O(*w*)–O(1″) and the O(*w*)–O(1‴) are hydrogen bonds. Whether this is so or not, the water molecule is surrounded by two O(1) atoms and by two ammonium ions in a skew tetrahedral arrangement.

Most of the hydrogen bonding system is evident from Fig. 3, but it is not apparent that the hydrogen bond triangle between N, O(*w*) and O(1‴) is a helix extending along the *b* axis.

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The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones. IV. Ammonium Nitranilate

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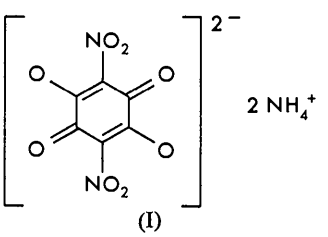
The structure of ammonium nitranilate has been refined with more experimental data than were included in the original determination. The carbon ring is planar and contains four carbon–carbon bonds of equal length (1·435 Å) and two considerably longer carbon–carbon bonds (1·551 Å). The carbon–oxygen bonds are of equal length (1·220 Å). The nitro group is out of the ring plane. It is twisted around the carbon–nitrogen bond and this bond is also out of the plane.

Introduction

The structure of ammonium nitranilate (I) reported by Jensen & Andersen (1964) has been refined with a more complete set of observed structure factors.



(I)

Experimental

The lattice constants of ammonium nitranilate have, by the least-squares method, been adapted to match the $\sin^2\theta$ values observed from a powder diagram taken in a Guinier–Hägg camera. Although these new constants scarcely differ from those reported in 1964 they are given here:

$a = 4{\cdot}712$ (0·001), $b = 7{\cdot}000$ (0·002), $c = 7{\cdot}847$ Å (0·002);
$\alpha = 111{\cdot}14$ (0·02), $\beta = 93{\cdot}45$ (0·02), $\gamma = 102{\cdot}24°$ (0·02)

(Values in brackets are standard deviations.)

These constants have been used in the calculations of bond lengths and bond angles.

With a crystal needle (dimensions 0·25 × 0·10 × 0·10 mm) the 1*kl* and 2*kl* reflexions were recorded. Only film halves with extended spots were measured and therefore a complete 360° Weissenberg diagram was prepared. This was done in two runs, and an overlap between the runs was used to scale them together. The intensities were corrected for spot extension, and converted to structure factors. No correction for absorption was made. 363 independent 1*kl* and 2*kl* reflexions were measured. 69 of these were also recorded in the old set, and they were used to scale the 1*kl* and 2*kl* reflexions. The total of independent structure factors is now 550. In the old determination 256 independent reflexions were included.

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The refinement

The structure was refined by three cycles of least squares. These were calculated with the Busing, Martin & Levy (1962) ORFLS program. The parameters from the 1964 publication were used as starting parameters except that the hydrogen atoms were excluded. The scattering factors selected by *International Tables for X-ray Crystallography* were used.

The following parameters were varied: 9 positional and thermal parameters for each atom; and 3 scale factors, one for the old data set, a second for the new $1kl$ structure factors, and a third for the new $2kl$ structure factors.

The quantity minimized in the calculations was $\Sigma w(F_o-F_c)^2$. The weighting scheme was that introduced by Hughes (1941) with

$$w=|F_o|^{-2} \quad \text{for} \quad F_o>4|F_{\min}|$$

and

$$w=0{\cdot}0625\ |F_{\min}|^{-2} \quad \text{for} \quad F_o<4|F_{\min}|\ .$$

The R index was 0·143 before the first cycle and 0·117 after. After the second and the third cycle R was 0·103. A three-dimensional difference synthesis, based on the result of the third least-squares cycle, was calculated. In this synthesis there were peaks at positions where the hydrogen atoms of the ammonium ion were expected to be found. Since the evidence for the location of the hydrogen atoms was poor, we refrain from giving the parameters for these atoms.

The final atomic parameters are given in Table 1. The observed and calculated structure factors are available on request from the author.

The standard deviations of bond lengths

The standard deviations of positional parameters in Table 1 are given in fractions of the cell edge. The average standard deviation in Å for all atoms is $\sigma(C,O,N)=0{\cdot}005$ Å. This gives a standard deviation on bond lengths of 0·007 Å, and differences in these lengths larger than 0·02 Å should therefore be significant.

The structure of the nitranilate ion

The intramolecular distances and angles are shown in Fig. 1. The carbon–oxygen bonds [C(2)–O(3) and C(3)–O(4)] are of equal length, and so are four of the carbon–carbon bonds [C(1)–C(2) and C(1)–C(3)].

If the differences in bond lengths (not greater than 0·007 Å, which is certainly not significant), and the deviations from planarity (given in Table 2) are disregarded, the molecules have *mmm* symmetry. Just the same was found for the chloranilate ion (described in part III) and what was said then about this molecular arrangement holds for the nitranilate ion also.

The out-of-plane displacements for atoms in the nitranilate ion are given in Table 2. These displacements show that the ring, within the limits of accuracy,

Table 2. *Out-of-plane displacements*

	From plane through C(1), C(2′), C(3′)	From plane through centre of molecule and parallel to the plane in the previous column
C(1)	0·000 Å	0·009 Å
C(2)	−0·018	−0·009
C(3′)	0·000	0·009
C(1′)	−0·018	−0·009
C(2′)	0·000	0·009
C(3)	−0·018	−0·009
O(1)	−0·196	−0·187
O(2)	0·029	0·038
O(3)	−0·020	−0·011
O(4)	−0·030	−0·021
N(1)	−0·059	−0·050

Table 1. *Final atomic parameters and standard deviations*

For the numbering of atoms see Figs. 1 and 2.

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

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
C(1)	7173	14	3367	8	4419	6
C(2)	8627	16	3929	9	3050	6
C(3)	8400	16	4372	9	6341	6
O(1)	2979	13	1527	8	5029	6
O(2)	3443	13	917	8	2218	6
O(3)	7748	12	3203	8	1393	5
O(4)	7309	12	4031	7	7603	5
N(1)	4429	12	1878	7	3886	6
N(2)	2298	13	2205	8	8956	6

(*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)	1·57	0·33	1·81	0·21	1·31	0·18	0·08	0·21	0·41	0·20	0·57	0·16
C(2)	2·50	0·44	2·48	0·24	1·29	0·18	−0·08	0·25	0·34	0·20	0·68	0·18
C(3)	2·17	0·35	2·29	0·22	1·37	0·18	0·30	0·22	0·53	0·20	0·80	0·17
O(1)	2·07	0·26	4·26	0·24	2·54	0·16	−1·11	0·20	0·72	0·17	1·12	0·17
O(2)	3·22	0·34	4·70	0·24	1·91	0·15	−2·26	0·22	−0·61	0·18	1·01	0·17
O(3)	3·16	0·33	5·10	0·25	1·25	0·15	−1·13	0·22	0·14	0·17	0·51	0·16
O(4)	2·33	0·28	3·84	0·21	1·63	0·14	−0·95	0·18	0·29	0·15	1·04	0·15
N(1)	1·86	0·30	1·73	0·19	1·83	0·16	0·28	0·19	0·28	0·18	0·61	0·15
N(2)	1·92	0·33	2·73	0·21	1·78	0·16	−0·50	0·20	0·26	0·18	0·88	0·16

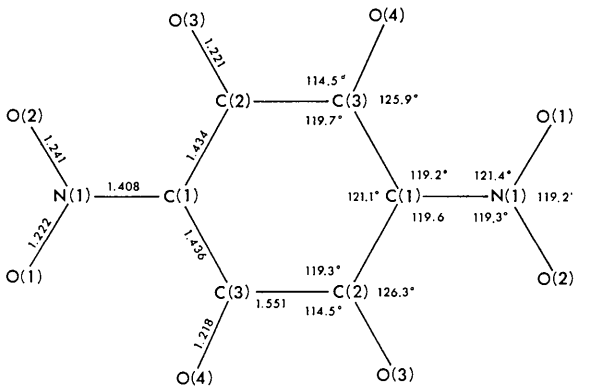

Fig. 1. Intramolecular distances (Å) and angles in the nitranilate ion.

is planar and that the oxygen atoms O(3) and O(4) lie in the ring plane. The atoms of the nitro group and C(1) are in the same plane [N(1) lies 0·005 Å from a plane through C(1), O(1), O(2)], but the nitro group does not lie in the ring plane. The nitro group is twisted around the C(1)–N(1) bond by 6·1°. The C(1)–N(1) bond is also out of the ring plane. These deviations from planarity are only partially characteristic for the nitranilate ion. In the structure of hydronium nitranilate (reported in part V) the deviation of the N(1) atom from the ring plane is the same as here (0·04 Å), but the angular twist around the C(1)–N(1) bond is 22·0°.

The crystal structure

Fig. 2 is a sketch of the structure viewed along the *a* axis. The molecules are stacked in columns running parallel to the *a* axis. The molecules are parallel within each column, and the perpendicular distance between neighbour molecules is 3·222 Å. The closest approach of molecules belonging to different columns is 3·134 Å between O(1) atoms. The ammonium ion has contact with eight oxygen atoms in the anions. It was mentioned above that four peaks in the three-dimensional difference synthesis could be attributed to hydrogen atoms. The positions of these peaks are consistent with the hydrogen bond system shown in Fig. 2 with dotted lines. The N–H bonds involved vary in length from 0·81 to 1·28 Å and the angles between them from 104 to 130°.

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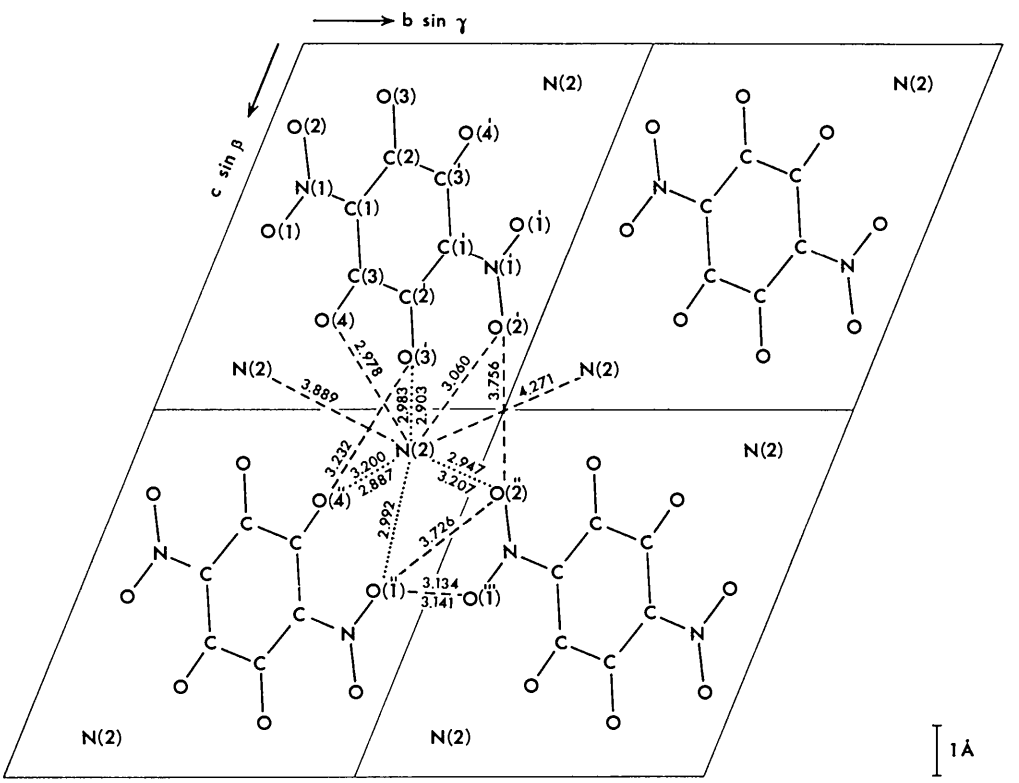

Fig. 2. Intermolecular distances in ammonium nitranilate.