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The Crystal Structure of Trimethylammonium Iodide; Refinement of Absorption for a Laminar Crystal

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The crystal structure of Me_3NHI has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, $P2_1/m$, $a = 7·13$, $b = 8·33$, $c = 5·62$ Å, $\beta = 104°48'$, $Z = 2$. Intensities were estimated visually from equi-inclination Weissenberg photographs; the structure was refined by full-matrix least squares to a final conventional R index of $0·147$ for 431 non-zero unique reflexions. The compound is isostructural with Me_3NHBr but not with Me_3NHCl. The N–C bond lengths are $1·45 \pm 0·06$ and $1·46 \pm 0·04$ Å, and the C–N–C angles 113 ± 2 and $109 \pm 2°$. There is a short, probably linear, N–H$\cdots$I hydrogen bond, with an N$\cdots$I distance of $3·46 \pm 0·04$ Å. A useful procedure for refining the linear absorption coefficient for a laminar crystal is described.

Introduction

A complete set of X-ray data for a crystal of trimethylammonium iodide was obtained in the course of our investigation of trimethylamine adducts of silyl halides. We have completed the structure determination because there is some interest in the N–H$\cdots$I hydrogen bond length, and because it provided an opportunity

to test a method for refining the absorption correction for a laminar crystal. For a very thin crystal of this type the absorption depends critically upon the crystal thickness, which may prove difficult to measure with the required precision. It has been suggested by Werner (1964) that the value of the 'R factor' should provide a sensitive test of whether the absorption had been calculated correctly. The absorption correction for a thin plate crystal depends only on the value of $\mu_A t$ (where μ_A is the linear absorption coefficient and t the crystal thickness); we have found that a plot of the generalized R index against $\mu_A t$ gives a well defined minimum, enabling the value of $\mu_A t$ for use in the final calculations to be estimated. This method is successful because it is possible to calculate the absorption correction rapidly and accurately for a thin plate crystal; a convenient procedure is given in the Appendix.

A previous determination (Mussgnug, 1941) of the unit-cell dimensions and space group of trimethylammonium iodide suggested that it was isostructural with the corresponding bromide, but not with the chloride. The crystal structure of trimethylammonium chloride has recently been determined by Lindgren & Olovsson (1968), yielding an N–H···Cl distance of 3·00 Å.

Experimental

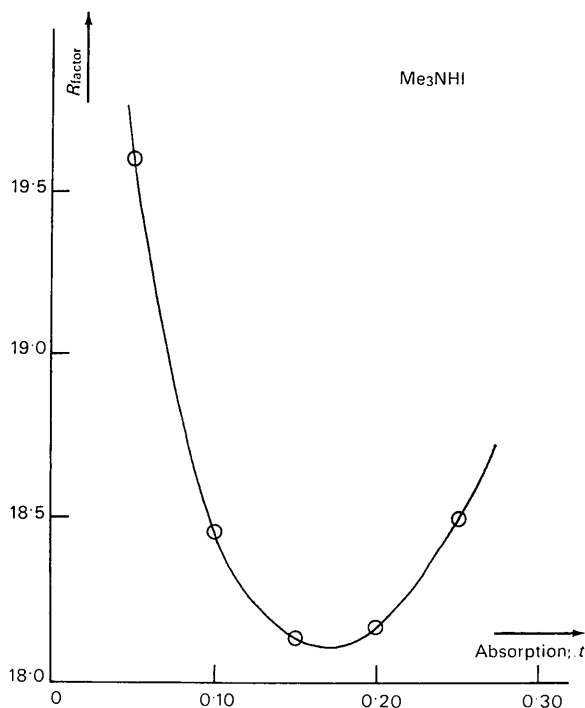Intensities were estimated visually in the usual manner from equi-inclination Weissenberg photographs (lay-

Fig. 1. Graph of generalized R index against absorption parameter.

ers $hk0$ to $hk3$ and $h0l$ to $h2l$) of a single thin laminar crystal (*ca.* 0·3 × 0·2 × <0·01 mm) taken with Ni-filtered Cu $K\alpha$ radiation. Higher layers were excluded on account of inferior spot-shapes. Lorentz and polarization corrections were applied, and absorption corrections calculated for several values of $\mu_A t$, assuming the crystal to be a thin plate perpendicular to (100) and totally immersed in the beam. The crystal structure was refined by full-matrix least squares (unit weights, ignoring extinction) for each value of $\mu_A t$, and the resulting generalized index $R_G = [\sum (F_{obs} - F_{calc})^2 / \sum F^2_{obs}]$ was plotted against $\mu_A t$ (Fig. 1), giving a smooth curve with a minimum at $\mu_A t = 0·17$. This value was then used in a final calculation of the absorption correction. Interlayer scale factors in each of the above calculations were determined by the linear least-squares method of Rae & Blake (1966). Accurate unit-cell dimensions were obtained from the $\alpha_1 - \alpha_2$ separations on the equiinclination photographs ($hk0$ to $hk3$, $h0l$ and $h1l$) by the method of Alcock & Sheldrick (1967), using $\lambda(\text{Cu } K\alpha_1) = 1·5405$ Å.

Crystal data

$(CH_3)_3NHI$, $M = 187$, monoclinic
$a = 7·133 \pm 0·004$, $b = 8·329 \pm 0·005$, $c = 5·619 \pm 0·014$ Å
$\beta = 104°48' \pm 4'$, $U = 322·9 \pm 0·8$ Å^3. $D_o = 1·924$,[2]
$D_c = 1·923$ for $Z = 2$, $\mu_A = 386·8$ cm^{-1}.

These values for the unit-cell dimensions are likely to be more precise than those quoted by Mussgnug, and give a much better agreement with his observed density. Systematic absences of reflexions occur only for $0k0$ with k odd; thus the space group is $P2_1$ or $P2_1/m$. The latter was suggested by Mussgnug's observation that the crystals did not exhibit a piezoelectric effect, and is confirmed by the successful refinement of the structure.

Structure determination and refinement

The iodine, nitrogen and one of the carbon atoms are situated in special positions $\pm(x, \frac{1}{4}, z)$ on the mirror planes, and the remaining carbon atoms in the general positions of the set $\pm(x, y, z; x, \frac{1}{2} - y, z)$. The iodine atoms were located by interpretation of the three-dimensional Patterson function, and the other atoms were found by difference Fourier synthesis. The structure was refined by full-matrix least squares using complex neutral-atom scattering factors given by Cromer (1965) and Cromer & Waber (1965) for all the atoms; the weighting scheme adopted on the basis of an analysis of variance was $w = 1/(6·178 + F_o + 0·0243 F_o^2)$ (this has been converted to an absolute scale of F_o so as to be consistent with the data in Table 1). In the final cycles a total of 17 independent parameters were refined, consisting of the overall scale factor, nine positional parameters, four anisotropic temperature factor components for iodine, an isotropic temperature fac-

tor for the nitrogen atom and an overall isotropic temperature factor for the carbon atoms, and the Zachariasen secondary extinction parameter (Larson, 1967) which refined to the value $9\cdot8 \pm 2\cdot8 \times 10^{-6}$ cm. The final value of $R=(\sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o|)$ was 0·150 for a total of 431 unique non-zero reflexions; the corresponding unweighted R index was 0·147. These values are a little higher than expected, possibly owing to poor spot-shape. A final three-dimensional difference Fourier synthesis revealed no unexpected features. Observed and calculated structure factors are shown in Table 1 and the results from the final least-squares cycle are given in Tables 2 and 3. These results together with the full covariance matrix and the estimated standard deviations in the unit-cell dimensions were used to calculate the bond lengths and angles and their standard errors. Fig. 2 shows the structure in projection down the z axis.

Trimethylammonium chloride and iodide both crystallize in the space group $P2_1/m$, and both possess $X\cdots Me_3N-H\cdots X\cdots Me_3N-H\cdots$ chains (X=Cl, I); however the chains pack together differently in the two structures, resulting in quite different unit-cell dimensions. In the iodide the N–C(1) and N–C(2) bond lengths are $1\cdot45 \pm 0\cdot06$ and $1\cdot46 \pm 0\cdot04$ Å respectively, and the C(1)–N–C(2) and C(2)–N–C(2) angles are 113 ± 2 and $109 \pm 2°$ respectively. These are in agreement with the corresponding results for the chloride (average N–C = 1·48 Å, average C–N–C = 111°) and other similar compounds. The centroid of the three carbon atoms (0·7226, 0·2500, 0·5209) lies within experimental error on the I–N vector; thus the N–H$\cdots$I hydrogen bond must be approximately linear. The N$\cdots$I distance of $3\cdot46 \pm 0\cdot04$ Å compares with a N$\cdots$Cl hydrogen bond length of 3·00 Å in the chloride. These values are both about 1·2 Å greater than the

Table 1. *Observed and calculated structure factors*

h	k	l	$|F_o|$	$|F_c|$

ionic radii given by Johnson (1968) for I^- (2·20) and Cl^- (1·82 Å). The other shortest non-bonded distances not involving hydrogen atoms are $I \cdots C(1) = 3\cdot96$ and $I \cdots C(2) = 4\cdot20$ Å, showing that the iodide ion is roughly equidistant from three methyl groups in an $I \cdots Me_3N-H \cdots I \cdots Me_3N-H \cdots$ chain.

The calculations were performed using the Cambridge University Titan computer and programs written
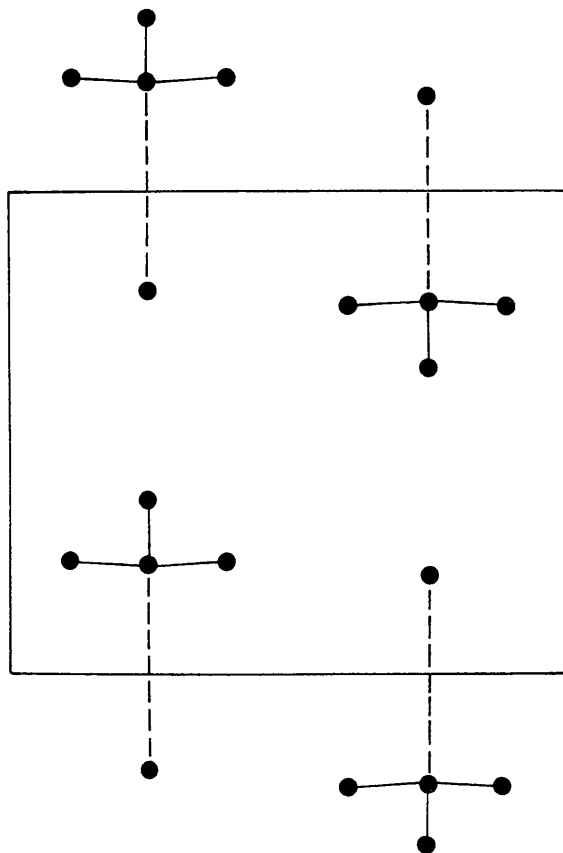

Fig. 2. The crystal structure as seen in projection along the z axis.

by one of us (G.M.S.). We are grateful to the S.R.C. for a maintenance grant to W.S.S.

APPENDIX

The calculation of the absorption correction for a thin laminar crystal and general Weissenberg geometry requires the value of $\mu_A t$, the oscillation zone axis $[uvw]$, and the orientation of the lamina with respect to the crystallographic axes. This orientation is conveniently and precisely specified by the Miller indices $(h'k'l')$ of the normal to the plane of the lamina. Consider the stereogram given in Fig. 3. $\mathbf{I}$ is the incident beam and $\mathbf{D}$ the reflected beam direction, $\mathbf{Q}$ is the oscillation zone axis making an acute angle with $\mathbf{I}$, and $\mathbf{N}$ is a face normal to the lamina. $\mathbf{M}$ is the normal to the reflecting planes (hkl); thus $\mathbf{D} \times \mathbf{M} = \mathbf{M} \times \mathbf{I} = \frac{1}{2}\pi - \theta$. If $\mathbf{D}, \mathbf{I}$ and $\mathbf{Q}$ form a set of opposite hand to that shown in Fig. 3, $\mathbf{M}$ should be given the indices $(-h, -k, -l)$; for a conventional camera geometry this occurs for reflexions appearing on the lower half of the film. The other angles are defined in the diagram; the signs of μ and ν are as given in International Tables for X-ray Crystallography (1959). We have found that the calculation procedure described below can easily be converted into an efficient subroutine for use in a data reduction program; it is much faster than methods involving numerical integration.

The angle δ will be positive (as drawn) if the angle between $\mathbf{Q}$ and the zone axis $\mathbf{M} \times \mathbf{N}$ $[u'v'w']$ is acute; otherwise it will be negative. If we denote the sign of δ by the index j,

$$j = \text{sign of } [a^2uu' + b^2vv' + c^2ww' + bc \cos \alpha(vw' + v'w) + ac \cos \beta((uw' + u'w) + ab \cos \gamma(uv' + u'v)]$$

where a etc. are the real unit-cell dimensions, and $u' = kl' - lk', v' = lh' - hl'$ and $w' = hk' - kh'$. The angles τ, σ and φ can be found as follows:

$$\cos \tau = (uh' + vk' + wl')/GF$$
$$\cos \sigma = \lambda(uh + vk + wl)/2G \sin \theta$$
$$\cos \varphi = \lambda[a^{*2}hh' + b^{*2}kk' + c^{*2}ll' + b^*c^* \cos \alpha^*(kl' + k'l) + a^*c^* \cos \beta^*(hl' + h'l) + a^*b^* \cos \gamma^*(hk' + h'k)]/2F \sin \theta ,$$

Table 2. Atom coordinates and isotropic vibrational amplitudes ($\text{Å}^2 \times 10^3$) with standard deviations

	x/a	y/b	z/c	$\bar{U}$
N	0·7772 (58)	0·2500	0·5716 (88)	42 (9)
C(1)	0·6393 (68)	0·2500	0·7217 (93)	42 (5)
C(2)	0·7642 (45)	0·1064 (37)	0·4205 (62)	42 (5)

Table 3. Atom coordinates and anisotropic vibrational amplitudes ($\text{Å}^2 \times 10^3$) with standard deviations

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
I	0·2029 (4)	0·2500	0·0351 (7)	21 (1)	59 (3)	59 (3)	0	−5 (1)	0

The anisotropic temperature factor takes the form:
$$\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)] .$$

where
$$G = (a^2u^2 + b^2v^2 + c^2w^2 + 2bcvw \cos \alpha$$
$$+ 2acuw \cos \beta + 2abuv \cos \gamma)^{1/2} \quad \text{and}$$
$$F = (a^{*2}h'^2 + b^{*2}k'^2 + c^{*2}l'^2 + 2b^*c^*k'l' \cos \alpha^*$$
$$+ 2a^*c^*h'l' \cos \beta^* + 2a^*b^*h'k' \cos \gamma^*)^{1/2};$$

λ is the X-ray wavelength, and a^* etc. the reciprocal cell-dimensions (in Å^{-1}).

From the spherical triangle QMN,

$$\cos |\delta| = (\cos \varphi - \cos \tau \cos \sigma)/\sin \tau \sin \sigma ,$$

and from the spherical triangles MQI and DQM respectively,

$$\cos \xi = (\sin \theta + \cos \sigma \sin \mu)/\cos \mu \sin \sigma$$
$$\cos \zeta = (\sin \theta - \sin \nu \cos \sigma)/\sin \sigma \cos \nu .$$

Thus from the spherical triangles NQI and DQN respectively,

$$\cos \kappa = \sin \tau \cos \mu \cos (\xi - j|\delta|) - \cos \tau \sin \mu$$
$$\cos \omega = \sin \tau \cos \nu \cos (\zeta + j|\delta|) + \cos \tau \sin \nu .$$

If χ is the acute angle of incidence (to the face normal), $\cos \chi = |\cos \kappa|$; the angle of reflexion ψ is defined by $\cos \psi = i \cos \omega$, where i is the sign of $\cos \kappa$. If $\cos \psi$ is positive, the incident and reflected beams are on the same side of the lamina. If the crystal is assumed to be completely bathed in the beam, the factor A by which the observed intensities must be divided to correct for absorption depends on the length of the path through the crystal; for negative $\cos \psi$ it is given by:

$$A = (1/t) \int_0^t \exp [-\mu_A(x \sec \chi + (x-t) \sec \psi)] \, dx$$

$$= \frac{\{1 - \exp [-\mu_A t(\sec \chi + \sec \psi)]\}}{(\sec \chi + \sec \psi) \exp (-\mu_A t \sec \psi)\mu_A t}$$

and if $\cos \psi$ is positive,

$$A = (1/t) \int_0^t \exp [-\mu_A x(\sec \chi + \sec \psi)] \, dx$$

$$= \frac{\{1 - \exp [-\mu_A t(\sec \chi + \sec \psi)]\}}{(\sec \chi + \sec \psi)\mu_A t} ,$$
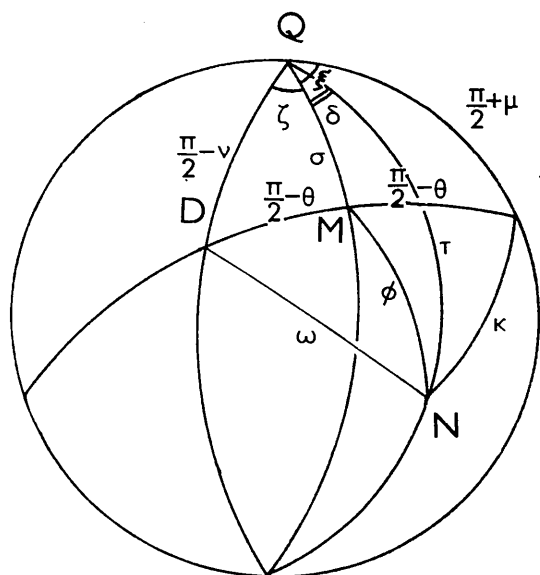

Fig. 3. Stereographic projection.

which is the expression used in this work. Reflexions for which the incident or reflected beams are nearly parallel to the plane of the lamina are likely to be relatively strongly influenced by edge effects, so we reject reflexions for which either $\cos \chi$ or $|\cos \psi|$ are less than 0·01.

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