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The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones.
VII. Hydronium Cyananilate (Cyananilic Acid Hexahydrate) and Hydronium Nitranilate (a Redetermination)

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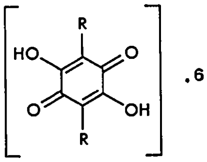
The refinement of hydronium nitranilate was based on full three-dimensional Mo data (1031 reflexions were observed, that is 52% of those in the range covered). The previous results have been confirmed. The hydrogen atoms have been located. The structure of a hydrated hydronium salt of cyananilic acid has been determined by three-dimensional diffractometer data (604 reflexions were observed, that is 71% of those in the range covered). The space group is $P2_1/c$ with $a=3{\cdot}567$, $b=19{\cdot}961$, $c=8{\cdot}927$ Å, $\beta=92{\cdot}51°$ and $Z=2$. The ring system, which is similar to that found in salts of nitranilic acid, contains four bonds of equal lengths (1·42 Å) and two considerably longer bonds (1·53 Å). The carbon–oxygen bonds are of nearly equal lengths (1·24 Å). The ring is planar, but the exocyclic atoms are out of this plane. The hydronium ions are linked by water molecules to form chains of composition $(H_7O^3)_n^{n+}$.

Introduction

In a previous paper (Andersen, 1967*a*) of this series we reported the crystal structure of a hydronium salt of nitranilic acid ($R=NO_2$ in formula I). We now report the structure determination of a similar compound, the hydronium salt of cyananilic acid ($R=CN$ in formula I).



(I)

The hydronium salts of nitranilic and cyananilic acids are to our knowledge the only organic substances in which hydronium ions have been found. We also report a refinement of the structure of hydronium nitranilate based on a new (more complete and more accurate) set of data. The most important new information gained by the present work on hydronium nitranilate is the positional parameters for the hydrogen atoms.

Experimental

Cyananilic acid was obtained from a sample of sodium cyananilate supplied by Dr K. Wallenfels (Universität Freiburg/Breisgau). When a stream of hydrogen chloride was passed through a saturated aqueous solution of this salt, flat yellow crystals with a composition corresponding to cyananilic acid hexahydrate separated. These crystals were recrystallized from nitrobenzene as recommended by Wallenfels, Bachmann, Hofmann & Kern (1965). Two different substances were obtained from the recrystallizations: one consisted of unstable orange prismatic crystals which turned to powder when separated from the mother liquor; the other separated only when the nitrobenzene solutions were allowed to stand for about a week. They had the same composition as those originally obtained from the sodium cyananilate solution saturated with hydrogen chloride. These crystals were used in the X-ray experiments. They were unfortunately rather small and flat. Accurate lattice constants (Table 1) were determined as described by Andersen (1967*b*).

Table 1. *Crystal data*

Values in parentheses are standard deviations.

(*a*) Hydronium cyananilate	(*b*) Hydronium nitranilate
$C_8H_2O_4N_2.6H_2O$	$C_6H_2O_8N_2.6H_2O$
$Z=2$	$Z=2$
Monoclinic	Monoclinic
$a=$ 3·567 (1) Å	$a=$ 3·657 (2) Å
$b=$19·961 (6)	$b=$19·399 (6)
$c=$ 8·927 (2)	$c=$ 9·184 (3)
$\beta=$92·51 (2)°	$\beta=$94·28 (3)°
Data collection Cu $K\alpha$	Data collection Mo $K\alpha$
μ(Cu $K\alpha$)$=13{\cdot}05$ cm^{-1}	μ(Mo $K\alpha$)$=1{\cdot}898$ cm^{-1}
$D_m=1{\cdot}554$ (16) g cm^{-3}	$D_m=1{\cdot}729$ g cm^{-3}
$D_c=1{\cdot}563$ g cm^{-3}	$D_c=1{\cdot}731$ g cm^{-3}
F.W. 298·22	F.W. 338·19
$F(000)=312$	$F(000)=352$
Systematic absences:	Systematic absences:
$h0l$ $l=2n+1$	$h0l$ $l=2n+1$
$0k0$ $k=2n+1$	$0k0$ $k=2n+1$
Space group $P2_1/c$	Space gioup $P2_1/c$
Dimensions of crystal used in data collection:	Dimensions of crystal used in data collection:
0·05 × 0·1 × 0·3 mm	0·3 × 0·3 × 0·3 mm

The density of the crystals was measured in bromoform-benzene mixtures. Results of these determinations and of photographic X-ray experiments are given in Table 1 together with other crystal data. The observed density and lattice constants indicate that the substance is a hexahydrate. Further confirmation of this was obtained by determination of the loss of mass on dehydration. This was 35·4%, in agreement with a calculated value of 36·2% for the hexahydrate. Dry cyananilic acid takes up moisture from the air, if kept in an open vessel, until the hexahydrate is formed.

The crystal data for hydronium nitranilate are also reported in Table 1. The composition of these crystals corresponds to one acid molecule and six water molecules. The 1967 work, however, clearly showed that the compound is a hydronium salt.

The three-dimensional intensity data for hydronium cyananilate were collected on an automatic diffractometer (scintillation counter and pulse-height discriminator) with nickel-filtered Cu $K\alpha$ radiation. The intensity was recorded by a $\theta/2\theta$ scan of 1·6° (in θ) (scan speed 1·25° min^{-1}), and for half the scan time at each end of the scanning interval. The 081 reflexion was measured after each group of 15 reflexions. These measurements provided material for calculation of scale factors for each group of 15 reflexions. The scale factors were in the range 1·00 to 0·96.

All reflexions (852) in the range $0{\cdot}05 \le \sin \theta/\lambda \le 0{\cdot}54$ were measured. Only 604 had intensities larger than twice the standard deviation of the measurement. The intensities were corrected for Lorentz and polarization effects and were converted to structure factors. No correction for absorption was applied.

The intensity data for hydronium nitranilate were collected with the same technique except that zirconium-filtered Mo $K\alpha$ radiation was used. Here the 080 reflexion was used as a standard. The scale factors were in the range 1·00 to 0·91. All reflexions (1999) in the range $0{\cdot}061 \le \sin \theta/\lambda \le 0{\cdot}71$ were measured. Only 1031 of the reflexions had intensities larger than twice the standard deviation of the measurement. These were corrected for Lorentz and polarization effects and converted to structure factors.

Structure determination of the cyananilate

Before the structure determination of hydronium cyananilate is described it should be mentioned that hydronium cyananilate and hydronium nitranilate belong to the same space group ($P2_1/c$); they have closely similar lattice constants and the unit-cell content of both substances is two anions (on symmetry centres) and 12 water molecules.

From corrected intensities measured photometrically on integrated Weissenberg films the Patterson projection along [100] was calculated. This showed much resemblance with the Patterson projection along [100] in hydronium nitranilate. It was decided to calculate an electron-density map on the basis of the 30 largest cyananilate structure factors assigned the phases of the corresponding structure factors in the nitranilate structure. In this map the locations of seven non-hydrogen atoms (out of 10) were determined. Structure-factor calculations for all observed reflexions based on these positions gave $R = 0{\cdot}47$. In a subsequent electron-density map positions for the remaining three atoms were determined. Refinement by Fourier methods yielded $R = 0{\cdot}18$.

Table 2. *Final positional and thermal parameters with estimated standard deviations*

(*a*) Hydronium cyananilate

For the numbering of atoms see Fig. 1. *W* stands for the oxygen atoms of the water molecules. Positional coordinates are $\times 10^4$ and $U_{ij} \times 10^4$ Å^2, where T.F. $= \exp [-2\pi^2 \sum \sum U_{ij} a_i^* a_j^* h_i h_j]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	−505 (11)	113 (2)	3003 (4)	435 (24)	376 (23)	208 (22)	−70 (19)	23 (16)	6 (18)
O(2)	3284 (10)	969 (2)	−1592 (4)	419 (25)	323 (23)	240 (21)	−50 (18)	46 (18)	44 (17)
W(1)	2816 (13)	851 (3)	5182 (5)	532 (31)	496 (29)	249 (23)	−50 (22)	46 (21)	−1 (20)
W(2)	906 (14)	2001 (3)	5675 (5)	659 (33)	489 (30)	370 (27)	8 (23)	23 (23)	−11 (22)
W(3)	−2489 (14)	2223 (2)	8382 (5)	455 (27)	419 (29)	477 (26)	60 (21)	−40 (21)	80 (22)
N(1)	3822 (16)	1642 (3)	2141 (6)	581 (37)	353 (31)	390 (31)	−91 (26)	−4 (26)	−55 (27)
C(1)	1378 (14)	595 (3)	755 (6)	273 (30)	254 (31)	176 (26)	−44 (22)	14 (22)	−56 (23)
C(2)	−206 (14)	84 (3)	1612 (5)	249 (31)	357 (32)	178 (29)	64 (24)	21 (22)	5 (23)
C(3)	1766 (14)	545 (3)	−820 (6)	287 (31)	248 (29)	235 (28)	−13 (24)	−5 (23)	13 (24)
C(4)	2748 (15)	1176 (3)	1501 (6)	335 (34)	305 (36)	180 (27)	24 (27)	36 (25)	36 (28)

(*b*) Hydronium nitranilate

For the numbering of atoms see Fig. 4 in Andersen (1967*a*). *W* stands for the oxygen atoms of the water molecules. Positional coordinates are $\times 10^4$ and $U_{ij} \times 10^4$ Å^2, where T.F. $= \exp [-2\pi^2 \sum \sum U_{ij} a_i^* a_j^* h_i h_j]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4964 (5)	1614 (1)	688 (2)	567 (13)	314 (9)	348 (8)	−169 (8)	76 (8)	−31 (7)
O(2)	1923 (6)	1430 (1)	2554 (2)	817 (15)	336 (9)	264 (8)	−114 (10)	132 (9)	−116 (7)
O(3)	98 (5)	113 (1)	2935 (2)	678 (12)	304 (9)	180 (7)	−135 (8)	31 (7)	−14 (6)
O(4)	2398 (6)	1000 (1)	8294 (2)	736 (14)	316 (9)	223 (7)	−202 (9)	27 (8)	31 (6)
W(1)	2258 (6)	890 (1)	5290 (2)	669 (14)	475 (11)	223 (8)	−87 (10)	26 (8)	18 (8)
W(2)	9870 (7)	2055 (1)	5543 (2)	673 (15)	467 (12)	372 (11)	−18 (10)	36 (10)	1 (8)
W(3)	6529 (6)	2301 (1)	8081 (2)	573 (13)	328 (9)	384 (10)	3 (9)	20 (8)	112 (7)
N(1)	2872 (6)	1256 (1)	1352 (2)	380 (11)	211 (8)	215 (8)	−14 (7)	−10 (7)	1 (6)
C(1)	1504 (6)	624 (1)	700 (2)	335 (12)	200 (9)	195 (8)	−23 (8)	14 (8)	−14 (7)
C(2)	155 (6)	105 (1)	1591 (2)	331 (11)	241 (10)	183 (8)	−7 (8)	11 (7)	−9 (7)
C(3)	1392 (6)	566 (1)	9142 (2)	339 (12)	234 (9)	197 (9)	−3 (9)	13 (8)	1 (7)

Table 2 (*cont.*)

U_{iso}=0·0431 for all hydrogen atoms.

	x	y	z
H(1)	1837 (227)	633 (42)	4353 (98)
H(2)	2051 (218)	593 (40)	6016 (94)
H(3)	1532 (225)	1280 (47)	5392 (86)
H(4)	− 146 (248)	2234 (42)	5064 (97)
H(5)	−577 (235)	2065 (38)	6547 (90)
H(6)	−4438 (236)	2511 (42)	8077 (83)
H(7)	−3576 (245)	1872 (44)	8564 (96)

U_{iso}=0·0400 for all hydrogen atoms.

	x	y	z
H(1)	1552 (119)	677 (20)	4421 (46)
H(2)	1641 (107)	597 (21)	5965 (46)
H(3)	685 (107)	1406 (22)	5490 (42)
H(4)	8666 (113)	2272 (22)	4779 (48)
H(5)	8592 (111)	2080 (23)	6376 (48)
H(6)	5214 (118)	2387 (22)	2741 (43)
H(7)	5341 (119)	1888 (22)	8331 (42)

Refinement of the structure on the basis of the diffractometer data was now made by least-squares calculations. These were performed with the *ORFLS* version included in the X-RAY 70 System (Stewart, Kundell & Baldwin, 1970) and *CRYLSQ* included in the X-RAY 72 System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The quantity minimized was $\sum w(F_o-F_c)^2$. The weighting scheme was $w=(a+F_o+bF_o^2)^{-1}$ with a=1·40 and b=0·10. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). No contributions from unobserved reflexions were included. The y and z starting parameters were taken from the two-dimensional calculations described above. The x coordinates were largely taken from the hydronium nitranilate structure. Four cycles of least-squares calculations were performed. In these the positional parameters and isotropic temperature factors for the carbon, nitrogen and oxygen atoms were included. The R index was 0·36 before the first of these cycles and 0·088 after the fourth cycle. These calculations were followed by two cycles of least-squares calculations in which anisotropic temperature factors were introduced. Three-dimensional difference electron-density maps calculated at this stage revealed the hydrogen-atom positions. Fig. 1 is a composition of these maps showing the hydrogen atom peaks. Finally, two cycles of least-squares refinement were performed in which all parameters except the thermal parameters for the hydrogen atoms were allowed to vary. In the last cycle the average ratio parameter shift/standard deviation was 0·02 (maximum value 0·10). The R index was 0·053. The parameters are given in Table 2(*a*).[*]

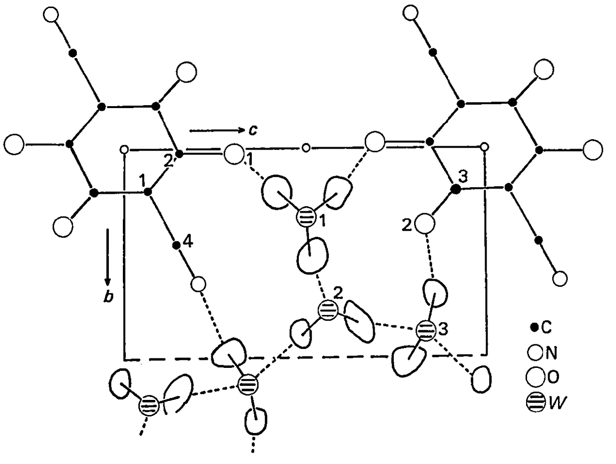


Fig. 1. Difference synthesis showing hydrogen-atom peaks and part of the crystal structure. Dotted lines indicate hydrogen bonds.

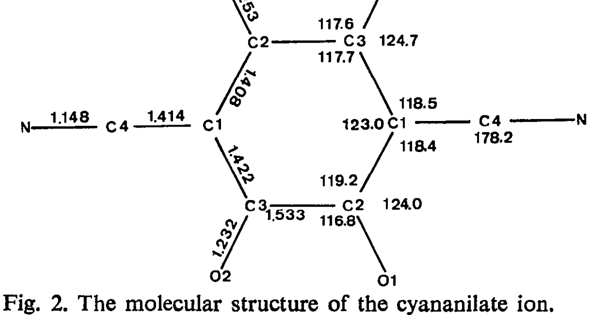


Fig. 2. The molecular structure of the cyananilate ion.

Refinement of the structure of hydronium nitranilate

The refinement and the location of hydrogen atoms was performed as described above for the cyananilate. The weighting parameters a=0·74 and b=0·04 produced mean values of $w(F_o-F_c)^2$ that were only slightly dependent on sin θ and the magnitudes of F_o. In the final cycle the average ratio parameter shift/standard deviation was 0·02 (maximum value 0·15), and the R index was 0·048. The final parameters are given in Table 2(*b*).[†]

The structure of the cyananilate and nitranilate ions

Details of the structure of the cyananilate ion are given in Fig. 2 and in Table 3 the bond lengths and angles have been compared with corresponding bond lengths and angles in the nitranilate ion (Andersen, 1967*c*, and the present determination). From Table 3 it may be seen that the ring systems in the three substances are closely similar. The rings contain in all three cases two bonds (equivalent by symmetry) of a length (1·54 Å) which is unusual between sp^2-hybridized carbon atoms. There are four considerably shorter bonds of almost

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[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30632 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

[†] See footnote above.

equal length (*ca* 1·42 Å, they are equivalent in pairs due to symmetry). The four C–O bonds (equivalent in pairs) are of nearly equal length (1·23 Å). They are rather short compared with C–O bonds in other non-carboxylic acid salts.

The carbon ring is planar in both anions, but all exocyclic atoms are out of the carbon-ring plane. The deviations of the atoms from the molecular planes are listed in Table 4.

Table 3. *Bond lengths* (Å) *and angles* (°) *in the cyananilate and nitranilate ions*

Standard deviations are in parentheses.

	Cyananilate ion in hydronium salt	Nitranilate ion in: hydronium salt	ammonium salt*
C(1)—C(2)	1·408 (7)	1·409 (3)	1·434 (8)
C(2)—C(3)	1·533 (7)	1·553 (3)	1·551 (9)
C(3)—C(1)	1·422 (7)	1·433 (3)	1·436 (8)
C(1)—C(4)†	1·414 (7)	1·440 (3)	1·408 (8)
C(4)—N	1·148 (8)		
C(2)—O(1)‡	1·253 (6)	1·236 (3)	1·221 (6)
C(3)—O(2)§	1·232 (6)	1·222 (3)	1·218 (8)
C(3)—C(1)–C(2)	123·0 (5)	122·7 (2)	121·1 (3)
C(4)†–C(1)–C(2)	118·4 (4)	119·5 (2)	119·6 (4)
C(4)†–C(1)–C(3)	118·5 (5)	117·7 (2)	119·2 (5)
C(1)—C(2)–C(3)	119·2 (4)	118·6 (2)	119·3 (5)
O(1)‡–C(2)–C(1)	124·0 (5)	127·2 (2)	126·3 (5)
O(1)‡–C(2)–C(3)	116·8 (5)	114·2 (2)	114·6 (5)
C(2)—C(3)–C(1)	117·7 (4)	118·7 (1)	119·7 (5)
O(2)§–C(3)–C(1)	124·7 (5)	126·5 (2)	125·9 (5)
O(2)§–C(3)–C(2)	117·6 (5)	114·8 (2)	114·5 (5)

* Andersen (1967*c*).
† In nitranilate structures the nitrogen in a nitro group.
‡ In nitranilate structures called O(3).
§ In nitranilate structures called O(4).

Table 4. *Least-squares planes and deviations*

(*a*) Deviations of atoms (Å) from a plane through the cyananilate ion

Equation of least-squares plane defined by the carbon atoms of the ring

$$-3{\cdot}169x+8{\cdot}700y-0{\cdot}924z=0$$

Deviations of atoms included in calculating the equation of the plane

C(1), C(2′), C(3′) all 0·010
C(1′), C(2), C(3) all −0·010

Deviations of the exocyclic atoms

C(4) 0·013, N(1) 0·019, O(1) −0·019, O(2) −0·051

(*b*) Deviations of atoms (Å) from planes through the nitranilate ion in the hydronium salt of nitranilic acid

Equation of least-squares plane I defined by the carbon atoms

$$-3{\cdot}313x+8{\cdot}042y-0{\cdot}159z=0$$

Deviations of atoms included in calculating the equation of the plane

C(1′), C(2), C(3) all 0·008
C(1), C(2′), C(3′) all −0·008

Deviations of the exocyclic atoms

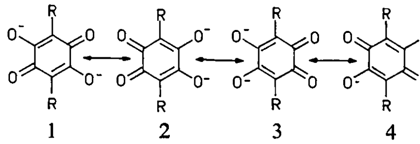
O(1) −0·358, O(2) 0·472, O(3) 0·011, O(4) 0·037, N(1) 0·037

Equation of plane II through the C(1) atom and the nitro-group oxygen atoms

$$-2{\cdot}744x+9{\cdot}538y-3{\cdot}533z=-0{\cdot}066$$

Deviation of the nitrogen atom from this plane 0·002. The dihedral angle between planes I and II is 22·9°.

If one ignores the fact that the ions are not entirely planar, and if some other small deviations are also neglected, the anilate ions have *mmm* symmetry. They may if we adopt this simplification be reasonably described by a resonance hybrid to which the following valence structures give equal contributions:



Two of the deviations from *mmm* symmetry deserve attention however. One is the difference between the C–O bond lengths in the hydronium nitranilate structure. This is 0·014 Å, which in view of the low standard deviations is significant. The other is the difference in the shorter bond lengths between the carbon atoms. This is 0·023 Å, which is also significant. The trend is

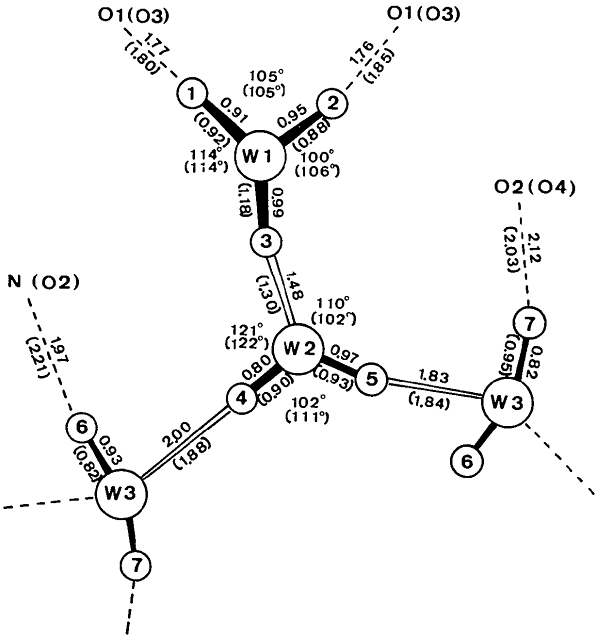


Fig. 3. Bond lengths (Å) and angles (°) in the $(H_7O_3)_n^{n+}$ complex. Figures in parentheses refer to the nitranilate structure, figures without parentheses to the cyananilate structure.

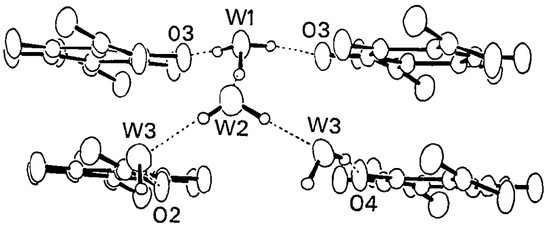


Fig. 4. The hydrogen bonding in hydronium nitranilate. Four nitranilate ions are shown (on centres: bottom left on centre 0,0,0, bottom right on 0,0,1, upper left on 1,0,0, upper right on 1,0,1).

the same for the difference between C–O bond lengths and between C–C bond lengths in hydronium cyananilate. It looks as if structure 4 above contributes more than structures 1, 2 and 3.

It is proposed that the nitranilate ions and cyananilate ions in the hydronium salts are perturbed by the short hydrogen bonds (described in the next section) that they receive from the hydronium ions. These short hydrogen bonds involve the O(1) atoms while the hydrogen bonds to the O(2) atoms are much longer (difference 0·3 Å). The nitranilate ions in the ammonium salt are more symmetrical than those in the hydronium salt. The C–O bonds are of nearly equal lengths (difference 0·003 Å) and so are the C–C bonds (difference 0·002 Å). There are no short hydrogen bonds in this salt.

The crystal structure

The anilate ions are stacked in columns along the lines $x,0,0$ and $x,\frac{1}{2},\frac{1}{2}$ (see Fig. 4 of Andersen, 1967*a*). The columns are surrounded on all sides by water molecules and hydronium ions. The perpendicular distance between neighbouring molecules within a column is therefore the only short contact between the anions: this distance is 3·3 Å.

The arrangement of the hydronium ions and the water molecules is the most interesting aspect of the crystal structure. In the previous X-ray study of hydronium nitranilate (Andersen, 1967*a*) the hydrogen-atom positions were not determined. Since all the hydrogen atoms in the water molecules have more than two oxygen atoms at hydrogen-bonding distance the possibility of bifurcated hydrogen bonds was proposed. The neutron-diffraction study by Williams & Peterson (1969) has, however, clearly shown that bifurcated hydrogen bonds are not found in the structure. The hydrogen-atom positions found in the present determinations are also in favour of normal hydrogen bonds. The hydrogen-bonding system is shown in Figs. 1, 3 and 4.

Table 5. *Bond lengths* (Å) *and angles* (°) *in the hydrogen-bonding systems in hydronium nitranilate and hydronium cyananilate*

W stands for the oxygen atoms of the water molecules. Standard deviations are in parentheses.

	Neutron diffraction (Williams & Peterson, 1971):	X-ray diffraction	
	Hydronium nitranilate	Hydronium nitranilate	Hydronium cyananilate
W(1)–H(1)	0·95*	0·92 (4)	0·91 (8)
W(1)–H(2)	1·00	0·88 (4)	0·95 (8)
W(1)–H(3)	1·18	1·18 (4)	0·99 (9)
W(2)–H(3)	1·27	1·30 (4)	1·48 (9)
W(2)–H(4)	0·98	0·90 (4)	0·80 (9)
W(2)–H(5)	0·99	0·93 (4)	0·97 (8)
W(3)–H(6)	0·95	0·82 (4)	0·93 (8)
W(3)–H(7)	0·96	0·95 (4)	0·82 (9)
W(1)–*W*(2)	2·45	2·440 (3)	2·441 (7)
W(2)–*W*(3)		2·753 (3)	2·786 (7)
H(1)–*W*(1)–H(2)	114·6	105	105
H(1)–*W*(1)–H(3)		114	114
H(3)–*W*(1)–H(2)		106	100
H(4)–*W*(2)–H(5)	111·8	111	102
H(4)–*W*(2)–H(3)		122	121
H(3)–*W*(2)–H(5)		102	111
H(6)–*W*(3)–H(7)	105·7	117	103

* Standard deviations are not given by Williams & Peterson.

The crystal structures of hydronium nitranilate and hydronium cyananilate are rather similar. This is shown by Table 5, where bond lengths and angles from the two structures are given. In all three structures the H(3) atom is significantly nearer to *W*(1) than to *W*(2) [*W*(1) stands for the oxygen atom in the tables, but in the following it is used to designate the H_3O^+ ions; similarly *W*(2) and *W*(3) in the following stand for the two water molecules in the asymmetric unit]. We therefore chose to describe the arrangement as containing H_3O^+ ions [*W*(1)] hydrogen bonded to water molecules *W*(2) and *W*(3) in infinite chains of composition $(H_7O_3)_n^{n+}$. The hydronium ions and the water molecules also hydrogen bond to the nitranilate ions. These bonds are shown in Fig. 4. In this figure four nitranilate ions (on centres 0,0,0; 1,0,0; 0,0,1; and 1,0,1), one *W*(1), one *W*(2) and two *W*(3) molecules are shown. Adjacent nitranilate ions are linked by hydrogen bonds. Such a link is shown on the right side of the figure. It goes from an O(4) atom (in the ion lying on the centre at 0,0,1) through *W*(3), *W*(2) and *W*(1) to an O(3) atom (in the ion lying on centre 1,0,1). A similar chain is shown in the left side of the drawing. It goes from an O(2) atom through *W*(3), *W*(2) and *W*(1) to an O(3) atom (lying on the centre 1,0,0). In the cyananilate structure a hydrogen bond to the nitrogen atom of the cyanide group replaces the hydrogen bond to a nitro-group oxygen atom.

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