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The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones. V. Hydronium Nitranilate, Nitranilic Acid Hexahydrate

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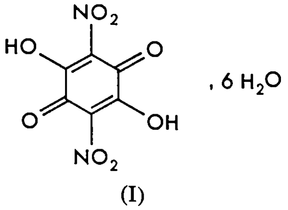
The structure of nitranilic acid hexahydrate has been determined by use of partial three-dimensional data. The cell dimensions are: $a=3\cdot657$, $b=19\cdot399$, $c=9\cdot184$ Å, $\beta=94\cdot28°$. The space group is $P2_1/c$ and $Z=2$. The geometry of the carbon ring system is similar to that found in chloranilate and nitranilate ions, and the carbon–oxygen bonds are of equal length (1·22 Å, the same as in nitranilate). There is thus strong evidence that the substance is hydrated hydronium nitranilate. The ring is planar, but the nitro group is out of the ring plane.

Introduction

The molecular structures of chloranilic acid and chloranilate ion were compared in one of the preceding papers (part III). The structure determination reported here has been made to provide data for a similar comparison between nitranilic acid (I) and the nitranilate ion.



(I)

We had expected the nitranilic acid molecule to be in the quinoidal form; the results, however, do not support our expectations. What we thought was nitranilic acid hexahydrate turned out to be hydronium nitranilate. Attempts to obtain crystals of anhydrous nitranilic acid have not been successful.

Experimental

The substance was prepared by a method given by Meyer (1924). It was recrystallized from saturated solutions in nitric acid by cooling or from solutions in acetone by slow evaporation. Crystals grown from nitric acid as well as from acetone have been used. The crystals form yellow needles.

The following lattice constants were determined from indexed powder photographs taken in a Guinier–Hägg camera:

$$a=3\cdot657\ (0\cdot002),\ b=19\cdot399\ (0\cdot006),\ c=9\cdot184\ \text{Å}\ (0\cdot003);$$
$$\beta=94\cdot28°\ (0\cdot03)$$

(Values in brackets are standard deviations.)

The formula weight of nitranilic acid hexahydrate is 338·2. With the observed lattice constants, assuming two formula units per unit cell, the calculated density is 1·731 g.cm^{-3}. The density determined by flotation is 1·729 g.cm^{-3}.

From the crystals listed in Table 1 equi-inclination Weissenberg diagrams were taken. One long and one short exposure were made of each layer, using the multiple-film technique. The intensities were estimated visually. Only film halves with extended spots were measured.

Table 1. *The size of crystals used for the intensity data collection*

Crystal	Size (mm)	Data collected
c(2)	0·21 × 0·13 × 0·08	*hk*0—*hk*3
a(3)	0·16 × 0·17 × 0·22	0*kl*—2*kl*
a(6)	0·5 × 0·5 × 0·5	2*kl*
b(1)	Small	*h*0*l*

The data from crystal *c*(2) were not used in the refinements since it was found that they had serious systematic errors (discrepancies varying with ω). The intensities measured from crystal *a*(3) and a few intensities from crystal *a*(6) (these reflexions had not been measured from crystal *a*(3) because only film halves with extended spots were measured) were put on the same scale by means of *hk*0 data from crystal *c*(2), and on an absolute scale by Wilson's method. The intensities were corrected for spot extension and converted to structure factors. No correction for absorption was made. This combined set of structure factors (in total 712) was used in the refinement of the structure. Within the limiting sphere for copper radiation there are 1527 reflexions. Of the 813 unobserved, 349 were too weak to be observed, and 464 were not covered by the experiments.

The trial structure

The following rules were observed to limit the reflexions:

hkl	no conditions
*h*0*l*	$l=2n$
0*k*0	$k=2n$;

therefore the space group $P2_1/c$ was assumed.

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Since there are only two acid molecules in the unit cell, they must lie on the special positions of the space group and hence be centrosymmetrical. The positions 0,0,0 and $0,\frac{1}{2},\frac{1}{2}$ were chosen.

The projection along [100]

The orientation of the acid molecules in the projection was found from the central part of the Patterson pro-

Table 2. *Final atomic parameters and standard deviations*

For the numbering of atoms see Figs. 2 and 4.

(*a*) Positional parameters ($\times 10^4$)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
C(1)	1528	18	627	3	699	5
C(2)	154	18	110	3	1590	5
C(3)	1403	18	563	2	9148	5
O(1)	4926	14	1613	2	690	4
O(2)	1952	15	1426	2	2555	4
O(3)	101	13	120	2	2932	4
O(4)	2411	14	999	2	8304	4
N(1)	2877	15	1253	2	1348	4
W(1)	2223	15	887	2	5283	3
W(2)	9843	15	2054	2	5542	4
W(3)	6484	15	2304	2	8081	4

(*b*) Thermal parameters (in the form $-\{\frac{1}{4}\Sigma\Sigma B_{ij}a_i^*a_j^*h_ih_j\}$)

	B_{11}	$\sigma(B_{11})$	B_{22}	$\sigma(B_{22})$	B_{33}	$\sigma(B_{33})$	B_{12}	$\sigma(B_{12})$	B_{13}	$\sigma(B_{13})$	B_{23}	$\sigma(B_{23})$
C(1)	0·45	0·41	2·39	0·20	2·21	0·20	−0·09	0·17	0·24	0·20	−0·34	0·15
C(2)	0·80	0·42	2·45	0·20	2·33	0·19	0·05	0·18	0·80	0·19	−0·20	0·15
C(3)	1·06	0·41	2·22	0·18	1·80	0·18	0·19	0·18	0·24	0·19	−0·02	0·14
O(1)	3·33	0·37	3·11	0·17	3·12	0·17	−0·13	0·17	1·21	0·17	−0·28	0·14
O(2)	4·35	0·36	3·42	0·17	2·14	0·16	−0·71	0·18	1·13	0·18	−0·57	0·12
O(3)	3·68	0·35	2·99	0·17	1·68	0·14	−0·80	0·15	0·68	0·16	−0·02	0·11
O(4)	3·96	0·35	2·93	0·17	2·02	0·14	−1·47	0·17	0·40	0·16	0·13	0·12
N(1)	1·52	0·36	2·28	0·16	1·81	0·15	−0·12	0·16	0·44	0·16	−0·05	0·13
W(1)	3·72	0·37	4·07	0·20	1·96	0·14	−0·62	0·18	0·61	0·16	0·10	0·13
W(2)	3·28	0·37	3·98	0·21	3·34	0·19	−0·35	0·19	0·24	0·19	−0·13	0·15
W(3)	3·16	0·37	3·06	0·17	3·07	0·18	0·12	0·15	0·50	0·16	0·77	0·13

Table 3. *Bond lengths and angles for nitranilate ion and chloranilate ion*

Column I is from hydronium nitranilate, column II is from the determination of ammonium nitranilate, column IV is from the determination of ammonium chloranilate monohydrate.

In columns I, II and III R = N, in column IV R = Cl. Values in brackets are standard deviations.

	I From this determination	II From ammonium nitranilate	III Mean of I and II	IV From ammonium chloranilate
C(1)–C(2)	1·411 Å (0·008)	1·434 Å (0·008)	1·427 Å	1·407 Å (0·009)
C(1)–C(3)	1·427 (0·007)	1·436 (0·008)		1·401 (0·006)
C(2)–C(3)	1·559 (0·007)	1·551 (0·009)	1·555	1·535 (0·008)
C(2)–O(3)	1·234 (0·007)	1·221 (0·006)	1·224	1·243 (0·006)
C(3)–O(4)	1·222 (0·006)	1·218 (0·008)		1·253 (0·008)
C(1)–R(1)	1·425 (0·007)	1·408 (0·008)	1·417	1·741 (0·006)
R(1)–O(1)	1·217 (0·006)	1·222 (0·008)	1·227	
R(1)–O(2)	1·229 (0·006)	1·241 (0·008)		
R(1)–C(1)–C(2)	119·4° (0·4)	119·6° (0·4)	119·2°	117·6° (0·3)
R(1)–C(1)–C(3)	118·4 (0·5)	119·2 (0·5)		119·0 (0·5)
C(2)–C(1)–C(3)	122·1 (0·5)	121·8 (0·3)	121·9	123·3 (0·5)
C(1)–C(2)–C(3)	118·5 (0·5)	119·3 (0·4)	119·2	118·7 (0·5)
C(1)–C(3)–C(2)	119·4 (0·5)	119·7 (0·5)		118·0 (0·5)
C(1)–C(2)–O(3)	126·9 (0·5)	126·3 (0·5)	126·2	125·2 (0·5)
C(1)–C(3)–O(4)	125·8 (0·5)	125·9 (0·5)		125·0 (0·5)
C(3)–C(2)–O(3)	114·6 (0·5)	114·5 (0·5)	114·6	116·1 (0·4)
C(2)–C(3)–O(4)	114·8 (0·5)	114·5 (0·5)		117·0 (0·5)
C(1)–R(1)–O(1)	119·2 (0·4)	121·4 (0·4)	120·3	
C(1)–R(1)–O(2)	120·0 (0·4)	119·3 (0·5)	119·7	
O(1)–R(1)–O(2)	120·8 (0·4)	119·2 (0·5)	120·0	

jection along [100]. The arrangement of the water molecules (also in projection) was found from space-filling considerations. The coordinates of this two-dimensional trial structure were refined by electron-density projections and by difference syntheses. A final electron-density projection is found in the upper part of Fig. 1.

The projection along [001]

From the result of the [100] projection a three-dimensional trial structure for the acid molecules was worked out. With coordinates from this model the $F(hk0)$ structure factors were calculated (water molecules were left out of this calculation).

The electron-density projection along [001] was now calculated, using data from crystal $c(2)$. The overlap prevented refinement of the x coordinates, but for two of the water molecules the x coordinate could be found and it could be seen that the x coordinate for the third water molecule was between 0·2 and 0·4.

Refinement with three-dimensional data

Three bounded projections were calculated with signs from calculated structure factors based on coordinates from the [100] and [001] projections, and further improvement of the coordinates was obtained by two three-dimensional difference syntheses. After these R was 0·163.

All positional parameters and individual isotropic temperature factors were now refined by diagonal least-squares (not block diagonal) calculations. The results of these calculations have been reported (Andersen, 1964). They agree roughly with the final results given below. The refinement was finished by two cycles of least-squares calculations. These were calculated with the Busing, Martin & Levy (1962) ORFLS program. The hydrogen atoms were not included. The scattering factors were those selected by *International Tables for X-ray Crystallography*. The quantity minimized was $\Sigma w(F_o-F_c)^2$, and the positional parameters, anisotropic temperature parameters and one scale factor were adjusted. The R index was 0·129 before the first cycle and 0·088 after the first and the second cycle. Table 2 gives the final parameters. The observed and calculated structure factors are available on request from the author.

With the result from the final least-squares calculation a three-dimensional difference synthesis was calculated. This showed no large peaks, and it was not possible to locate the hydrogen atoms.

Standard deviations of bond lengths

The standard deviations of positional parameters in Table 2 are given in fractions of the cell edges. The average standard deviation is 0·005 Å, which gives a standard deviation for bond lengths σ(C–C, C–O, C–N, N–O) = 0·007 Å.

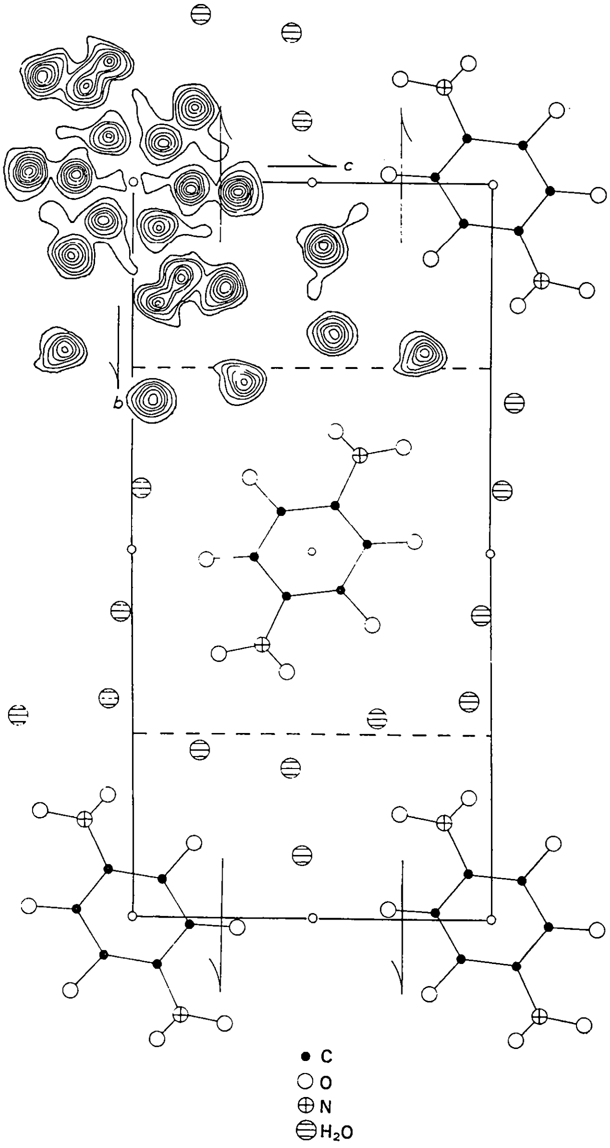

Fig. 1. Electron-density projection along [100].

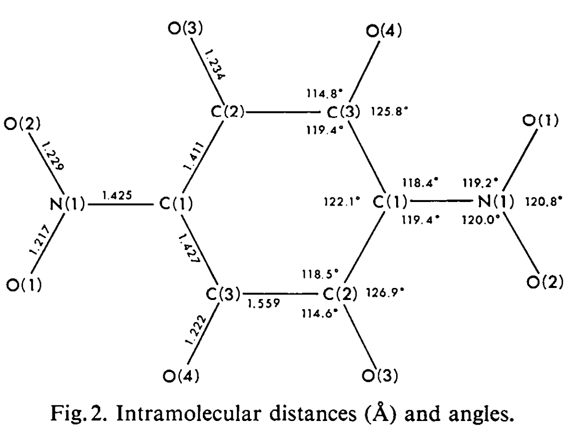

Fig. 2. Intramolecular distances (Å) and angles.

The molecular structure

The intramolecular distances and angles are shown in Fig. 2, and in Table 3 they are compared with the corresponding set of distances and angles determined in the study of ammonium nitranilate and ammonium chloranilate monohydrate. From columns I and II of Table 3 it is seen that the structure found in the hexahydrate and in ammonium nitranilate agree within the limits of accuracy. This is the strongest evidence we have that the hexahydrate is a nitranilate. In particular the length 1·559 Å of the C(2)–C(3) bond is convincing. That the C(1)–C(2) and C(1)–C(3) bonds are found to be of equal length might be due to disorder, and the same explanation could be given also for the equality of the carbon–oxygen bonds (although they most likely would turn out as 1·27 instead of 1·22 Å). The long C(2)–C(3) bond would, however, not be explained by the assumption of disorder.

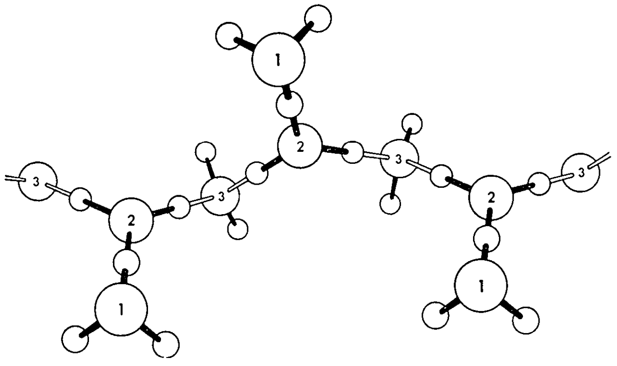

Fig. 3. The arrangement of water molecules in hydronium nitranilate.

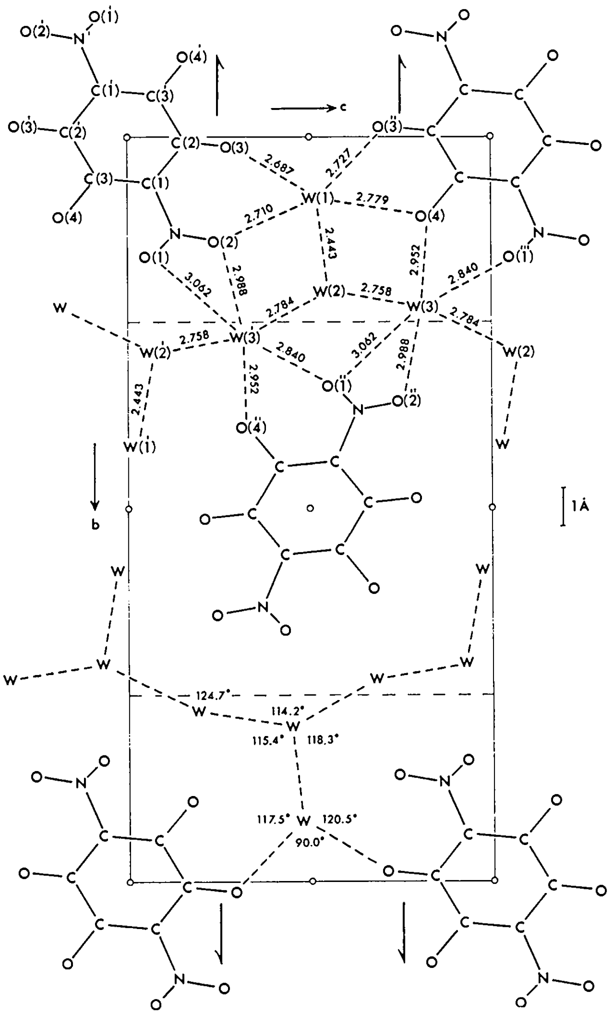

Fig. 4. Intermolecular distances (Å).

Robertson (1965) has recently reviewed some structures in which abnormally long bonds have been found between two trigonally hybridized carbon atoms. Among the structures which Robertson reviews are ammonium oxalate monohydrate (Robertson, 1965), lithium oxalate (Beagley & Small, 1964), and ammonium oxamate (Beagley & Small, 1963). The central carbon–carbon bonds in these structures are 1·569, 1·561 and 1·564 Å respectively. The oxalate ion in ammonium oxalate monohydrate is twisted (dihedral angle 26·6°), the other two anions are planar. Robertson concludes: 'Clearly there must be some factor connected with the presence of two neighbouring carbonyl groups and perhaps also of ionic charge, which is responsible for the remarkable lengthening of the bond in all these cases'. The C(2)–C(3) bonds in nitranilate and chloranilate are well characterized by Robertson's statement. They are long and they have adjacent carbonyl groups which carry ionic charge.

The molecular structure of the chloranilate ion is similar to that of the nitranilate ion. This is seen from columns III and IV of Table 3. There is a tendency for the carbon–carbon bonds to be shorter in the chloranilate ion than in the nitranilate ion, and the reverse is the case with the carbon-oxygen bonds. These deviations are only just significant. It would be interesting to have the molecular structure of a few more salts of hydroxyquinones, *e.g.* salts of tetrahydroxy-*p*-benzoquinone and fluoranilic acid. This would make it possible to find out whether there is a relation between acidic strength and the detailed structure of the anion.

In Table 4 the out-of-plane displacements are given for hydronium nitranilate and for ammonium nitranilate. It may be seen that, on the whole, the deviations from planarity are the same in the two determinations. It is interesting to note, however, that the nitro group is more twisted around the C–N bond in hydronium nitranilate than in ammonium nitranilate. The twists are 22·0 and 6·1° respectively. The atoms of the nitro groups and the C(1) atoms are in the same plane in both structures. In hydronium nitranilate the nitrogen atom lies 0·003 Å from the plane through C(1), O(1), O(2), and in the ammonium salt this distance is 0·005 Å.

Table 4. *Out-of-plane displacements*

	Hydronium nitranilate		Ammonium nitranilate
	I	II	III
	From plane through C(1), C(2′), C(3′)	From plane through origin and parallel to the plane in column I	Similar to column II
C(1)	0·000 Å	0·009 Å	0·009 Å
C(2)	−0·018	−0·009	−0·009
C(3′)	0·000	0·009	0·009
C(1′)	−0·018	−0·009	−0·009
C(2′)	0·000	0·009	0·009
C(3)	−0·018	−0·009	−0·009
O(1)	0·322	0·331	−0·187
O(2)	−0·475	−0·466	0·038
O(3)	−0·019	−0·010	−0·011
O(4)	−0·054	−0·045	−0·021
N(1)	−0·050	−0·041	−0·050

The crystal structure

The most distinctive part of the crystal structure of hydronium nitranilate is the arrangement of the water molecules. This is shown in Fig. 3. Water molecules (2) [in the following *W*(2) *etc.*] and *W*(3) form a zigzag chain that runs parallel to the *c* axis. These water molecules are presumably hydrogen bonded with *W*(2) as donor molecules. In Fig. 4 all the short intermolecular distances are given. It is seen that *W*(3) has short distances to O(4) and O(1‴) on the one side and to O(1″) and O(2″) on the other side. The directions from *W*(3) to these atoms form angles in a range from 112 to 125°, and the four atoms are probably acceptors in two bifurcated hydrogen bonds, *W*(3) being donor; by these two bonds and by the bonds to *W*(2) molecules *W*(3) is surrounded by four nearly tetrahedral hydrogen bonds. The distance between *W*(2) and *W*(1) is abnormally short (2·443 Å). Furthermore, *W*(1) has short distances to O(2), O(3), O(3″) and O(4). These are all within hydrogen bonding distance, and there is probably one bifurcated hydrogen bond to O(2) and O(3) and another to O(3″) and O(4). By such an arrangement *W*(1) and *W*(2) will both be apices of flat nearly trigonal pyramids formed of hydrogen bonds. This may be the reason for the abnormally short distance between them. Craven, Martinez-Carrera & Jeffrey (1964) found a short (2·38 Å) distance between two water molecules in dilituric acid trihydrate. The first of these two water molecules was threefold hydrogen bonded to three water molecules (as *W*(2) is in hydronium nitranilate), the second had four atoms at hydrogen bond distance, namely the first water molecule and three oxygen atoms from dilituric acid molecules (*W*(3) in hydronium nitranilate has four oxygen atoms from nitranilate molecules). According to the interpretation given by Craven, Martinez-Carrera & Jeffrey, the hydrogen bonding around the second water molecule is distorted trigonal planar.

Wicke, Eigen & Ackermann (1954) have pointed out that the ion $H_9O_4^+$, with a structure resembling that of the central four water molecules in Fig. 3, is the most probable structure for the hydronium ion in acid aqueous solutions, and there seems to be general agreement that this structure is consistent with all known experimental facts (when the solutions are not extremely concentrated). According to our interpretation of the crystal structure of hydronium nitranilate the hydronium ion in this solid should be formulated as an infinite chain with composition $(H_7O_3)_n^{n+}$.

The nitranilate ions are stacked in columns along the line $x,0,0$ and $x,\frac{1}{2},\frac{1}{2}$. The anions are parallel within each of these columns, and the perpendicular distance between neighbour molecules is 3·306 Å. There is no other short contact between nitranilate ions. It is noted that going along the assumed hydrogen bonds from O(4), O(1‴) to *W*(3) and further to *W*(2) and *W*(1) one returns to the O(3″) and O(4) of the molecule above the one from which the start was made. The same is the case when passing the atoms O(1), O(2)–*W*(3′)–*W*(2)–*W*(1)–O(2), O(3).

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