O(*w*)-H(2) 83°, H(2)-O(*w*)-H(2) 126°, H(2)-O(*w*)-H(3) 117°, and H(3)-O(*w*)-H(1) 116°.

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The Crystal and Molecular Structure of Hydroxyquinones and Salts of Hydroxyquinones. III. Ammonium Chloranilate Monohydrate

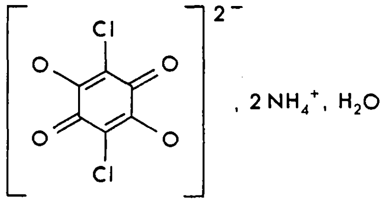
By E. Krogh Andersen*

Chemical Laboratory, Royal Veterinary and Agricultural College, Copenhagen, Denmark

(*Received* 18 *July* 1966)

The structure of ammonium chloranilate monohydrate has been determined with three-dimensional data. The cell dimensions are $a = 16{\cdot}988$, $b = 4{\cdot}780$, $c = 14{\cdot}101$ Å, $\beta = 118{\cdot}01°$. The space group is $C2/c$ and $Z = 4$. The carbon ring system is not in quinoidal form. It is planar and contains four carbon–carbon bonds of equal length (1·404 Å) and two considerably longer carbon–carbon bonds (1·535 Å). The C–O bonds are of equal length (1·248 Å). The chlorine and oxygen atoms are within the accuracy of the determination in the ring plane.

The structure determination of ammonium chloranilate monohydrate (I) was made in order to find what the molecular rearrangement is when chloranilic acid forms salts.



(I)

Experimental

Ammonium chloranilate monohydrate was prepared by slow evaporation of an aqueous chloranilic acid solution supersaturated with ammonia. The crystals are dark red violet needles with the *b* axis along the needle direction.

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

$$a = 16{\cdot}988\ (0{\cdot}003),\ b = 4{\cdot}780\ (0{\cdot}001),$$
$$c = 14{\cdot}101\ (0{\cdot}003)\ \text{Å};$$
$$\beta = 118{\cdot}01°\ (0{\cdot}02°)$$

(Values in brackets are standard deviations.)

The molecular weight of ammonium chloranilate monohydrate is 261·07. With the observed lattice constants, assuming 4 molecules per unit cell, the calculated density is 1·718 g.cm^{-3}. The observed density determined by flotation is 1·718 g.cm^{-3}.

From the crystals listed in Table 1 equi-inclination Weissenberg diagrams were taken. A long and a short exposure were taken of each layer, using the multiple-film technique. Intensities were estimated visually. Only film halves with extended spots were measured. The intensities were corrected for spot extension and converted to structure factors. The intensities measured from crystal *b*(2) were not corrected for absorption, but those measured from crystal *k*(1), which was ground to a sphere, were corrected with the aid of the tables in *International Tables for X-ray Crystallography* (1959). The data from crystal *b*(2) were put on the same relative scale by data from crystal *c*(1). The data from the [010] and [101] setting of crystal *k*(1) were also put on the same relative scale. The data from *k*(1) were finally combined into one set with which the final refinement of the structure was made. Within the limiting sphere

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* Present address: Chemical Laboratory, The University of Odense, Denmark.

for copper radiation there are 1222 reflexions. The combined set of data from crystal $k(1)$ contained 885 reflexions. Of the 337 non-observed reflexions, 181 were too weak to be observed on the films and 156 were not covered by the experiments. The residual between 198 structure factors estimated in both settings of crystal $k(1)$ was 0·079. This residual gives some measure of the reliability of the intensity estimates.

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

Crystal	Axis of rotation	Size (mm)	Data collected
$b(2)$	[010]	$0{\cdot}75\times0{\cdot}125\times0{\cdot}05$	$h0l\rightarrow h2l$
$k(1)$	[010]	Sphere 0·232 radius	$h0l\rightarrow h2l$
$k(1)$	[101]	Sphere 0·232 radius	$\rightarrow h+l=9$
$c(1)$	[001]	Unknown	$hk0$

The trial structure

In the Weissenberg diagrams the following conditions could be seen to limit the reflexions:

hkl	$h+k=2n$
$h0l$	$l=2n;\ h=2n$
$0k0$	$k=2n\,.$

This leads to the space groups $C2/c$ and Cc. Since the crystals exhibited no piezoelectricity the space group $C2/c$ (no. 15) was assumed.

The unit cell contains 4 chloranilate ions, 8 ammonium ions and 4 water molecules. The general positions in $C2/c$ are eightfold and the chloranilate ions must therefore lie on special positions. The site:

$$c\ (0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0)+\tfrac{1}{4},\tfrac{1}{4},0;\ \tfrac{3}{4},\tfrac{1}{4},\tfrac{1}{2}$$

with symmetry $\bar{1}$ was chosen for them.

The water molecules were placed on

$$e\ (0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0)+0,y,\tfrac{1}{4};\ 0,y,\tfrac{3}{4}$$

which is the only special position with symmetry 2.

The ammonium ions were placed on general positions.

The projection along [010]

The orientation of the chloranilate ions was found from the Patterson projection along [010]. Structure factors were calculated with the coordinates for atoms of the anions from the Patterson projection and with the ammonium ions placed half way between oxygen atoms in neighbouring anions. With signs from these calculations the electron density projected along the [010] direction was calculated. This showed that the structure was essentially correct, but the ammonium ions were rather badly placed.

The x and z coordinates were now refined by difference syntheses. The refinement was finished with four cycles of diagonal (simple) least-squares calculations. These included individual isotropic temperature factors. The final R was 0·123. At this stage an electron-density projection and a difference synthesis were calculated. The results of these are shown in Fig. 1, which also gives the numbering of the atoms.

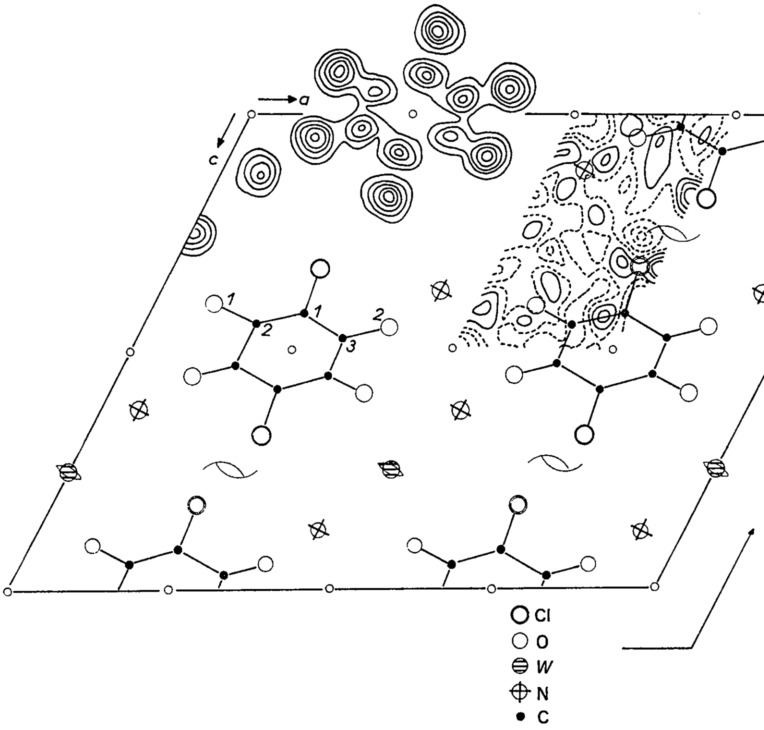


Fig. 1. Electron-density projection along [010]. Contours at equal intervals (in chlorine every second is left out). Difference synthesis (broken contours are negative).

The three-dimensional trial structure

A three-dimensional trial structure was now set up for the chloranilate ion. This was done by means of the result from the [010] projection and standard bond lengths for the bonds in the anions.

It was not possible to propose y coordinates for the water molecule or for the ammonium ion. The electron density was therefore calculated along the lines $(0{\cdot}5,y,0{\cdot}25)$ and $(0{\cdot}44,y,0{\cdot}37)$. These are the lines along which the water molecule and the ammonium ion will be found. These calculations were carried out with signs for the structure factors calculated for the chloranilate ions alone and with structure factors observed from crystal $b(2)$. From these line syntheses the y coordinates for the oxygen of the water molecule and for the nitrogen of the ammonium ion were found to be 0·55 and 0·225 respectively.

Refinement of the structure

The structure was now refined by four cycles of diagonal (simple) least-squares calculations. In these the positional parameters, isotropic temperature factors and one scale factor were adjusted. The results of these calculations have been published (Andersen, 1964). They agree roughly with the final results given below (deviations in bond lengths up to 0·04 Å).

Until this stage only the data obtained with crystal $b(2)$ had been used. The refinement of the structure was finished with the data recorded from crystal $k(1)$. This was done by least-squares calculations with the Busing, Martin & Levy (1962) ORFLS program.

The quantity minimized in these calculations was $\Sigma\, w(F_o-F_c)^2$. The weighting scheme was that introduced by Hughes (1941). In the calculations the positional parameters, anisotropic temperature factors and one scale factor were adjusted. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962).

Table 2. *Final atomic parameters and standard deviations*

For the numbering of atoms see Figs. 2 and 3.

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

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cl	2253	1	2970	3	3235	1
C(1)	2396	3	5462	11	4203	4
C(2)	1704	3	5791	12	4476	4
C(3)	1812	3	2016	12	324	4
O(1)	997	3	4435	10	4083	4
O(2)	1174	3	1727	9	528	3
N(1)	4386	3	2122	13	3726	5
O(w)	5000		5484	12	2500	

The R index was 0·215 before the first cycle and 0·187 after. After the second cycle R was 0·169. It was now observed that 7 of the observed structure factors were considerably in error. With these 7 structure factors left out two more cycles of least-squares calculations were carried out. The R was 0·104 before these calculations and 0·086 after. The parameters obtained in these final calculation are given in Table 2. The observed and calculated structure factors are available on request from the author.

A three-dimensional difference synthesis was now calculated. In this synthesis there were peaks at positions where the hydrogen atoms of the ammonium ion were expected to be found; but the hydrogen atoms belonging to the water molecule could not be seen. Since the evidence for the location of the hydrogen atoms was poor (there were many equally large peaks at other positions) we refrain from giving the parameters for these atoms.

The structure of the chloranilate ion

The intramolecular distances and angles in the chloranilate ion are shown in Fig. 2, and in Table 3 they are compared with corresponding values for bonds and angles in the chloranilic acid molecule and in the chloranil molecule. In paper II of this series it was suggested that the following structures contribute to the ground state of the chloranilic acid molecule:

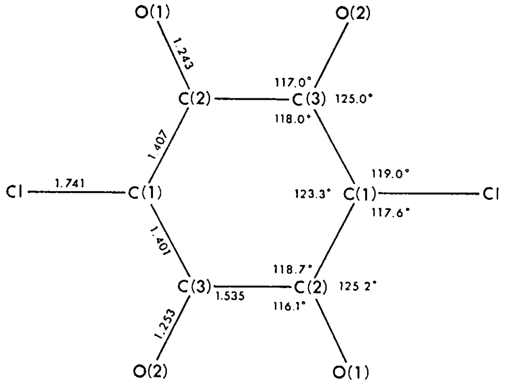


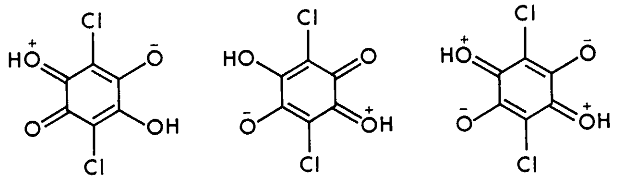
Fig. 2. Intramolecular distances (Å) and angles in the chloranilate ion.

Table 2 (*cont.*)

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

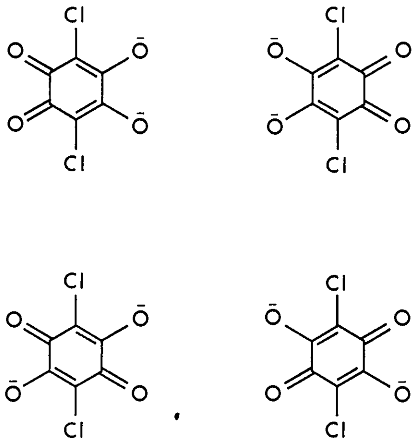
v

	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}	$\sigma(B_{23})$
Cl	1·39	0·06	1·76	0·06	1·56	0·06	−0·03	0·04	0·76	0·04	−0·54	0·05
C(1)	1·44	0·18	1·09	0·18	1·61	0·19	0·10	0·17	0·66	0·16	−0·10	0·17
C(2)	0·79	0·16	1·65	0·20	2·03	0·20	−0·16	0·18	0·43	0·15	−0·36	0·19
C(3)	0·90	0·17	1·88	0·20	1·55	0·18	−0·15	0·18	0·55	0·15	0·00	0·19
O(1)	1·21	0·14	2·39	0·18	3·60	0·20	−0·44	0·15	1·16	0·14	−1·27	0·17
O(2)	1·49	0·15	2·46	0·18	2·64	0·17	0·29	0·15	1·31	0·13	0·70	0·15
N(1)	1·50	0·19	2·67	0·23	3·84	0·26	0·51	0·19	1·32	0·19	−0·35	0·22
O(w)	2·39	0·24	2·06	0·20	3·08	0·26	0·0		1·17	0·21	0·0	

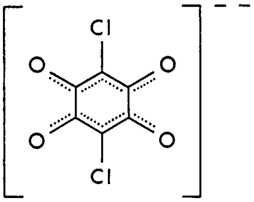


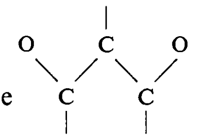
These would account for the increased acidity and for the particular molecular structure found in chloranilic acid.

It is tempting to suggest that the structure found for the chloranilate ion receives contributions from such structures as:



These structures could be combined to one:



The dotted line along the  indicates that the π electrons involved in these bonds are strongly delocalized.

The chloranilate ion is planar within the accuracy of the structure analysis. The distances from the atoms to a plane through three carbon atoms in symmetrical position are given in Table 4. The largest out-of-plane deviation is 0·032 Å for the O(2) atom. This is scarcely significant and none of the planes used in Table 4 is the 'best' plane through the atoms of the molecule.

Table 4. *Out-of-plane displacements*

	I From plane through C(1)C(2′)C(3′)	II From plane through the centre of the molecule and parallel to the plane in column I
C(1)	0·000 Å	−0·003 Å
C(2)	0·006	0·003
C(3′)	0·000	−0·003
C(1′)	0·006	0·003
C(2′)	0·000	−0·003
C(3)	0·006	0·003
Cl	−0·001	−0·004
O(1)	0·015	0·012
O(2)	0·035	0·032
Centre of molecule	0·003	0·000

If the small differences in length between the C(1)–C(2) and C(1)–C(3) bonds and between the C(2)–O(1) and C(3)–O(2) bonds are disregarded, and if also the small deviations from planarity are ignored, the chloranilate ion has *mmm* symmetry. A highly symmetrical anion is also found in the nitranilate ion described in the next paper. Other anions of organic hydroxyl compounds have recently been found to have highly

Table 3. *Bond lengths and angles in chloranilate ion compared with corresponding bonds and angles in chloranil and chloranilic acid*

Values in brackets are standard deviations.
The values for chloranil are from Chu, Jeffrey & Sakurai (1962).

Bonds and angles	Chloranil	Chloranilic acid	Chloranilate ion
C(1)–C(2)	1·477 Å	1·446 Å	1·407 Å (0·009 Å)
C(1)–C(3)	1·342	1·346	1·401 (0·006)
C(2)–C(3)	1·477	1·506	1·535 (0·008)
C(2)–O(1)	1·195	1·225	1·243 (0·006)
C(3)–O(2)		1·320	1·253 (0·008)
C(1)–Cl	1·714	1·719	1·741 (0·006)
Cl—C(1)–C(2)	116°15′	117·5°	117·6° (0·3°)
Cl—C(1)–C(3)	122 23	120·9	119·0 (0·5)
C(2)–C(1)–C(3)	121 22	121·6	123·3 (0·5)
C(1)–C(2)–O(1)	121 22	124·0	125·2 (0·5)
C(1)–C(2)–C(3)	117 16	118·1	118·7 (0·5)
C(3)–C(2)–O(1)	121 22	117·9	116·1 (0·4)
C(1)–C(3)–C(2)	121 22	120·2	118·0 (0·5)
C(2)–C(3)–O(2)		117·2	117·0 (0·5)
C(1)–C(3)–O(2)		122·5	125·0 (0·5)

symmetrical structures. The croconate ion, for example, has five carbon atoms in a regular pentagon and five C–O bonds of equal length (Baenziger & Hegenbarth, 1964). The structure of the dipotassium salt of diketocyclobutenediol has been determined (Macintyre & Werkema, 1964). The structure of the anion in this salt (called squarate ion) is found to be a planar regular square with C–C bonds of 1·444 and 1·469 Å length and with C–O bonds of 1·260 and 1·258 Å.

The *pK* values for the substances discussed above are given in Table 5. It may be seen that all the substances are unusually strong acids. This is no doubt partly due to the high symmetry af their anions. The compounds are comparable to the strong inorganic oxyacids, sulphuric and perchloric acid, to which anions (sulphate and perchlorate) of exact tetrahedral symmetry correspond.

Table 5. *The pK values for some acidic organic hydroxyl compounds*

	pK_1	pK_2	Reference
Chloranilic acid	0·58	3·18	Schwarzenbach & Suter (1941)
Nitranilic acid	−3·5	−0·5	Schwarzenbach & Suter (1941)
Diketocyclobutenediol	~1	2·2	Cohen, Lacher & Park (1959)
(Sulphuric acid)	−3	1·7	

It is generally found that the strengths of acids depend on the number of equivalent oxygen atoms in their anions. Either resonance or the spread of charge (between the oxygen atoms) is given as an explanation for this observation.

The crystal structure

The chloranilate ions are stacked in columns running parallel to the *b* axis. In Fig. 3 one anion from each column in the unit cell is shown. The chloranilate ions are parallel within each column, and the perpendicular distance between two molecules is 3·30 Å, a value very similar to that found in chloranilic acid and in chloranilic acid dihydrate (3·25 Å).

The closest approach of molecules belonging to different columns is the 3·514 Å between two chlorine atoms related by a screw axis. Such short halogen–halogen distances are often found in structures containing covalently bonded chlorine. It was found in the structure of anhydrous chloranilic acid and in the dihydrate of chloranilic acid. The Cl···Cl distances in these two structures were 3·335 and 3·435 Å respectively.

The hydrogen atoms for which there was weak evidence in a three-dimensional difference synthesis are consistent with the hydrogen-bonding system shown in Fig. 3 with dotted lines. The ammonium ion should in such a system be donor in four hydrogen bonds of which the one is bifurcated. The atoms O(1‴) and O(2″) receive each one prong of the bifurcated hydrogen bond. The other three hydrogen bonds have Cl″, O(2) and O(*w*) as acceptor atoms. The lengths of the N–H bonds vary from 0·99–1·11 Å and the angles between them from 91° to 129°.

The hydrogen atoms of the water molecule were not located; but from the crystal structure it seems plausible [the angle O(1″)–O(*w*)–O(1‴) is 95·4°] that the

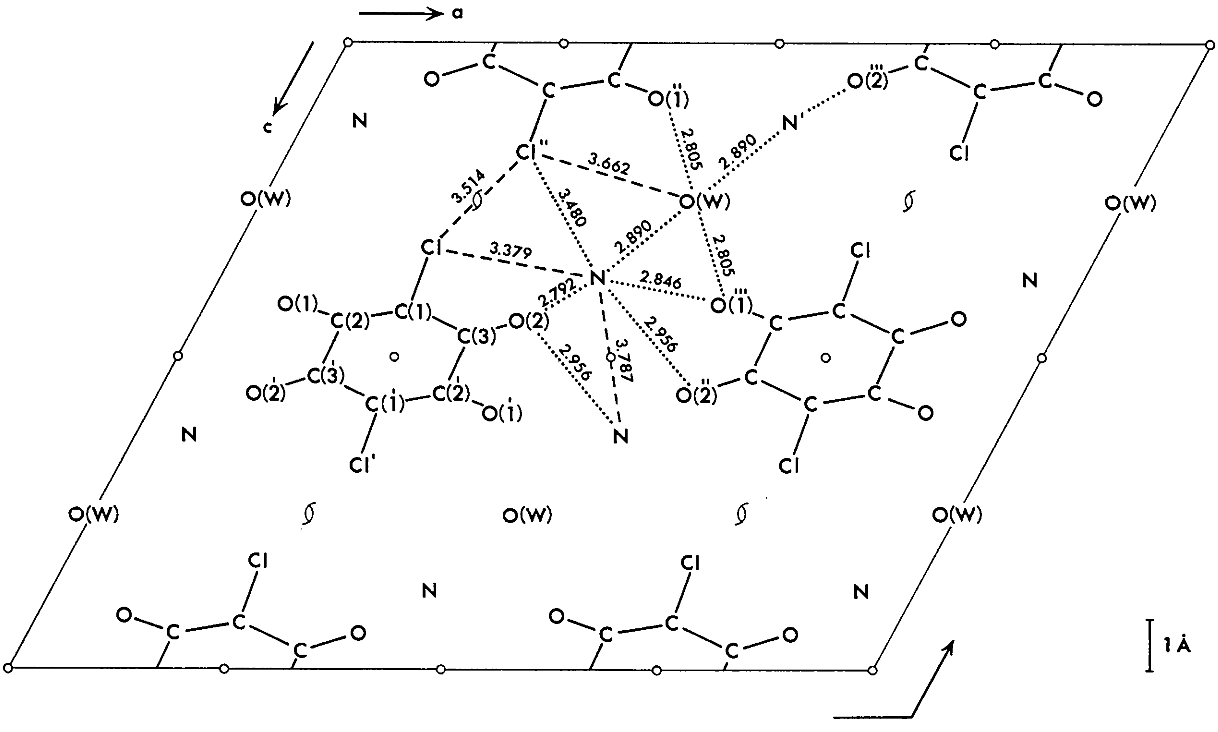


Fig. 3. Intermolecular distances (Å) in ammonium chloranilate monohydrate.

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

BY E. KROGH ANDERSEN*

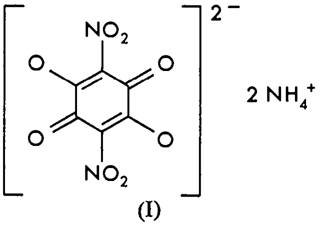
Chemical Laboratory, Royal Veterinary and Agricultural College, Copenhagen, Denmark and X-ray Laboratory, Mineralogical-Geological Institute, The University of Copenhagen, Denmark

(*Received* 18 *July* 1966)

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:

$$a=4\cdot712\ (0\cdot001),\ b=7\cdot000\ (0\cdot002),\ c=7\cdot847\ \text{Å}\ (0\cdot002);$$
$$\alpha=111\cdot14\ (0\cdot02),\ \beta=93\cdot45\ (0\cdot02),\ \gamma=102\cdot24°\ (0\cdot02)$$

(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 $1kl$ and $2kl$ 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 $1kl$ and $2kl$ reflexions were measured. 69 of these were also recorded in the old set, and they were used to scale the $1kl$ and $2kl$ reflexions. The total of independent structure factors is now 550. In the old determination 256 independent reflexions were included.

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* Present address: Chemical Laboratory, The University of Odense, Denmark.