380. *The Crystal and Molecular Structure of Tetraethylammonium Iodide.*

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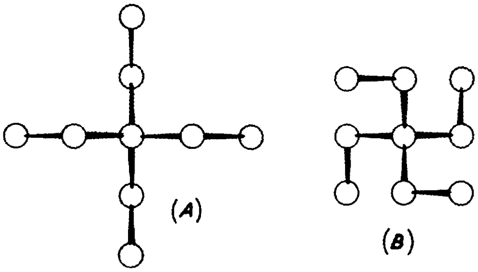
Tetraethylammonium iodide forms a very distorted wurtzite-type structure, each ion having four neighbours of the opposite charge at the corners of a very flattened tetrahedron. The conformation of a tetraethylammonium ion is that which in projection forms a Nordic cross (swastika). Partly owing to steric effects the bond angle N–C–C is about 12° greater than the regular tetrahedral value.

Only two shapes, *A* and *B* (Fig. 1), are likely for the tetraethylammonium ion. Even in these conformations the distances between the carbon atoms of a terminal methyl and an adjacent methylene group would be less than 3 Å if the N–C–Me bond angle had the regular tetrahedral value, and the bonds the single covalent bond lengths. The normal contact distance between two such groups in neighbouring molecules is 4 Å.

Fig. 1.



Form *A* was found in the molecular compound of tetraethylammonium bromide with succinimide (preceding paper), but detailed examination of the bond distortion was not possible. The crystal structure of tetraethylammonium iodide has therefore been determined with a view to further examination of the form of the complex ion.

Crystals of tetraethylammonium iodide were examined goniometrically by Slavik,[1] who assigned them to the tetragonal class $\bar{4}2m$ and determined the axial ratio $c : a$ as 0·5544. Wyckoff [2] made an *X*-ray diffraction study and concluded that the iodine atoms

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[1] Slavik, *Z. Kryst.*, 1902, **36**, 274.
[2] Wyckoff, *Z. Kryst.*, 1928, **67**, 550.

were in a body-centred array. On the morphological evidence he assumed the space-group to be one of those in the class $\bar{4}2m$. It is shown here that this assumption is incorrect and that the space-group is $I\bar{4}$. The assignment to a wrong crystal class was made because suitable faces did not develop. Unfortunately, it has led to this substance's being quoted as an example of the comparatively rare class $\bar{4}2m$.

Crystals suitable for X-ray work were obtained by recrystallisation of a commercial sample (B.D.H.) from hot water. Such a crystal had the form of a tetrahedron with smaller faces of a second tetrahedron truncating its corners (Slavik's Fig. 7). Filtered Cu-K_α radiation was used for the X-ray examination. Oscillation and zero- and first-layer equi-inclination Weissenberg photographs were taken for rotation about the c and a axes. They confirmed the tetragonal symmetry. The only systematically absent reflections were those with $h + k + l \neq 2n$. This corresponds to a body-centred lattice. Intensities of various classes of reflections showed the relationships $F_{hkl} = F_{hk\bar{l}}$; $F_{hkl} = F_{\bar{k}hl}$; $F_{hhl} = F_{h\bar{h}l}$; but $F_{hkl} \neq F_{h\bar{k}l}$. Since in all space-groups of the class $\bar{4}2m$, $F_{hkl} = F_{h\bar{k}l}$ it was concluded that the point symmetry was $\bar{4}$ and the space-group $I\bar{4}$. Cell dimensions from measurements of high-angle reflections on Weissenberg photographs calibrated with copper powder lines were $a = b = 8{\cdot}87 \pm 0{\cdot}02$ Å; $c = 6{\cdot}95 \pm 0{\cdot}02$ Å. They were in good agreement with the values given by Wyckoff. The density by flotation was $\rho = 1{\cdot}56 \pm 0{\cdot}01$ g./c.c. That calculated from cell dimensions on the assumption of two formula units NEt_4I in the unit cell is 1·57 g./c.c. The intensities of 57 of the 61 independent $hk0$ reflections within the Cu-K_α sphere of reflection were measured on the c axis zero-layer Weissenberg photographs by visual comparison with a scale of spots of known intensity ratios prepared from the same crystal. From these, structure factors F_{obs} were derived.

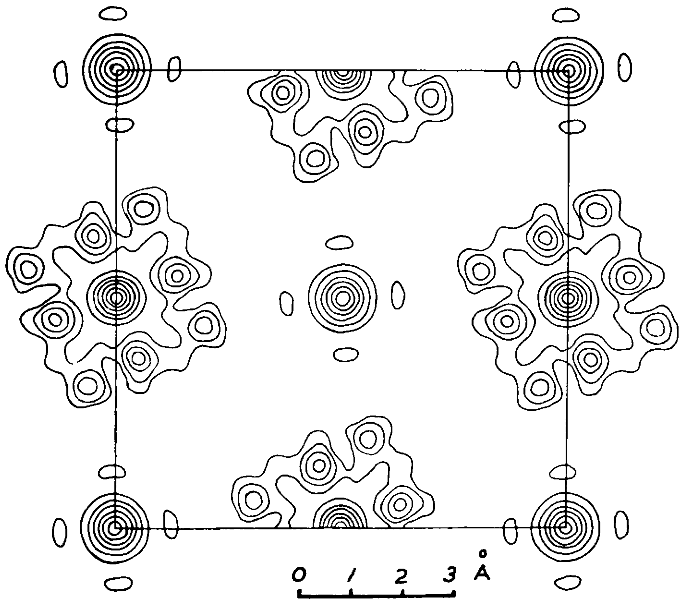
TABLE 1. *Observed and calculated structure factors.*

h	k	l	F_c	F_o
2	0	0	118	114
4	0	0	65	78
6	0	0	51	60
8	0	0	26	34
10	0	0	18	18
1	1	0	44	38
2	2	0	72	74
3	3	0	79	74
4	4	0	50	55
5	5	0	38	34
6	6	0	27	24
7	7	0	20	20
8	8	0	14	12
1	3	0	100	98
1	5	0	50	57
1	7	0	34	36
1	9	0	25	25
1	11	0	14	18
2	4	0	66	68
2	6	0	62	75
2	8	0	36	40
2	10	0	21	22
3	1	0	66	81
3	5	0	34	33
3	7	0	18	18
3	9	0	19	18
4	2	0	65	65
4	6	0	52	48
4	8	0	28	26
4	10	0	14	18
5	1	0	50	60
5	3	0	54	46
5	7	0	23	22
5	9	0	22	22
6	2	0	45	50
6	4	0	30	33
6	8	0	17	18
7	1	0	40	44
7	3	0	34	30
7	5	0	29	25
8	2	0	34	37
8	4	0	31	32
8	6	0	23	27
9	1	0	24	25
9	3	0	12	11
9	5	0	12	14
10	2	0	22	25
10	4	0	22	26
11	1	0	17	18

In the space-group $I\bar{4}$ there are four 2-fold special positions with co-ordinates (a) $\frac{1}{2}0\frac{1}{4}$, (b) $\frac{1}{2}0\frac{3}{4}$, (c) 000, (d) $00\frac{1}{2}$, and the corresponding body-centred co-ordinates. The point symmetry at each of these positions is $\bar{4}$. Since the c axis is comparatively short no structure can be formed in which one ion occupies (a) and the other (b). Similarly (c) and (*d*) cannot both be used. The formally different ways of selecting one of (*a*) or (*b*) and one of (*c*) or (*d*) lead to structures which are identical apart from trivial interchange of axes or origin. The iodide ions may therefore be taken to be at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and the nitrogen atoms at $0\frac{1}{2}\frac{1}{4}$ and $\frac{1}{2}0\frac{3}{4}$. The tetraethylammonium ion has a 4-fold axis of rotation inversion parallel to the *c* axis.

The projection of the structure on a plane perpendicular to *c* has a centre of symmetry, and the iodine atom at the origin makes its maximum possible positive contribution to each structure amplitude. This is almost equal to the total possible contribution from the remaining cell contents. It is therefore most probable that all F_{hk0} will have positive signs. The Fourier F synthesis calculated with all signs taken as positive is shown in Fig. 2. All atoms except hydrogen are resolved. F_{hk0} values were then calculated on the basis of the observed atomic co-ordinates. Scattering factors employed were those of McWeeney [3] for carbon and nitrogen and of Thomas and Fermi [4] for iodine. All calculated structure amplitudes were positive. This confirms the initial assumption on which the F synthesis was based. The absolute scale of observed structure factors and an average temperature factor were determined from a plot of log F_c'/F_c' against $\sin^2 \theta$, where F_c' is the structure factor calculated for atoms at rest and F_o' the observed structure factor on an arbitrary scale. From the slope of the graph the value of the temperature factor was found as $B = 3{\cdot}1$ Å^{-2}. F_o and F_c, the calculated structure amplitudes corrected for thermal vibration, are shown in Table 1. The discrepancy factor $R = \sum||F_o| - |F_c||/\sum|F_o|$ is 0·094. For comparison, the value of R_I, the discrepancy between the iodine contribution alone and F_o reduced to the same scale, was $R_I = 0{\cdot}196$. The systematic errors in the atomic co-ordinates caused by termination of Fourier series at the limit of the sphere of reflection were now determined by Booth's "backshift" method.[5] The corrected co-ordinates are listed in Table 2. For the present purpose a 3-dimensional analysis which

FIG. 2. *Electron density projected perpendicular to* [001]. *Contours at intervals of* 2 *electrons*/Å^2, *except for the iodine atoms at the origin and the centre where the interval is* 20 *electrons*/Å^2.



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[3] McWeeney, *Acta Cryst.*, 1951, **4**, 513.

[4] Internationale Tabellen zur Bestimmung von Krystallstrukturen, Band II, Borntraeger, Berlin, 1935.

[5] Booth, *Proc. Roy. Soc.*, 1946, *A*, **188**, 77.

would give the z co-ordinates was not considered necessary since the information required could be deduced from the projection in the following way. The tetraethylammonium ion is seen directly to have form B (Fig. 1). If the inner carbon atoms are assumed to be at the vertices of a regular tetrahedron with the nitrogen at the centroid, then the N–C bond length is 1·49 Å, consistent with independently determined covalent radii. There is a geometrical relationship between the X and Y co-ordinates of the atoms as listed in Table 2, the $C_{(1)}$–$C_{(2)}$ bond length, and the N–$C_{(1)}$–$C_{(2)}$ bond angle. The variation in the bond angle for any probable values of the $C_{(1)}$–$C_{(2)}$ bond length l was calculated. For $l = 1·52$ the angle is 121° 9′ and as l changes up to 1·57 the angle alters steadily to 121° 44′. It is concluded that the bond angle is approximately 12° greater than the regular tetrahedral angle. In contrast it has been reported that, in the crystal structure of tetra-*n*-propylammonium bromide,[6] the CH_2 groups of the complex ion adopt the conformation A (Fig. 1), the central N–C bond has length 1·55 ± 0·04 Å, and that an angle of 105° is found between two bonds of the nitrogen atom.

TABLE 2. *Atomic co-ordinates.* (*For carbon atoms, values before application of backshift correction are shown in parentheses.*)

	x	y	z
I	0	0	0
N	½	0	¼
$C_{(1)}$	0·367 (0·370)	0·048 (0·047)	—
$C_{(2)}$	0·442 (0·442)	0·190 (0·192)	—

The general packing of the structure is determined largely by the size and shape of the tetraethylammonium ion. Fig. 3 shows that these ions are in contact with each other as well as with their iodine neighbours. There are no iodine–iodine contacts. The *a* dimension is determined by the sum of the effective radii of the two ions, but contacts between tetraethylammonium ions alone are sufficient to fix *c*. As a result of this the arrangement is a very distorted form of the wurtzite (ZnS) type of structure, each ion being surrounded by four of the opposite kind located at the corners of a very flattened tetrahedron. Formally the wurtzite-type cubic unit cell is replaced by the tetragonal cell of height 6·95 Å and an *a* dimension of 12·5 Å at 45° to the *a* axis of the body-centred cell. The principal contact distances of Fig. 3 are consistent with known ionic and van der Waals radii for the relevant groups. The electrostatic attractions due to the iodide ions are applied to the positive ions in directions roughly perpendicular to the $\bar{4}$ axis in such a way that they might increase the deformation of the N–$C_{(1)}$–$C_{(2)}$ bond angle. Possibly this, as well as the repulsion between the over-crowded groups, may be a cause of the distortion.

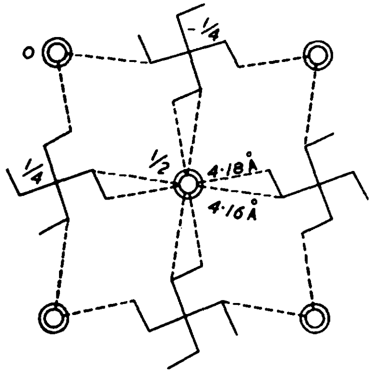

FIG. 3. *Projection of structure perpendicular to* [001].
Double circles = iodine. Co-ordinates along *c* axis show for I and N. Tetraethylammonium ions indicated in skeletal form. Broken lines show contacts between iodine and the complex ion. Each methyl group at the corner of a Nordic cross is also at the contact distance of 3·92 Å from two methyl groups belonging to the complex ion immediately above or below, and located at the two neighbouring corners of the cross.

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[6] Zalkin, *Acta Cryst.*, 1957, **10**, 557.