GIMARC, B. M. (1969). Private communication.
GIRLING, R. L. & AMMA, E. L. (1967). *Inorg. Chem.* **6**, 2009.
HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-ray Crystallography (1965). Vol. I, pp. 99, 545. Birmingham: Kynoch Press.
KOJIMA, T. & NISHIKAWA, T. (1957). *J. Phys. Soc. Japan*, **12**, 680.
KUNCHUR, N. R. & TRUTER, M. R. (1958). *J. Chem. Soc.* p. 2551.
LANCASTER, J. E. & STOICHEFF, B. P. (1956). *Canad. J. Phys.* **34**, 1016.
LANE, T. J., SEN, D. N. & QUAGLIANO, J. V. (1954). *J. Chem. Phys.* **22**, 1855.
LEWIS, P. H. & RUNDLE, R. E. (1953). *J. Chem. Phys.* **21**, 986.
LIDE, D. R. JR & MANN, D. E. (1958). *J. Chem. Phys.* **28**, 572.
MALONE, J. F. & MCDONALD, W. S. (1967). *Chem. Comm.* p. 444.
NISHIKAWA, T. (1957). *J. Phys. Soc. Japan*, **12**, 668.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd. ed., p. 246. Ithaca: Cornell Univ. Press.
ROLLETT, J. S. (1965). *Computer Methods in Crystallography*, p. 22. New York: Pergamon Press.
SNOW, A. I. & RUNDLE, R. E. (1951). *Acta Cryst.* **4**, 348.
SPOFFORD, W. A. III (1968). *A Fortran Least-Square Plane Program for the IBM* 1620. Unpublished results.
SPOFFORD, W. A. III & AMMA, E. L. (1968). *Chem. Comm.* p. 405.
SPOFFORD, W. A. III & AMMA, E. L. (1969). 157th National Meeting of the American Chemical Society, paper INOR 133.
SPOFFORD, W. A. III, GENTILE, P. S., BOLDRINI, P., CARFAGNO, P. & AMMA, E. L. (1970). Chem. Comm. p. 40.
TAYLOR, I. F. & AMMA, E. L. (1970). To be published.
TRUTER, M. R. (1967). *Acta Cryst.* **22**, 556.
VIZZINI, E. A. & AMMA, E. L. (1966). *J. Amer. Chem. Soc.* **88**, 2872.
VIZZINI, E. A., TAYLOR, I. F. & AMMA, E. L. (1968). *Inorg. Chem.* **7**, 1351.
VRANKA, R. G. & AMMA, E. L. (1966). *J. Amer. Chem. Soc.* **88**, 4270.
VRANKA, R. G. & AMMA, E. L. (1967). *J. Amer. Chem. Soc.* **89**, 3121.
WEINIGER, M. S., O'CONNOR, J. E. & AMMA, E. L. (1969). *Inorg. Chem.* **8**, 424.
WEISS, E. (1964). *J. Organometal. Chem.* **2**, 314.
WEISS, E. (1965). *J. Organometal. Chem.* **4**, 101.
WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 182.

Acta Cryst. (1970). B**26**, 1483

Crystal and Molecular Structure of α-Chlorotropane Monohydrate

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The crystals of α-chlorotropane monohydrate, $C_8H_{14}ClN\,.\,H_2O$, are monoclinic: space group $P2_1/c$, $a=14{\cdot}285$ (1), $b=6{\cdot}416$ (2), $c=25{\cdot}238$ (2) Å, $\beta=126{\cdot}11$ (2)°, $Z=8$. The piperidine ring is in a very deformed chair form. The CH_3 group is in the equatorial position.

Introduction

The object of the investigation of α-chlorotropane (see Fig. 1) was to establish the attachment of the methyl group to the piperidine ring, the nitrogen atom of which forms no other bonds than two N–C bonds. In related structures the position of the methyl group is probably influenced by either the quaternization of the nitrogen atom or the forming of hydrogen bonds between adjacent molecules (Schenk, MacGillavry, Skolnik & Laan, 1967; Visser, Manassen & de Vries, 1954).

This primary object was not realized because during the investigation it became clear that water of crystallization is present in the ratio of 1:1. The water molecules form hydrogen bonds with the nitrogen atoms of the tropane molecules. Possibly as a result of this the methyl group is found in the equatorial position.

Experimental

α–Chlorotropane was prepared from pseudotropine, following Archer, Lewis & Zenitz (1958). The liquid compound freezes at approximately 10°C. An attempt to obtain single crystals by putting some liquid into a small glass capillary and cooling in a Weissenberg camera failed. However, in a tightly closed flask placed in a freezing box a number of long thin needles were found after a month. Weissenberg pictures showed the crystals to be monoclinic with the unique axis along the needle axis.

From calibrated Weissenberg diagrams taken at −140°C the cell constants were calculated to be $a=14{\cdot}285$ (1), $b=6{\cdot}416$ (2), $c=25{\cdot}238$ (2) Å, $\beta=126{\cdot}11$ (2)° (the standard deviations in parentheses are in units of the last digit). From the systematic absences $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$ it was concluded that the space group is $P2_1/c$. From a density determination by flotation it was concluded that there are 8 molecules in the unit cell (*i.e.* two molecules in the asymmetric unit). Since the crystals are deliquescent this determination was rather inaccurate. Reciprocal planes hkl with k from 0 to 5 were registered with

Cu $K\alpha$ radiation on Weissenberg photographs at −140°C. The intensities were estimated visually and reduced in the usual manner. No absorption correction was applied.

Structure determination and refinement

The two chlorine atoms were found from a Patterson synthesis and all other atoms except the two methyl carbon atoms were located from a Fourier synthesis phased on the chlorine contributions. The methyl groups appeared unambiguously in the next Fourier synthesis, together with two additional peaks, which filled up an empty column around the screw axis with a radius of 3 Å. It was concluded from their distances from the nitrogen atoms and their mutual separation distances that they might be oxygen atoms of water molecules. The next refinement confirmed this conclusion.

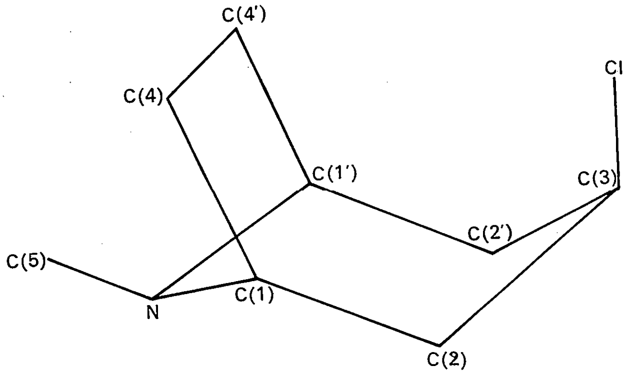

Fig. 1. Numbering of atoms in α-chlorotropane.

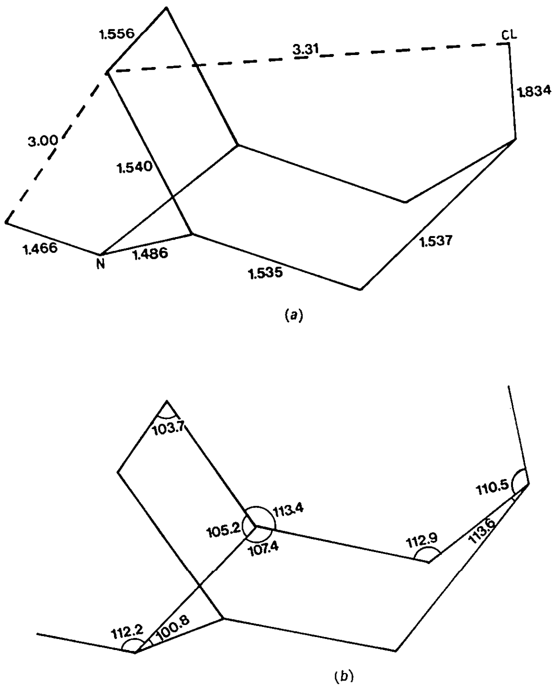

Fig. 2. Mean values of (*a*) corresponding bond lengths and some other interatomic distances, (*b*) valence angles.

In the block-diagonal least-squares refinement the weighting scheme of Cruickshank (1961) and the scat-

Table 1. *Final fractional coordinates* (× 10⁴) *and thermal parameters*

	a	*b*	*c*	*B*
Cl(*A*)	2629 (2)	5306 (4)	3365 (1)	*
Cl(*B*)	1234 (2)	2186 (4)	5095 (1)	*
N(*A*)	1601 (6)	9767 (12)	1878 (3)	2·44 (12) Å^2
C(3, *A*)	3103 (7)	7127 (16)	3003 (4)	2·84 (16)
C(2, *A*)	2601 (7)	6442 (16)	2295 (4)	2·65 (16)
C(1, *A*)	1429 (7)	7478 (15)	1783 (4)	2·33 (14)
C(4, *A*)	0501 (7)	6985 (15)	1890 (4)	2·68 (14)
C(4′, *A*)	0627 (8)	8742 (16)	2349 (4)	2·85 (17)
C(1′, *A*)	1625 (7)	0048 (15)	2467 (4)	2·35 (14)
C(2′, *A*)	2819 (8)	9355 (16)	3052 (4)	2·92 (17)
C(5, *A*)	0655 (8)	0927 (17)	1303 (5)	3·47 (19)
N(*B*)	3850 (6)	7843 (12)	5544 (3)	2·39 (12)
C(3, *B*)	2377 (7)	0455 (15)	5720 (4)	2·42 (15)
C(2, *B*)	3566 (8)	1150 (16)	5911 (4)	2·77 (16)
C(1, *B*)	3882 (7)	0114 (15)	5481 (4)	2·62 (15)
C(4, *B*)	3013 (8)	0595 (16)	4740 (4)	2·81 (16)
C(4′, *B*)	2105 (8)	8797 (15)	4488 (4)	2·63 (16)
C(1′, *B*)	2561 (7)	7453 (15)	5107 (4)	2·37 (14)
C(2′, *B*)	2078 (8)	8155 (16)	5483 (4)	2·86 (16)
C(5, *B*)	4430 (8)	6724 (17)	5310 (4)	3·17 (17)
O(1)	3643 (5)	1544 (11)	2103 (3)	3·15 (12)
O(2)	4825 (5)	8951 (11)	1808 (3)	3·40 (13)

* The anisotropic thermal parameters β_{11}, β_{22}, β_{33}, $2\beta_{12}$, $2\beta_{23}$, $2\beta_{13}$ are for Cl(*A*) +0·0069 (1), +0·0189 (8), +0·00137 (5), +0·0018 (7), +0·0016 (3) and +0·0031 (2) respectively and for Cl(*B*) +0·0059 (2), +0·0194 (8), +0·00210 (6), +0·0050 (6), +0·0016 (4) and +0·0040 (2) respectively.

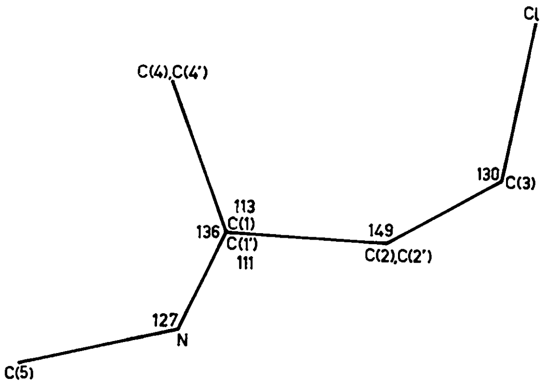

Fig. 3. The mean values of the corresponding angles between planes perpendicular to the molecular mirror plane.

tering factors from *International Tables for X-ray Crystallography* (1962) were used. Five cycles of isotropic refinement with individual scaling factors for each reciprocal layer with k = constant lowered the R index from 32 to 13%. At this stage the scaling factors were fixed and the chlorine atoms were refined anisotropically in the next two cycles. The hydrogen atoms, except those of the water molecules, were introduced, partly at the calculated positions, partly at positions found from a difference synthesis. The hydrogen parameters ($B = 3$ Å^2) were kept fixed in the final least-squares cycle. The final R value was 9·8% for 1665 independent reflexions.

The crystal structure

The final parameters of all atoms are given in Table 1. Bond lengths and valence angles are listed in Table 2. The mean values of corresponding bond lengths and valence angles are given in Fig. 2. Fig. 3 shows the mean values of the angles between planes perpendicular to the molecular mirror planes. In Fig. 4 Newman projections along some bonds have been drawn. A projection of the crystal structure along the [010] axis is given in Fig. 5.

A list of structure factors is available on request from our laboratory.

Discussion

Accuracy of the determination

An inspection of Table 2 leads to two conclusions.

(1) The two crystallographically inequivalent molecules are not significantly different.

(2) The molecular symmetry m [a mirror plane through the atoms C(5), N, C(3) and Cl] is not influenced by the packing.

These conclusions make it possible to check the e.s.d.'s calculated by the least-squares method. If it is assumed that corresponding bond lengths are independent measurements of the same quantity, the mean value and its experimental standard deviation can be calculated in the usual way. An experimental s.d. for each measurement of the bond length can be derived from this. The above quantities are included in Table 2. The same is done for the bond angles. A comparison of the calculated e.s.d.'s with the experimental s.d.'s of the individual measurements of Table 2 leads to a third conclusion:

(3) The e.s.d.'s are of the same magnitude as the experimental s.d.'s and thus are a good estimate of the accuracy of the determination. However, it should be

Table 2. *Bond lengths and valence angles*

E.s.d.'s are given in parentheses.

	Molecule *A*		Molecule *B*				
Bond lengths	Value	Value of the mirror image	Value	Value of the mirror image	Mean	Experimental s.d. of the mean	Experimental s.d. of an individual value
C(1)–C(2)	1·537 (11) Å	1·522 (10) Å	1·548 (18) Å	1·533 (18) Å	1·535 Å	0·005 Å	0·010 Å
C(2)–C(3)	1·548 (14)	1·510 (15)	1·534 (15)	1·555 (14)	1·537	0·009	0·018
C(1)–C(4)	1·535 (17)	1·524 (15)	1·550 (11)	1·553 (14)	1·540	0·007	0·014
C(1)–N	1·485 (12)	1·479 (15)	1·469 (12)	1·509 (10)	1·486	0·008	0·016
N—C(5)	1·475 (11)		1·458 (17)		1·466	0·006	0·010
C(3)–Cl	1·839 (13)		1·830 (8)		1·834	0·003	0·005
C(4)–C(4′)	1·547 (15)		1·564 (14)		1·556	0·006	0·010
Bond angles							
C(5)–N—C(1)	111·8 (6)°	113·1 (9)°	112·6 (9)°	111·2 (7)°	112·2°	0·4°	0·8°
C(1)–N—C(1′)	100·7 (8)		100·8 (6)		100·8	0·1	0·1
N—C(1)–C(4)	104·7 (9)	105·7 (7)	105·9 (7)	104·5 (8)	105·2	0·3	0·6
N—C(1)–C(2)	107·3 (6)	106·8 (9)	108·1 (9)	107·4 (7)	107·4	0·3	0·6
C(2)–C(1)–C(4)	112·9 (8)	114·4 (8)	113·8 (8)	112·6 (8)	113·4	0·4	0·8
C(1)–C(4)–C(4′)	104·4 (8)	103·3 (10)	103·0 (8)	104·2 (6)	103·7	0·3	0·6
C(1)–C(2)–C(3)	112·4 (9)	113·5 (7)	112·3 (7)	113·3 (10)	112·9	0·3	0·6
C(2)–C(3)–Cl	109·8 (7)	111·5 (9)	110·8 (7)	110·0 (5)	110·5	0·3	0·6
C(2)–C(3)–C(2′)	113·5 (8)		113·6 (9)		113·6	0·1	0·1

emphasized that this applies only to the accidental errors.

Molecular geometry

In α-chlorotropane the chair-type piperidine ring is deformed more than in pseudotropine (Schenk, MacGillavry, Skolnik & Laan, 1967). Though the bond angles of the ring do not differ very much from those in pseudotropine, the deformation is clearly shown in the Newman projections along the three bonds, in which the dihedral ring angles deviate 3, 3 and 8° respectively from the corresponding pseudotropine values [see Fig. 4(*a*), (*b*), (*c*)]. As a result of this the C(1)–C(2)–C(3)–C(2′)–C(1′) part of the molecule is more planar. This is also demonstrated by an increase of 7° in the dihedral angle C(1,1′)–C(2,2′)–C(3) (149° for α-chlorotropane (Fig. 3) and 142° for pseudotropine). The deformation is apparently due to the steric interaction of the axial chlorine atom and the bridge atoms C(4) and C(4′).

Crystal structure

In several cases some sort of pseudosymmetry is found between independent molecules in the asymmetric unit. In this case the 2_1 axis is a pseudo 4_1 axis.

In the immediate neighbourhood of $\frac{1}{4},y,\frac{1}{4}$ a helix of water molecules is generated by this pseudo axis. The O–H···O distance is 2·76 Å, indicating the formation of hydrogen bonds. The α-chlorotropane molecules are connected to this helix by N···H–O bonds of 2·86 Å and conform to the pseudosymmetry (see Fig. 5).

Nuclear magnetic resonance spectrum

The n.m.r. spectrum of α-chlorotropane shows a multiplet at $\delta=4\cdot04$ p.p.m. which is ascribed to the C(3) proton. From a first-order analysis two coupling constants are found, $J_1=5\cdot6$ c.p.s. and $J_2=1\cdot5$ c.p.s. From the Newman projection along C(2)–C(3) (see Fig. 4) it is found that the dihedral angles made by the two C(2) protons with the C(3) proton are 35 and 85° respectively. Using the Karplus equation $J=8\cdot5\cos^2\varphi-0\cdot28$ $(0\le\varphi\le90°)$ (Williams & Fleming, 1966) we

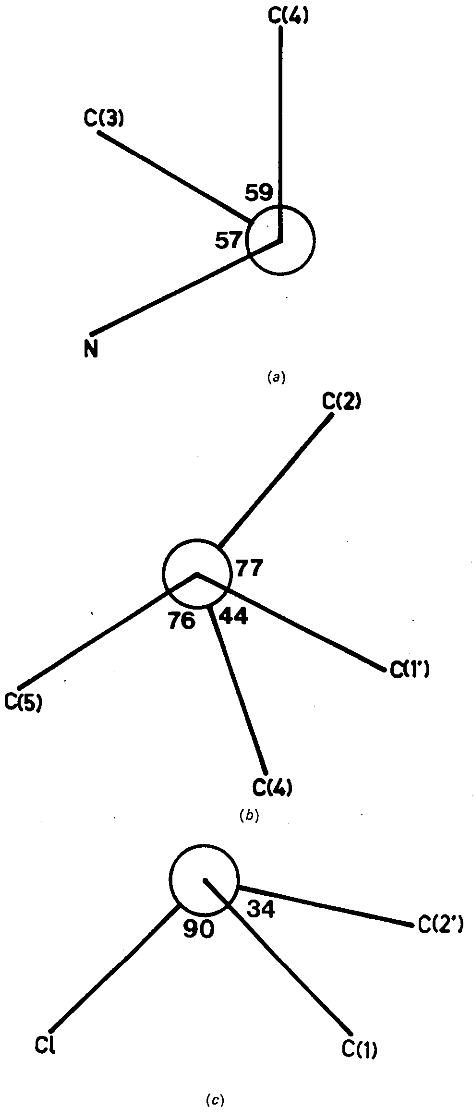

Fig. 4. Newman projections along some of the bonds. The dihedral angles are the mean values of all corresponding angles in the two independent molecules. (*a*) Along C(1)–C(2), (*b*) along N–C(1), (*c*) along C(2)–C(3).

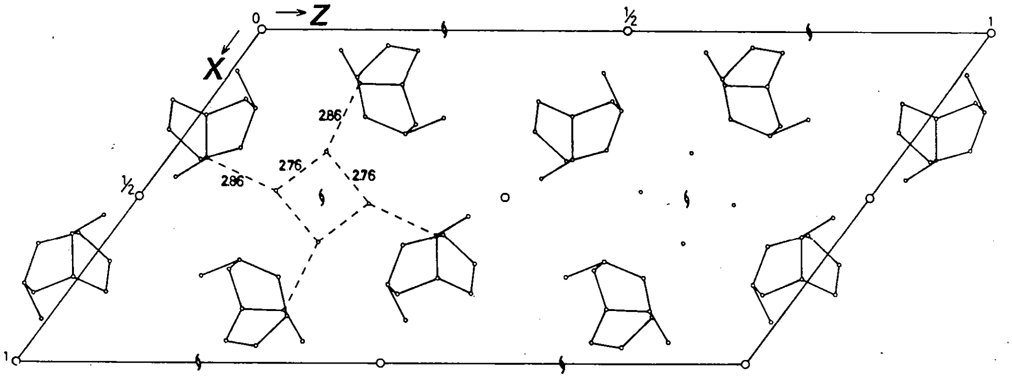

Fig. 5. Projection of the crystal structure along the *y* axis. The lengths of the hydrogen bonds are indicated.

calculate coupling constants of 5·5 and 0·2 c.p.s. The first is in very good agreement with J_1.

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References

Archer, S., Lewis, T. R. & Zenitz, B. (1958). *J. Amer. Chem. Soc.* **80**, 958.

Cruickshank, D. W. J. (1961). In *Computing Methods and the Phase problem in X-ray Crystal Analysis.* Oxford: Pergamon Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Schenk, H., MacGillavry, C. H., Skolnik, S. & Laan, J. (1967). *Acta Cryst.* **23**, 423.

Visser, J. W., Manassen, J. & de Vries, J. L. (1954). *Acta Cryst.* **7**, 288.

Williams, D. H. & Fleming, I. (1966). *Spectroscopic Methods in Organic Chemistry*, p. 104. New York: McGraw-Hill.

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Neutron Diffraction Study of NH_4Br and NH_4I

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NH_4Br, which has the caesium-chloride structure, and NH_4I, which has the sodium chloride structure, have been studied by neutron diffraction, mainly to determine the orientation and vibrational behaviour of the NH_4 groups. For NH_4Br, a model with eight $\frac{1}{2}$-hydrogen atoms in $\langle 111 \rangle$ directions, and isotropic, Gaussian libration of the hydrogen atoms, seemed to provide an adequate destription of the diffraction results with physically plausible parameters. For NH_4I, the hydrogen distribution has broad peaks in the six $\langle 100 \rangle$ directions and unusually large vibration amplitudes for the ions; the most profitable method of refinement was to describe the hydrogen distribution by Kubic Harmonics.

Introduction

NH_4Br has the caesium chloride structure in the temperature range −38 to 138°C. It is obvious that the NH_4 tetrahedra must be oriented with N–H bonds in $\langle 111 \rangle$ directions. Two orientations are possible and it has been established by Levy & Peterson (1953) that there is complete disorder between them.

Above 138°C NH_4Br transforms to the sodium chloride structure but crystals large enough for neutron difiraction break up in the transition. Therefore, to study ammonium halides in the sodium chloride phase, we used crystals of NH_4I, which has this structure above −17·6°C. In this structure there is no obvious way in which the tetrahedral NH_4 ion can fit in with the octahedral symmetry of the NH_4 site. Several possible models were discussed by Levy & Peterson (1953) but none of them was clearly established.

Collection and analysis of data on NH_4Br

A single crystal of NH_4Br was grown from an aqueous solution doped with urea. Its approximate dimensions were 7 × 4 × 2 mm. Data were collected on a four-circle computer-controlled neutron diffractometer at the Australian Atomic Energy Commission. The instrument has been described by Pryor, Ellis & Dullow (1969).

At room temperature 50 reflexions were measured with a wavelength of 1·05 Å, and 30 at a wavelength of 1·55 Å. The crystal was then mounted in a silica tube packed with alumina wool. A fine heater wire was spiralled inside the tube and supplied from a stabilized d.c. supply. At 120°C, 50 reflexions were measured at wavelength 1·05 Å and, at 136°C, 50 reflexions at 1·17 Å. In every case three symmetry-related equivalents of each reflexion were measured.

The observed intensities were corrected for absorption, using an absorption coefficient, μ, of 2·5 cm^{-1}, with the program *CDRABS* (written by G. W. Cox and M. M. Elcombe, of A.A.E.C.). This program also provides values of the mean path length $\bar{T} = \int T \exp(-\mu T) dv / \int \exp(-\mu T) dv$, where T is the path length in the crystal, which is required for extinction corrections. In these ammonium salts, as in all other hydrogen-containing materials, the true value of the absorption coefficient, μ, is not known. However in these refinements, described next, for extinction and structural parameters, no result was altered outside 1 estimated standard deviation by varying μ between 2·0 and 3·0 cm^{-1}.

The absorption-corrected data were subjected to a preliminary refinement based on the structural model described below. Comparison of the observed and calculated structure factors indicated that the data were