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The Crystal and Molecular Structure of Ammonium Nitranilate

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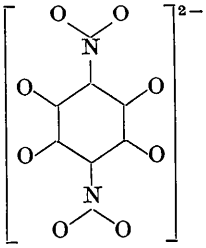
The structure of ammonium nitranilate has been determined. The crystals belong to the triclinic space group $P\bar{1}$ with cell parameters:

$$a=4\cdot709,\ b=7\cdot001,\ c=7\cdot848\ \text{Å};$$
$$\alpha=111\cdot14^\circ,\ \beta=93\cdot48^\circ,\ \gamma=102\cdot21^\circ.$$

The nitranilate ions form layers nearly parallel to the $(1\bar{2}0)$ plane. The six carbon atoms in one ring and the four oxygen atoms attached to them are, within the limits of accuracy, in the same plane. The nitro group is out of this plane. It is twisted around the C–N bond, and the C–N bond is also out of the plane. The ammonium ion has near contact with eight oxygen atoms.

Introduction

The formula for ammonium nitranilate is:



$2\,NH_4^+$.

Several bond structures can be suggested for the anion; no indication of bond types has therefore been made in the formula.

Our aim has partly been to find the packing conditions for ammonium ions and the large flat anion, and partly to establish the molecular structure (particularly the character of the C–C and C–O bonds).

Experimental

The substance was prepared by a method described by Meyer (1924), and it was purified by recrystallization from aqueous solutions. The crystals are triclinic with the following lattice constants:

$$a=4\cdot709,\ b=7\cdot001,\ c=7\cdot848\ \text{Å (all } \pm 0\cdot01\ \text{Å)};$$
$$\alpha=111\cdot14^\circ,\ \beta=93\cdot48^\circ,\ \gamma=102\cdot21^\circ\ (\text{all } \pm 0\cdot1^\circ)\ .$$

The crystals are yellow needles with the a axis along the needle direction. The needles are often flat with (001) as a predominant face. They have a distinct cleavage in the $(1\bar{2}0)$ plane. Examination between crossed Nicol prisms showed extinction nearly parallel to the cleavage. This was taken to be an indication that the flat anion is roughly parallel to the $(1\bar{2}0)$ plane.

The molecular weight of ammonium nitranilate is 264·14. With the observed lattice constants, assuming one formula unit per unit cell, the calculated density is 1·880 g.cm^{-3}. The observed density determined by the flotation method in benzene–bromoform is 1·877 g.cm^{-3}.

The substance showed no piezoelectricity when tested in a very sensitive detector, and Wilson's statistical test — using $hk0$ intensities — was clearly in favour of a centre of symmetry. Therefore the space group $P\bar{1}$ was assumed. From two batches of crystals, one prepared by the authors and the other kindly supplied by the late Dr E. Güntelberg, small needles with nearly square cross section were selected. From these the crystals used in the X-ray experiments were cut.

Rotation and Weissenberg diagrams taken with [100], [010], and [001] as rotation axes showed the crystal system to be triclinic. Preliminary lattice constants were determined from the rotation photographs. Accurate constants were later found from indexed powder photographs taken with Cu $K\alpha$ radiation in a Guinier Hägg camera with quartz as internal standard. A calibration for the camera was calculated from observed quartz lines and lattice constants for quartz ($a=4\cdot913$, $c=5\cdot405$ Å) recorded by Swanson & Fuyat (1954). In this calculation and in the calculation of lattice constants the weighted mean of α_1 and α_2 wavelengths for copper radiation 1·5418 Å has been used. The resulting $\sin^2\theta_c$ are compared with the observed values in Table 1.

The structure was determined from projections along [100], [010], [001], and [110].

From the crystals listed in Table 2 zero layer Weis-

Table 1. *Comparison of observed and calculated* $\sin^2\theta$ *values for ammonium nitranilate*

(Cu $K\alpha$ radiation)

Indices *hkl*	Intensity estimated	$10^5\times\sin^2\theta_o$	$10^5\times\sin^2\theta_c$
001	*m–s*	1139	1135
010	*m*	1489	1487
$0\bar{1}1$	*m*	1625	1627
100	*vw*	2870	2870
Quartz	*m–s*	3283	
$\bar{1}10$	*wm*	3309	3320
$\bar{1}01$	*w*	3455	3462
011	*vvw*	3615	3617
101	*w*	4538	4548
002			4540
$\bar{1}11$	*w*	4909	4907
Quartz	*vs*	5317	
110	*w*	5393	5394
020	*w*	5943	5950
$\bar{1}02$	*w*	6320	6324
$\bar{1}2\bar{1}$	*m*	6424	6433
$0\bar{2}2$	*w*	6514	6510
$\bar{1}20$	*m*	6752	6745
$\bar{1}1\bar{2}$	*w*	6950	6956
012	*vw*	8017	8017
Quartz	*vw*	9848	
003	*vw*	10221	10214
$12\bar{2}$	*w*	10373	10363
$\bar{2}10$	*m*	10900	10893
120			10893
200	*mbr*	11473	11480
Quartz	*vw*	11882	
Quartz	*w*	13131	
$1\bar{2}\bar{1}$	*w*	13482	13475
013	*w*	14679	14686
$\bar{2}\bar{1}3$	*w*	14986	14984

Table 2. *The size of crystals used for intensity data collection*

Crystal	Size	Data collected
a_2	*	$0kl$
b_7	0·1 × 0·1 × 0·15 mm	$h0l$
c_5	0·04 × 0·05 × 0·08	$hk0$
ab_2	0·06 × 0·08 × 0·1	$h\bar{h}l$

* The size of a_2 was probably about 0·1 × 0·1 × 0·1 mm, but the crystal was lost during experiments.

senberg diagrams were taken. A long and a short exposure, using multiple-film technique, were taken of each layer. Intensities were estimated visually by comparison with an intensity scale prepared for each crystal. The intensities were converted to structure factors. No correction for absorption was made (the linear absorption coefficient for Cu radiation is 25 cm^{-1}). The $hk0$ and $h\bar{h}l$ intensities were estimated twice on one set of films taken with crystals c_5 and ab_2. The residual between these intensity estimates when converted to structure factors was 3·0%. The $0kl$ and $h0l$ intensities were estimated twice on two sets of films. The one set was taken from crystals a_2 and b_7, the other from crystals a_1 and b_2 (no data taken from crystal a_1 and b_2 were used in later stages of the structure determination). The residual between these estimates when converted to structure factors was 7·8%. These residuals give a measure of the reliability of our intensity estimates.

The trial structure

Patterson projections along the [100] and the [001] axes were prepared. The [001] projection clearly showed the majority of interatomic distance vectors to lie approximately in the $(1\bar{2}0)$ plane. Accordingly the [100] projection was scaled up to match the $(1\bar{2}0)$ plane. It was only possible to choose one orientation of the molecule as proposed on the basis of standard bond lengths so that the positions and heights of the Patterson peaks were accounted for. The approximate NH_4^+ position was found by space considerations.

Refinement of the structure

The [100] projection was refined by standard methods. Structure factors were calculated on an electronic computer (DASK).

Atomic scattering factors were introduced as

$$f_n=A_n\exp\{-a_n(\sin^2\theta/\lambda^2)\}\\ +B_n\exp\{-b_n(\sin^2\theta/\lambda^2)\}+C_n\exp\{-c_n(\sin^2\theta/\lambda^2)\}$$

where the constants A_n, a_n, ... for carbon, nitrogen, and oxygen were calculated by Appel (1959) to fit the scattering curves by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The constants for hydrogen were by Forsyth & Wells (1959).

Electron densities were calculated on a modified Hägg–Laurent machine constructed by V. Frank (1957). In the first five cycles of electron-density projections R decreased from 43 to 19% (hydrogen was not included in the calculation of the structure factors; non-observed reflexions were omitted).

Further refinement was accomplished by difference syntheses. From peaks in the second of these and from the spectroscopically known symmetry and size of the ammonium ion it was possible to chose positions for the hydrogen atoms. Two further cycles brought the residual down to 15·1%. The appearance of the F_o-F_c synthesis now made it evident, that little reduction in R could be expected with isotropic temperature factors. Similarly with the projection along [110], where the refinement was stopped after five cycles with a residual $R=20{\cdot}8\%$ (hydrogen included, isotropic temperature factor). This projection showed even more marked anisotropy.

Introduction of anisotropic temperature factors

For purposes of refinement it was naturally of no consequence whether the observed anisotropy was due to anisotropic thermal vibrations or other causes. Instead of the isotropic temperature factor $T(\sin\theta)=\exp-(B\sin^2\theta/\lambda^2)$ a temperature factor of the form proposed by Cruickshank (1956)

$$T(hkl) = \exp - (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{23}kl + 2B_{31}lh)$$

was used. It must be kept in mind that this temperature factor will only in special cases give rise to an ellipsoidal charge distribution. The condition for this to be the case is that the atomic form factor is of the form $f(\sin\theta/\lambda) = \text{const.}\exp - (a\sin^2\theta/\lambda^2)$ (Gaussian shape). As mentioned above, the form factors used here were given as a sum of three Gaussian shapes, so that the anisotropic charge distribution assumed is a sum of three ellipsoidal distributions, *i.e.* not ellipsoidal. For the determination of the six parameters B_{ij} three projections are necessary, each giving three independent constants, but in such a manner that overlap cannot be avoided in information given by any two projections (a reflexion occurring in both of two zones leads by its temperature factor to a relationship between the anisotropy constants from one zone and from the other). The B_{ij}'s were determined by a distorted lattice method (Cochran 1954) used on each of the projections along [100], [110], and [010]. The parameters necessary for performing the homogeneous distortions were arrived at by the following steps. First it was assumed that the anisotropic charge distributions were ellipsoidal (the following is thus not quite consistent with the remarks above concerning these distributions). The main axes for each anisotropic atom were easily established from the difference maps. Next the magnitudes of distortions were estimated by means of the heights and positions of the anisotropy peaks in connection with graphs, giving for each type of atom the projected electron density as computed with the isotropic (mean) temperature factor. Finally the following equation was used for each atom and for three different reflexions in each zone:

$$f(\sin\theta'/\lambda)\exp - (B\sin^2\theta'/\lambda^2) = f(\sin\theta/\lambda)\exp - (\Sigma_{ij}B_{ij}h_ih_j)\ .$$

Here f is the atomic form factor and B the isotropic (mean) temperature factor. θ and θ' are the Bragg

Table 3. *Observed and calculated structure factors*

(- - - indicates that the reflexion was not observed)

H	K	L	Fobs	Fcal
0	2	-10	---	-2.72
0	3	-10	2.20	-2.54
0	4	-10	3.48	3.03
0	0	-9	2.86	1.59
0	1	-9	2.24	-1.81
0	2	-9	3.98	3.70
0	3	-9	2.50	-1.32
0	4	-9	4.68	4.08
0	5	-9	2.90	-2.74
0	6	-9	2.92	-3.83
0	0	-8	6.90	6.96
0	1	-8	5.40	5.17
0	2	-8	6.58	-5.74
0	3	-8	8.06	-8.25
0	4	-8	5.92	-5.76
0	5	-8	3.58	2.88
0	6	-8	---	1.81
0	7	-8	2.86	3.21
0	0	-7	2.82	-3.04
0	1	-7	2.00	-1.99
0	2	-7	12.02	-13.10
0	3	-7	12.72	13.98
0	4	-7	---	0.01
0	5	-7	---	0.88
0	6	-7	5.96	5.04
0	7	-7	5.96	-6.33
0	8	-7	---	1.10
0	0	-6	2.74	-2.26
0	1	-6	1.88	0.46
0	2	-6	17.90	17.63
0	3	-6	6.44	-7.48
0	4	-6	3.46	-3.24
0	5	-6	---	-0.72
0	6	-6	4.90	4.73
0	7	-6	3.58	3.90
0	8	-6	---	-1.26
0	0	-5	1.46	-2.21
0	1	-5	2.78	-1.78
0	2	-5	13.64	13.50
0	3	-5	2.04	2.68
0	4	-5	2.18	3.18
0	5	-5	1.94	-0.32
0	6	-5	3.40	-2.85
0	7	-5	---	-0.19
0	8	-5	6.56	-6.30
0	0	-4	1.40	-1.00
0	1	-4	4.16	-2.96
0	2	-4	7.32	7.82
0	3	-4	3.76	0.90
0	4	-4	17.20	-18.88
0	5	-4	1.30	-2.04
0	6	-4	1.98	-1.13
0	7	-4	2.38	-0.85
0	8	-4	7.16	7.47
0	0	-3	18.26	-17.70
0	1	-3	7.40	-7.28
0	2	-3	6.44	-5.44
0	3	-3	4.40	-3.52
0	4	-3	5.24	5.14
0	5	-3	---	-0.42
0	6	-3	2.42	-2.78
0	7	-3	4.48	5.21
0	8	-3	---	-0.70
0	0	-2	11.56	-11.19
0	1	-2	2.50	-2.83
0	2	-2	27.50	-28.76
0	3	-2	1.26	1.12
0	4	-2	15.68	15.78
0	5	-2	1.84	0.66
0	6	-2	---	0.43
0	7	-2	---	-0.12
0	8	-2	---	0.83
0	0	-1	17.28	-18.45
0	1	-1	14.68	14.40
0	2	-1	6.64	6.33
0	3	-1	12.74	11.62
0	4	-1	21.40	21.51
0	5	-1	9.40	-9.70
0	6	-1	3.40	-3.72
0	7	-1	---	-0.75
0	8	-1	1.30	1.53
0	1	0	13.60	-13.88
0	2	0	16.02	-16.48
0	3	0	4.52	-4.16
0	4	0	14.48	-14.48
0	5	0	6.88	7.34
0	6	0	---	-0.90
0	7	0	---	-0.86
0	8	0	2.46	-1.89
0	1	1	9.96	-9.77
0	2	1	12.74	-11.90
0	3	1	6.86	7.86
0	4	1	2.28	-1.65
0	5	1	2.36	2.16
0	6	1	4.06	-4.18
0	7	1	2.24	-2.27
0	1	2	20.30	21.86
0	2	2	6.52	-6.61
0	3	2	12.84	-12.51
0	4	2	2.94	-2.10
0	5	2	4.18	-3.42
0	6	2	10.00	10.66
0	7	2	---	-0.94
0	1	3	14.80	-14.61
0	2	3	20.36	18.07
0	3	3	---	-0.74
0	4	3	---	1.79
0	5	3	9.10	9.10
0	6	3	3.22	-3.59
0	1	4	14.26	13.19
0	2	4	10.16	10.06
0	3	4	2.42	-2.83
0	4	4	2.38	-2.73
0	5	4	2.90	-2.20
0	6	4	---	-0.66
0	1	5	3.84	3.89
0	2	5	---	-0.22
0	3	5	1.80	-1.29
0	4	5	---	-0.82
0	5	5	2.10	-1.68
0	1	6	2.14	1.64
0	2	6	9.56	-9.96
0	3	6	3.64	3.10
0	4	6	---	0.28
0	1	7	6.80	-6.41
0	2	7	2.54	2.94
0	3	7	3.20	3.05
0	1	8	3.92	-3.28
0	2	8	1.42	0.91
0	0	-9	2.63	1.59
1	-1	-9	---	2.57
0	0	-8	7.30	6.96
1	-1	-8	2.51	2.31
2	-2	-8	2.60	-2.88
0	0	-7	2.60	-3.04
1	-1	-7	4.16	-3.94
2	-2	-7	1.11	0.95
3	-3	-7	2.17	2.52
0	0	-6	2.91	-2.26
1	-1	-6	---	-0.23
2	-2	-6	9.21	9.50
3	-3	-6	11.45	-10.34
0	0	-5	1.56	-2.21
1	-1	-5	4.24	-4.40
2	-2	-5	9.18	-9.35
3	-3	-5	5.42	4.90
4	-4	-5	1.48	-0.69
0	0	-4	1.52	-1.00
1	-1	-4	2.32	-2.08
2	-2	-4	5.69	-5.06
3	-3	-4	1.03	-0.20
4	-4	-4	3.64	-2.66
0	0	-3	19.80	-17.70
1	-1	-3	---	1.81
2	-2	-3	6.90	-5.99
3	-3	-3	2.05	0.06
4	-4	-3	2.91	3.16
0	0	-2	11.29	-11.19
1	-1	-2	13.50	13.77
2	-2	-2	0.80	0.91
3	-3	-2	2.52	3.18
4	-4	-2	4.56	-5.14
5	-5	-2	---	0.45
0	0	-1	19.29	-18.45
1	-1	-1	17.75	18.07
2	-2	-1	13.35	13.66
3	-3	-1	---	-1.78
4	-4	-1	1.33	0.64
5	-5	-1	1.73	1.87
1	-1	0	20.36	-20.45
2	-2	0	1.67	-0.70
3	-3	0	2.27	0.66
4	-4	0	1.05	1.24
5	-5	0	1.76	1.33
1	-1	1	0.66	-1.35
2	-2	1	8.55	8.50
3	-3	1	5.66	5.70
4	-4	1	6.16	7.26
5	-5	1	2.91	-4.62
1	-1	2	26.56	22.93
2	-2	2	6.37	6.55
3	-3	2	6.82	-7.49
4	-4	2	1.03	-1.67
5	-5	2	2.73	2.58
1	-1	3	17.47	-16.96
2	-2	3	7.64	8.19
3	-3	3	---	1.92
4	-4	3	---	-0.50
5	-5	3	---	1.09
1	-1	4	14.81	12.83
2	-2	4	15.03	-15.32
3	-3	4	1.85	-1.89
4	-4	4	3.06	-3.10
5	-5	4	3.13	-2.64
1	-1	5	4.87	-4.80
2	-2	5	13.36	-12.89
3	-3	5	1.48	2.87
4	-4	5	---	0.62
1	-1	6	2.22	-1.84
2	-2	6	2.63	-2.48
3	-3	6	---	0.29
4	-4	6	3.41	-4.04
1	-1	7	5.32	-5.78
2	-2	7	10.26	10.42
3	-3	7	5.15	-5.23
4	-4	7	---	0.40
1	-1	8	---	0.26
2	-2	8	---	-0.15
3	-3	8	---	-1.48
1	-1	9	1.54	1.73
2	-2	9	---	-1.07
0	0	-9	3.00	1.59
1	0	-9	3.53	3.23
2	0	-9	---	-1.16
0	0	-8	7.31	6.96
1	0	-8	5.18	-4.61
2	0	-8	5.37	-4.29
3	0	-8	---	0.54
0	0	-7	2.46	-3.04
1	0	-7	2.38	-2.41
2	0	-7	1.55	2.19
3	0	-7	4.28	-3.80
4	0	-7	---	1.40
0	0	-6	2.76	-2.26
1	0	-6	19.60	20.28
2	0	-6	1.90	0.79
3	0	-6	4.15	-3.28
4	0	-6	5.60	-4.35
5	0	-6	---	-0.34
0	0	-5	1.77	-2.21
1	8	-5	---	0.43
2	0	-5	5.87	6.30
3	0	-5	3.34	-2.88
4	0	-5	1.02	-0.24
5	0	-5	2.61	2.31
0	0	-4	1.57	-1.00
1	0	-4	8.43	-8.18
2	0	-4	5.37	-6.33
3	0	-4	9.27	9.39
4	0	-4	2.00	1.58
5	0	-4	5.05	-3.62
0	0	-3	17.90	-17.70
1	0	-3	18.91	-19.60
2	0	-3	24.20	24.36
3	0	-3	5.07	3.90
4	0	-3	12.50	-12.89
5	0	-3	2.00	-0.09
0	0	-2	11.00	-11.19
1	0	-2	20.80	-22.07
2	0	-2	4.05	-4.22
3	0	-2	4.74	4.60
4	0	-2	11.77	12.85
5	0	-2	5.18	-4.56
0	0	-1	17.51	-18.45
1	0	-1	12.17	13.41
2	0	-1	18.61	-18.07
3	0	-1	1.11	0.13
4	0	-1	3.61	2.57
5	0	-1	4.24	4.26
1	0	0	9.86	-10.40
2	0	0	39.00	-39.22
3	0	0	2.74	0.51
4	0	0	5.28	4.39
5	0	0	1.82	-2.40
1	0	1	5.20	5.87
2	0	1	13.62	14.28
3	0	1	6.27	-5.90
4	0	1	1.34	-0.42
5	0	1	4.26	4.44
1	0	2	14.98	13.34
2	0	2	6.41	6.89
3	0	2	1.25	-0.52
4	0	2	5.11	-4.85
5	0	2	1.92	1.45
1	0	3	30.41	28.38
2	0	3	9.09	9.71
3	0	3	22.00	-21.20
4	0	3	---	-0.86
5	0	3	4.18	3.54
1	0	4	---	-1.64
2	0	4	3.61	-3.83
3	0	4	14.00	14.30
4	0	4	2.42	-1.92
1	0	5	13.91	-13.70
2	0	5	6.80	7.27
3	0	5	5.65	4.77
4	0	5	2.26	-2.34
1	0	6	13.36	-12.19
2	0	6	1.32	0.73
3	0	6	---	1.01
4	0	6	---	-0.45
1	0	7	7.10	6.72
2	0	7	---	-0.78
3	0	7	---	-0.35
1	0	8	1.46	0.58
2	0	8	2.50	-2.80
1	0	9	---	-1.81
0	-8	0	2.37	-1.89
1	-8	0	---	0.22
2	-8	0	---	-1.98
3	-8	0	---	0.20
0	-7	0	---	-0.86
1	-7	0	---	1.62
2	-7	0	---	0.08
3	-7	0	---	1.54
4	-7	0	2.90	-3.08
0	-6	0	---	-0.90
1	-6	0	---	-3.07
2	-6	0	---	0.88
3	-6	0	2.65	3.10
4	-6	0	---	-0.33
5	-6	0	---	0.45
0	-5	0	7.25	7.34
1	-5	0	---	1.42
2	-5	0	---	-0.27
3	-5	0	7.36	-8.28
4	-5	0	---	0.98
5	-5	0	---	1.33
0	-4	0	14.51	-14.48
1	-4	0	4.50	-3.17
2	-4	0	12.29	13.49
3	-4	0	---	-0.13
4	-4	0	---	1.24
5	-4	0	3.96	-2.72
0	-3	0	4.35	-4.16
1	-3	0	6.34	-4.48
2	-3	0	16.30	-17.78
3	-3	0	---	0.66
4	-3	0	6.47	6.37
5	-3	0	---	-0.68
6	-3	0	---	1.61
0	-2	0	17.71	-16.48
1	-2	0	54.25	66.40
2	-2	0	---	-0.70
3	-2	0	9.06	-7.37
4	-2	0	5.95	-4.60
5	-2	0	---	0.19
6	-2	0	---	-1.29
0	-1	0	11.60	-13.88
1	-1	0	20.32	-20.45
2	-1	0	6.97	7.00
3	-1	0	16.41	16.90
4	-1	0	---	0.15
5	-1	0	---	1.23
6	-1	0	---	-0.54
1	0	0	11.11	-10.40
2	0	0	40.30	-39.22
3	0	0	2.12	0.51
4	0	0	5.66	4.39
5	0	0	---	-2.40
1	1	0	17.37	-19.17
2	1	0	21.80	25.30
3	1	0	4.14	5.75
4	1	0	---	-1.79
5	1	0	---	-2.32
1	2	0	42.65	-42.80
2	2	0	12.92	10.48
3	2	0	8.89	7.68
4	2	0	7.00	-7.03
5	2	0	---	-0.91
1	3	0	19.19	18.83
2	3	0	3.90	4.55
3	3	0	4.96	-4.12
4	3	0	---	-3.89
1	4	0	5.84	4.35
2	4	0	3.43	1.47
3	4	0	7.11	-5.97
4	4	0	---	0.43
1	5	0	---	-0.64
2	5	0	---	-0.79
3	5	0	---	-1.85
1	6	0	---	-3.03
2	6	0	---	0.25
3	6	0	---	1.53
1	7	0	---	1.81

angles for the reflexion concerned in the undistorted and the distorted lattice respectively. The B_{ij}'s are the only unknowns.

Introduction of anistropic temperature factors decreased R from 15·1 to 10·8%. Two further cycles brought this down to the final value for the [100] projection $R=8\cdot9\%$. The R for the [110] projection was finally 9·6% (after a total of 8 F_o-F_c syntheses) and 8·6% for the [010] projection (2 F_o-F_c syntheses). When the final parameters were used for calculation of the $hk0$ structure factors (the projection not used during the refinement), they showed $R=11\cdot2\%$. This is a not too unsatisfactory value, as the exposure made for the collection of $hk0$ data was rather shorter than the others.

The over-all R factor for the 337 reflexions was 9·5% (structure factors with $F_o=0$ omitted). F_o and F_c are listed in Table 3.

The NH_4^+ ion

During the refinement it was tried whether a spherically symmetric charge distribution (but vibrating anisotropically) around the centre of the NH_4^+ ion would improve the agreement between the F_o and F_c values. Such improvement has been reported by Jeffrey & Parry (1952). The form factor for NH_4^+ given by these authors was for the present work resolved as a sum of 3 Gaussian shapes to fit into the existing program for the electronic computer. In the [110] projection the residual increased from 11·2% to 14·0% (no other parameters were altered). This was taken as an indication that the NH_4^+ ion does not rotate freely. For the [100] projection a similar calculation led to the same result. Further attempts in this direction were then discontinued.

Standard deviation of bond lengths

The standard deviation of atomic coordinates was calculated for y and z coordinates from a formula given by Cochran (1951). The final electron-density projection and the final difference synthesis along [100] was used. For oxygen atoms the standard deviation in the y coordinates was: $\sigma(y)=0\cdot004$ Å. This value holds for carbon atoms and nitrogen atoms also. These atoms had, owing to smaller temperature factors, about the same central curvature of electron density as had oxygen atoms.

For the z coordinate the result was:

$$\sigma(z)=0\cdot005\ \text{Å}$$

for oxygen atoms. The [110] projection, which was used (in combination with the [100] projection) for determination of the x coordinate showed such similarity to the above mentioned projection that we felt justified in using as standard deviation for all coordinates and all atoms

$$\sigma=0\cdot005\ \text{Å}.$$

This leads to a standard deviation in bond lengths

$$\sigma(1\text{–}2)=0\cdot007\ \text{Å}.$$

Where two bond lengths are found to differ by more than 0·02 Å, the difference can be regarded as significant.

Description of the crystal structure

Fig. 1 is the final electron-density projection along the [100] direction. It may be seen that all atoms are clearly resolved. The ellipticity of the atoms, in particular the oxygen atoms, which made the use of anisotropic temperature factors necessary, is clearly seen. Fig. 2 is the final difference map along [100]. Only half of a unit cell, corresponding to the upper half of Fig. 1, has been drawn.

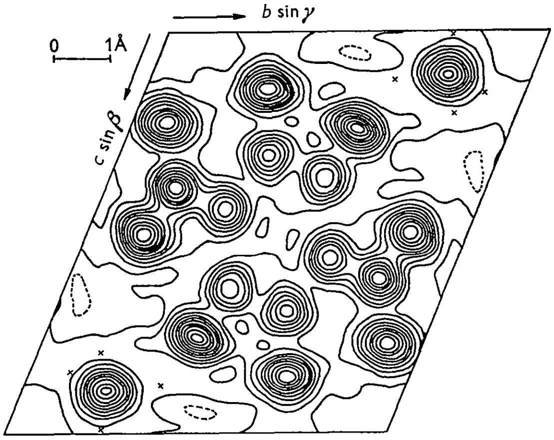


Fig. 1. Electron-density projection along [100]. Contours are 0, 1, 2, ... e.Å^{-2}, broken contour −1 e.Å^{-2}. Crosses are positions of hydrogen atoms.

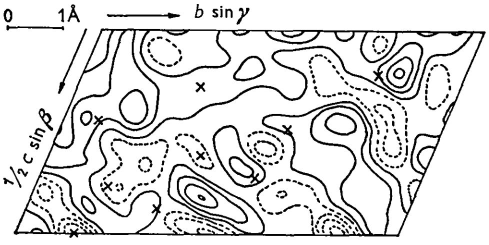


Fig. 2. F_o-F_c synthesis along [100]. Contours are 0·2 e.Å^{-2} apart. Broken contours are negative. Crosses are positions of carbon, nitrogen, and oxygen atoms.

The electron density projection along [110] is shown in Fig. 3. Some atoms are overlapping, *e.g.* N(1)–C(1) and C(2)–C(3). These atoms are clearly resolved in the [010] projection. Table 4 gives the final positional and thermal vibration parameters for all atoms. The atoms may be identified by Fig. 4(*a*) where a molecule has been drawn with intramolecular distances and angles.

Table 4. *Positional and thermal vibration parameters* ($\times 10^4$)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1)*	7162	3394	4408	260	135	102	49	46	26
C(2)	8643	3962	3070	260	151	102	57	46	26
C(3)	8366	4356	6346	260	151	102	57	46	26
O(1)	2964	1518	5023	260	257	102	−89	87	26
O(2)	3406	0922	2220	439	315	116	−44	90	−9
O(3)	7823	3223	1404	420	363	92	50	51	−7
O(4)	7346	4027	7586	420	260	92	−02	61	3
N(1)*	4433	1901	3886	260	135	102	49	46	26
N(2)	2345	2245	8955	389	165	102	−87	46	−84
H(1)†	3680	2470	120						
H(2)	9550	8920	1520						
H(3)	6330	8330	2020						
H(4)	8130	6430	1200						

* Only isotropic temperature factors have been used for these atoms.
† Hydrogen atoms have been given same thermal parameters as N(2).

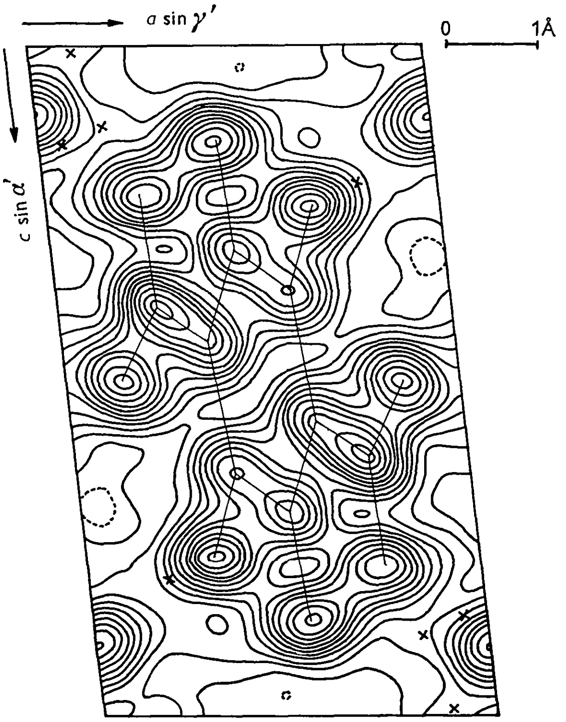


Fig. 3. Electron-density projection along [110]. Contours are 0, 1, 2, ... e.Å^{-2}, broken contour −1 e.Å^{-2}. Crosses are positions of hydrogen atoms.

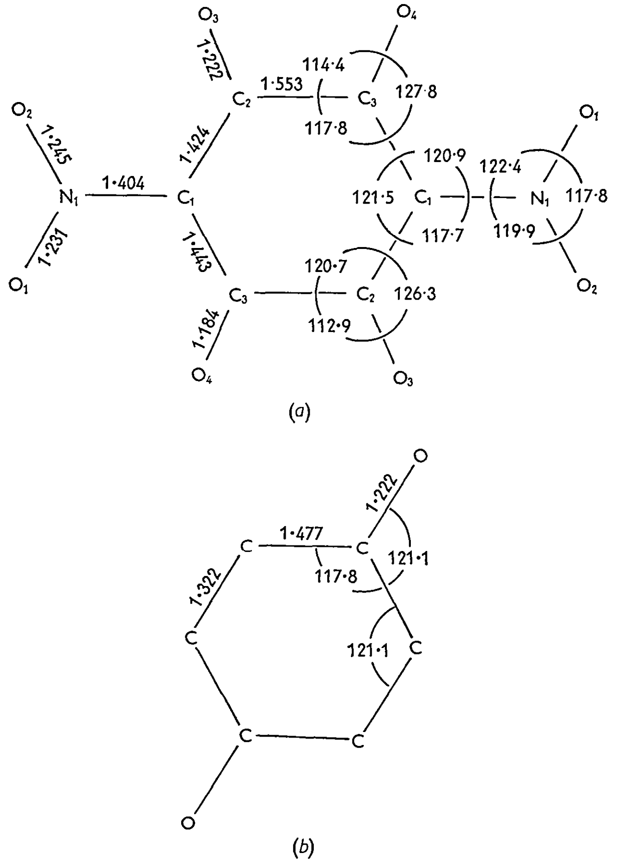


Fig. 4. (*a*) Bond distances and angles in nitranilate ion. (*b*) Bond distances and angles in benzoquinone (Trotter, 1960).

Fig. 5 is a sketch of the structure viewed along the *a* axis. The structure can be described as a layer structure with the flat anions lying parallel and nearly in the same plane ($1\bar{2}0$). The shorter atomic distances have been inserted (where two distances have been inserted along one bond the longer of them is between atoms in adjacent layers). It may be seen that no short distances are found between oxygen atoms of adjacent anions. The shortest is the 3·12–3·14 Å between nitro-group oxygen atoms. Distances between atoms in nitranilate ions in neighbouring layers are all above 3·3 Å.

The ammonium ion has near contact with eight oxygen atoms. These are very evenly distributed around the ammonium ions, two at a distance of some 3·2 Å and six at about 2·9 Å. The shortest ammonium–ammonium distance is 4·709 Å along the *a* axis; all others are longer than 7 Å. The molecular structure of benzoquinone is of interest in discussion of the geometry — and bonding of the nitranilate ion. From Fig. 4(*a*) and (*b*) it is seen that the nitranilate ion differs

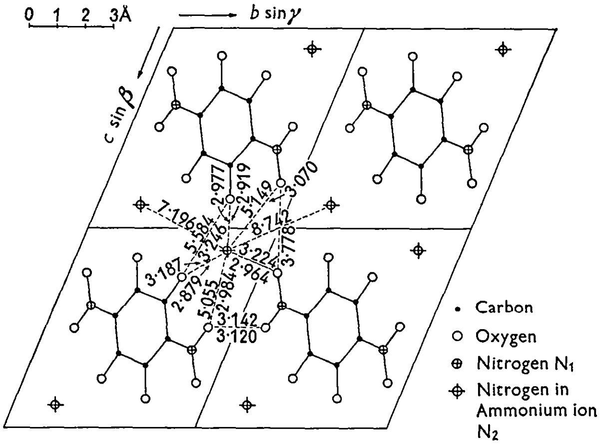


Fig. 5. Sketch of structure viewed along the *a* axis.

widely from the quinoid structure which is usually accepted for nitranilic acid. The carbon ring has in pure benzoquinone two short and four longer carbon–carbon bonds, whereas nitranilate has two long and four shorter bonds. There is an indication of the C(1)–C(2) bond being shorter than the C(3)–C(1) bond, but the difference is only about equal to the accuracy of our results. The carbon–oxygen bonds are slightly shorter than the lengths found in carboxylate ions (1·25–1·23 Å in oxalate ion (Jeffrey & Parry, 1952)). The C–O bonds are different by 0·04 Å. Although we do not want to stress arguments concerning bond characters based on these small differences, we have noted that the differences between C(1)–C(2) and C(3)–C(1), and between C(2)–O(3) and C(3)–O(4) are in favour of the retention of a small amount of quinoid structure. The carbon atoms and the oxygen atoms O(3) and O(4) are, within our accuracy, in the same plane. Table 5 shows the perpendicular distances of the atoms from a plane $4{\cdot}66x+0{\cdot}550y+1{\cdot}450z=1$ through C(1)C(3) and the center of the molecule.

Table 5. *Deviation of atoms from plane through* C(1)C(3) *and the centre of the molecule*

Atom	Deviation (Å)	
C(2)	−0·0017	Not significant
O(1)	−0·139	Difference significant
O(2)	+0·062	
O(3)	+0·014	Scarcely significant
O(4)	+0·0046	
N(1)	−0·024	Significant
N(2)	+0·360	Significant

The nitro group is out of this plane. It is twisted around the C(1)–N(1) bond and the C(1)–N(1) bond is also bent out of the plane defined above. The twist has been found in many nitro compounds, particularly in aromatic substances with large substituents in neighbour positions to the nitro group. In such compounds there may be short contacts between the bonded atoms (overcrowding). This is indeed the case in the nitranilate ion where nitro-group oxygen atoms come as near as 2·61 Å to O(3) and O(4).

It is more difficult to find a reason for the fact that the C(1)–N(1) bond is out of the ring plane. It has been found in a structure more accurately determined than ours, namely 4-nitroaniline, by Trueblood, Goldish & Donohue (1961). The perpendicular distance from N(1) to a plane through O(1), O(2) and C(1) was 0·0036 Å. This means that C(1) and the nitro group are in the same plane.

Further discussion of the molecular structure is deferred until completion of the structure determinations, already begun, of potassium nitranilate, nitranilic acid and ammonium chloranilate.

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