The conformation of the hydrogen atoms around the C(6)–C(8) bond is staggered.

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Refinement of the Structure of Ammonium Triiodide, NH_4I_3

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A new study closely confirms the structure and dimensions ascribed by R.C.L. Mooney in 1935, but indicates the triiodide ion to be linear.

The initial investigation by Mooney (1935) into the structure of ammonium triiodide, NH_4I_3, confirmed the assignment of this polyiodide to the orthorhombic system made by Groth (1908) on the basis of morphology. Mooney found that the unit cell contained four molecules and that the systematic absences were consistent with the space group *Pmcn*, limiting the atomic positions of the triiodide group to planes with x coordinates $x=\frac{1}{4}$ and $x=\frac{3}{4}$. The structural analysis was carried out through trial-and-error methods based on 144 qualitatively visually estimated intensities collected photographically by the oscillation method. She found the triiodide unit to be both non-linear (177°) and asymmetric with interiodine distances of 2·82 and 3·10 Å.

In view of the recent theoretical interest in crystalline polyiodides, in particular the work of Brown & Nunn (1966) on the configuration of the triiodide ion, it was considered worth while to attempt the refinement of this structure. In this connexion it was hoped that an examination of the thermal parameters of the triiodide iodine atoms would support their hypothesis that the asymmetric electrostatic environment of the anion stabilizes the asymmetric anion geometry.

This refinement confirms to a remarkable degree Mooney's structure for this compound.

Experimental

Crystals of ammonium triiodide suitable for X-ray analysis were prepared from a concentrated aqueous solution of A.R. grade ammonium iodide and resublimed iodine. The composition of this solution was adjusted with reference to Briggs's (Briggs, Ballard, Alrich & Wikswo, 1940) phase diagram for the system iodine–ammonium iodide–water to ensure that the only solid phase formed on evaporation was the anhydrous triiodide. The crystals so prepared were freed from mother liquor by rapid suction filtration on a sintered glass disk and then rapidly transferred to a dry Lindemann glass tube which was then sealed. As ammonium triiodide readily decomposes with loss of iodine, a number of crystals were packed into the one tube and some of these intentionally destroyed during the sealing process in order to create a significant iodine partial pressure within the tube from the outset. It was found that specimens prepared in this way could be preserved intact out of the X-ray beam for periods in excess of one month. However, as Mooney observed, as soon as a small crystal was brought into the X-ray beam, decomposition began with free iodine being deposited on the tube walls adjacent to the crystal.

The cell dimensions as determined from single-crystal photographs agreed with those found by Mooney and the same systematic absences were observed. In Table 1 the cell dimensions measured in this study and those of Mooney are compared; for convenience in the subsequent refinement calculations the axial labelling has been changed to conform to *International Tables for X-ray Crystallography* (1952) standard orientation for space group *Pnma*.

Table 1. *Comparison of cell dimensions*

	This work	Mooney
a	10·819 Å	10·82 Å
b	6·640	6·64
c	9·662	9·66

Six levels of data about the *b* axis and the first level about the *a* axis were collected photographically using Zr-filtered Mo *K* radiation and a Nonius Weissenberg goniometer. All photographs used for intensity measurement were taken using multiple-film packs of four Ilford Industrial Type G films interleaved with tin foil. Intensities were measured by visual estimation against a calibrated strip and were brought to a common scale using the *a* axis data. The Lorentz–polarization correction was applied but no absorption correction was made as the instability of the compound in the X-ray beam necessitated the use of three separate crystals to record the 516 independent reflexions used in this refinement. The crystals used all had maximum dimensions less than 0·02 mm.

The refinement of the structure was carried out using a structure factors/least squares program developed for the Elliott 503 computer. The program makes use of the block-diagonal approximation to the full least-squares matrix and employs the Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) weighting scheme. The scattering factor curves for iodine were taken from *International Tables for X-ray Crystallography* (1962), modified for the charge distribution of the triiodide unit and corrected for dispersion.

Refinement was commenced with the iodine atoms in the positions found by Mooney; at this stage the residual, $R=\sum(F_o|-|F_c|)/\sum|F_o|$, stood at 0·32. Five least-square cycles were performed using isotropic temperature factors and a partial shift factor of 0·8. At this stage further refinement was attempted using anisotropic temperature factors, but no progress could be made until the contribution to the structure factors of the ammonium group nitrogen atom was included. A trial nitrogen position was assumed from the isomorphous compound CsI_3, and after three further cycles with isotropic temperature factors, the refinement with anisotropic factors progressed smoothly using a smaller partial shift factor at 0·5 to a final residual of 0·183. No attempt was made to refine the structure further by the inclusion of the ammonium group hydrogen atoms. The positional and temperature factor parameters of the ammonium group nitrogen atom and the triiodide anion iodine atoms are given in Table 2.

The positional parameters of the nitrogen atom are not very accurate as indicated by the estimated standard deviations. This not unexpected result is also reflected in the anisotropic temperature factors; the nitrogen atom values have an e.s.d. of 0·0175 as compared with 0·0024 for the iodine atoms. The significant interatomic distances and angles are given in Table 3.

Table 3. *Interatomic distances and angles*

I(1)–I(2)	3·1134 ± 0·0037$_5$ Å
I(2)–I(3)	2·7912 ± 0·0039
I(1)–I(2)–I(3)	180·0 ± 0·0022°
I(1)–N	3·624 ± 0·0678, 3·679 ± 0·0678 Å
I(3)–N	3·776 ± 0·0680, 3·875 ± 0·0680

Discussion

As stated above, this refinement supports the analysis made by Mooney in that it confirms her conclusions regarding the asymmetry of the triiodide ion.

However, the refinement gives no evidence for a nonlinear triiodide ion as reported by Mooney for this compound, and which others (Tasman & Boswijk, 1954; Mooney-Slater, 1959) have reported in the structures of other triiodides [CsI_3 and $(C_6H_5)_4AsI_3$]. It was thought at first that this discrepancy between this refinement and the previous work on ammonium triiodide and its analogues indicating an interbond angle of ~176° in the triiodide ion might be explained by the hypothesis that ammonium triiodide undergoes a phase transition in the temperature range 0–30°C. However, a preliminary survey of several physical properties of this compound, including nuclear quadrupole and nuclear magnetic resonances, has not yielded any evidence for such a transition. The struc-

Table 2. *Atomic parameters*

(*a*) Positional parameters (Å)

	X	*Z*
N	9·0356 ± 0·0637	4·5453 ± 0·0654
I(1)	1·6970 ± 0·0030	3·3540 ± 0·0025
I(2)	4·1242 ± 0·0027	5·3039 ± 0·0025
I(3)	6·2580 ± 0·0030	7·1033 ± 0·0029

Thermal parameters (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N	0·0646	0·0614	0·0652	0·0	0·0	0·0
I(1)	0·0376	0·0306	0·0193	0·0	0·0	−0·0116
I(2)	0·0343	0·0317	0·0175	0·0	0·0	0·0
I(3)	0·0360	0·0392	0·0258	0·0	0·0	−0·0175

ture and crystallography of the tetraphenylarsonium triiodide (in which the bent triiodide ion is reported to have bonds of equal length) is sufficiently different from that of ammonium triiodide for environmental or packing effects to be responsible for differences in anion geometry. In the case of CsI_3 the structures are closely similar; a similar explanation can scarcely be envisaged. However, the most recent structural study (Tasman & Boswijk, 1954) was a refinement carried out by Fourier methods using 98 0*kl* reflexions and we may question the reliability of the I–I–I interbond angle. In commencing our refinement with Mooney's positional parameters, the residual of 0·32 indicated clearly that her structure does not completely fit our observational data.

In the light of the studies made by Brown & Nunn on the effect of the crystalline environment on the configuration of the triiodide ion, the lattice field over the anion in ammonium triiodide is expected to be unsymmetrical, thus stabilizing the configuration with unequal interiodine bonds. This hypothesis is supported by the similarity of the thermal parameters of each of the three iodine atoms which together make up the anion. The short I–N distance of 3·624 Å may be evidence for a form of hydrogen bonding between the ammonium group and the triiodide ion. This would raise the possibility of rotation or torsion of the cation about the N–H···I axis as is the case in NH_4I (Plumb & Hornig, 1953).

Copies of the observed and calculated structure factors listing are available from the authors upon request.

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The Crystal Structure of Trigonal Diboron Trioxide*

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Diboron trioxide, B_2O_3, crystallizes in space group $P3_1$ with cell dimensions $a=4{\cdot}336$, $c=8{\cdot}340$ Å. The cell contains three B_2O_3 units. The structures previously proposed by Berger and by Strong & Kaplow are incorrect. The structure was determined by the superposition frequency method, and refined by least-squares to $R=0{\cdot}059$ from diffractometer data. The structural unit is an infinite chain or ribbon of BO_3 triangles, very similar to the metaborate ribbon, $(BO_2)_{\infty}^{-\infty}$. These ribbons are interconnected, so that each oxygen atom has four oxygen neighbours at 2·30–2·43 Å distance. Both boron atoms are trigonally coordinated to oxygen with bond lengths 1·34–1·40 Å.

Introduction

Although diboron trioxide† (B_2O_3) plays a central role in modern glass technology and research, neither the structure of B_2O_3 I‡ nor the vitreous solid form have been satisfactorily determined. B_2O_3 will not crystallize from the melt under ambient pressure conditions. Solid diboron trioxide was known only in the vitreous state until Kracek, Morey & Merwin (1938) found B_2O_3 I to form as a fine powder during dehydration of metaboric acid under carefully controlled conditions. After failing to grow a useful single crystal by this process, Berger (1952, 1953) was forced to use data from powder photographs in an attempt to determine the structure. The basic units of Berger's structure were two different irregular tetrahedra of oxygen atoms each surrounding a boron atom. This structure has been considered unsatisfactory in several respects (*e.g.* Wells, 1962), particularly as it results in two

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† Terminology suggested by the Advisory Subcommittee on the Nomenclature of Boron Compounds, American Chemical Society [*Inorg. Chem.* (1968). 7, 1945].

‡ Terminology introduced by Prewitt & Shannon (1968) for the phase previously designated α-B_2O_3.