations from planarity are probably not typical for the free (in dilute gas or solution) acid molecules.

Table 3. *Out-of-plane displacements* (Å)

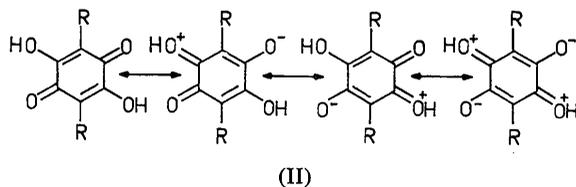
	From plane through C(1), C(3), C(2')	From plane through origin and parallel to the plane in the previous column
C(1)	0.0000	-0.0005
C(2)	0.0010	0.0005
C(3)	0.0000	-0.0005
C(1')	0.0010	0.0005
C(2')	0.0000	-0.0005
C(3')	0.0010	0.0005
Fluorine	-0.0272	-0.0277
O(1)	-0.0030	-0.0035
O(2)	0.0426	0.0421
H	-0.07	-0.07
Fluorine'	0.0282	0.0277
O(1')	0.0040	0.0035
O(2')	-0.0415	-0.0420
H'	0.07	0.07

Fig. 1 shows a drawing of the fluoranilic acid molecule. Bond angles and bond lengths in fluoranilic acid and chloranilic acid are given in Table 4. The corre-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30635 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

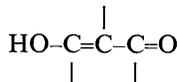
sponding distances and angles in the structures are seen to agree well. The C(1)–halogen bond is skew in the same sense with respect to the ring in all three structures [the halogen–C(1)–C(2) angle is significantly smaller than the halogen–C(1)–C(3) angle].

The ring system is particularly interesting. Benzoquinone (Trotter, 1960) and benzoquinones with four identical substituents [e.g. chloranil (R=Cl) (Chu, Jeffrey & Sakurai, 1962) and tetrahydroxyquinone (Klug, 1965)] have highly symmetrical structures. The bond lengths in the rings of these compounds are closely similar. They contain two identical (by symmetry) double bonds and four single bonds of equal length. The single bonds in the ring of the anilic acids, however, are remarkable in their division in two pairs: a long pair (1.50 Å) and a short pair (1.45 Å). This is found consistently in all three determinations and is in accordance with the resonance theory which would suggest contributions to the ground state of the molecules from structures such as:



These valence structures would account for the distribution of the carbon single bonds in short and long pairs, and for the acidity (the electron deficiency on the hydroxyl oxygen facilitates the release of the proton).

Similar valence structures have been proposed to contribute to the structures of other molecules containing the system



[e.g. ascorbic acid (Hvoslef, 1968), tetroneic acid (MacDonald & Alleyne, 1963; Lawrence & MacDonald, 1969), and dialuric acid (Bolton, 1965)]. This has been suggested primarily to account for the bond lengths in the molecules and for the rather unusual acidic strength of the substances.

The C–OH bonds in the structures of these compounds and in the anilic acids are short (*c.* 1.32 Å) as compared with C–OH bonds in phenols (*c.* 1.38 Å) and alcohols (*c.* 1.42 Å).

The crystal structure

The crystal structure of fluoranilic acid is closely similar to the structure of anhydrous chloranilic acid. The

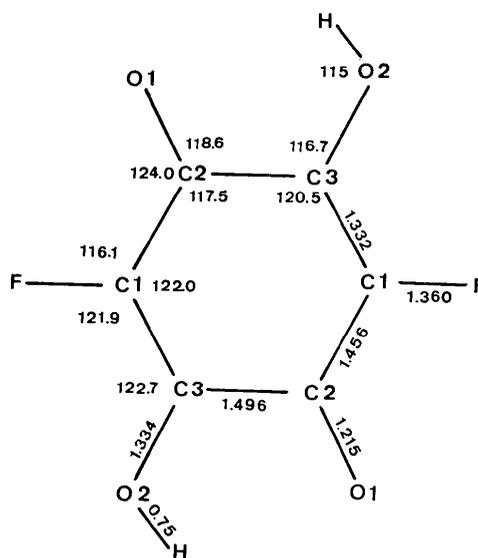


Fig. 1. The molecular structure of fluoranilic acid.

Table 4. Bond lengths (Å) and angles (°) in the chloranilic acid and fluoranilic acid molecules

Standard deviations in parentheses.

Bonds and angles	In chloranilic acid (Andersen, 1967a)	In chloranilic acid dihydrate (Andersen, 1967b)	In fluoranilic acid (this paper)
C(1)—Halogen	1.717 (5)	1.720 (5)	1.360 (4)
C(1)—C(2)	1.445 (6)	1.446 (8)	1.456 (3)
C(2)—C(3)	1.501 (7)	1.512 (7)	1.496 (4)
C(1)—C(3)	1.346 (6)	1.345 (8)	1.332 (4)
C(2)—O(1)	1.222 (4)	1.229 (6)	1.215 (3)
C(3)—O(2)	1.322 (5)	1.317 (7)	1.334 (3)
O(2)—H	0.90	0.98	0.75 (5)
Halogen—C(1)—C(2)	117.9 (3)	117.1 (4)	116.1 (2)
Halogen—C(1)—C(3)	120.9 (4)	121.0 (4)	121.9 (2)
C(2)—C(1)—C(3)	121.2 (5)	122.0 (5)	122.0 (3)
C(1)—C(2)—O(1)	123.8 (4)	124.2 (4)	124.0 (3)
C(1)—C(2)—C(3)	117.9 (3)	118.2 (5)	117.5 (2)
C(3)—C(2)—O(1)	118.2 (4)	117.6 (5)	118.6 (2)
C(1)—C(3)—C(2)	120.6 (4)	119.8 (4)	120.5 (2)
C(2)—C(3)—O(2)	116.6 (4)	117.8 (5)	116.7 (2)
C(1)—C(3)—O(2)	122.7 (4)	122.4 (5)	122.7 (3)
C(3)—O(2)—H	114	106	109 (3)

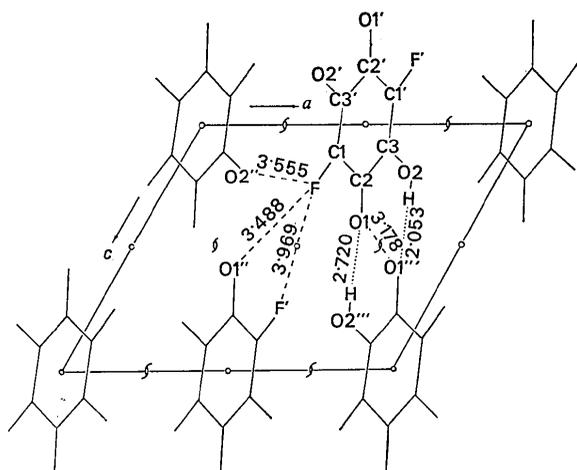


Fig. 2. The crystal structure of fluoranilic acid.

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

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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 $a=13.518$ (3), $b=5.933$ (2), $c=10.315$ (2) Å, $Z=4$; $D_m=1.746$ (10), $D_x=1.755$ 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

We thank Dr K. Wallenfels of Freiburg University for providing the fluoranilic acid sample used in this investigation and Dr K. J. Watson for his help in solving the structure by the Dewar program. The investigation was made possible by a grant from the Carlsberg Foundation. All calculations were performed at NEUCC, Lyngby.

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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