[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Structure of Tetramethylammonium Pentaiodide[1,1a]

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Tetramethylammonium pentaiodide is end-centered monoclinic with a_0 = 13.34, b_0 = 13.59, c_0 = 8.90 Å., β = 107° 50′, $\rho_{\text{calcd.}}$ = 3.06, Z = 4. The structure, based on space group, C2/c, consists of nearly square iodine nets within which V-shaped I_5^- ions can be distinguished. Iodine–iodine distances within the ion are 2.93 Å. and 3.14 Å., *versus* 2.67 Å. for the distance in I_2. Other iodine–iodine distances within one net are 3.55 A. or greater, while the nets are 4.3 Å. apart. The structure of the I_5^- ion bears no relation to the square ICl_4^- ion, where the I–Cl distance is close to the sum of the covalent radii. It is suggested that iodide does not tend to use its *d*-orbitals above the valence shell for covalent bonds with iodine, and the complex ions result from the interaction of an iodide ion with polarizable iodine molecules. Resonating structures result in enough covalent character of the iodide–iodine bond to weaken the iodine–iodine bond. The relation between polyhalide ions and "polyiodine" polymer complexes is discussed briefly.

Introduction

Polyhalide ions, IX_{2n}^-, are well known and several have received structural study by Wyckoff[2] and especially by Mooney.[3] Of those so far studied, iodine is the central atom of the ion. It is generally assumed that the bonding is mainly covalent with the central iodine atom making use of *d*-orbitals above the valence shell for the formation of bonds,[3,4] and this assumption is generally supported by the structures reported. Thus ICl_2^- and $IClBr^-$ are linear ions, and ICl_4^- is a planar, square ion, with I–X bonds very nearly equal to the sums of the covalent radii (Table I).

TABLE I

Ion	Bond	Length	R in Å.[5]
ICl_2^-	I–Cl	2.34[3d]	2.32
IClBr	I–Cl	2.38[3b]	2.32
	I–Br	2.50[3b]	2.47
ICl_4^-	I–Cl	2.34[3c]	2.32
I_3^-	I–I	2.82, 3.10[3a]	2.67

The triiodide ion seems anomalous. The reported distances are much greater than the sum of the covalent radii, and the ion is asymmetric. Unfortunately, highly accurate iodine positions could not be obtained and it has often been assumed that the ion is symmetric.[4] Polyiodides up to I_9^- occur,[6] while the higher polyhalides have not been made with the lighter halogens. This is in contrast with the case of molecules, IX_{2n+1}, where the higher members occur only if X is fluorine. Moreover, the polyiodides are more stable the larger the accompanying cation, and the higher members can be prepared only if the cation is as large or larger than tetramethylammonium ion.[6]

These data do not support the general assumption that the polyiodide compounds are similar to the other polyhalides. The study of the structure of tetramethylammonium pentaiodide was, therefore, undertaken to help determine the nature of the bonding in polyiodides.

Structure Determination

Preparation of the Compound.—Crystals of $N(CH_3)_4I_5$ were prepared by slowly cooling from the boiling point a saturated alcohol solution of $N(CH_3)_4I$ to which a two- or threefold excess of I_2 had been added. If a larger excess of I_2 was used $N(CH_3)_4I_9$ precipitated, while a smaller excess yielded some $N(CH_3)_4I_3$. Both seem to occur as separate phases, identifiable by optical means. Glacial acetic acid was used to recrystallize the $N(CH_3)_4I_5$.

Physical Data.—Crystals of $N(CH_3)_4I_5$ are deeply colored, red, monoclinic needles, with lattice constants in true ångströms, a_0 = 13.34, b_0 = 13.59, c_0 = 8.90, β = 107°50′. By flotation in methyl iodide–methylene iodide mixtures the density has been found to lie between 2.98 and 3.04 g./cc. The calculated density for $4N(CH_3)_4I_5$ per unit cell is 3.06.

Geuther has examined the crystals optically and reported them to be monoclinic with β = 72° 20′ (or 107° 40′)[6] in good agreement with our value. His optically determined axial ratios were 0.9866:1:0.6553, *versus* 0.982:1:0.655 which we find by X-ray diffraction.

X-Ray diagrams have been made with CuKα radiation and a Weissenberg camera, also MoKα radiation, and a Buerger precession camera. For all observed reflections $(h + k) = 2n$, and for all $(h0l)$ reflections, $h = 2n$ and $l = 2n$. The space group is, therefore, either Cc or C 2/c.

Parameter Determination.—Reflections $(h0l)$, $(hk0)$, $(0kl)$ and (hhl) were obtained by either Weissenberg or precession cameras, and sometimes both. Intensities of the reflections of the Weissenberg diagrams were estimated by the multiple film technique, while a similar method using timed exposures was employed for estimation of reflections on precession diagrams. In the latter case a General Electric XRD-3 diffraction unit, with regulated current and voltage, was employed. Over three hundred independent reflections were observed.

Intensities were corrected for Lorentz and polarization factors, and the resulting values were used to obtain the Patterson function projected onto (010), (001), (100) and $(1\bar{1}0)$. In all cases, coincidences on the Patterson projections made interpretation difficult, but all the Patterson projections may be interpreted in terms of one fourfold set, 4e, and two general, eightfold sets of the space group C 2/c.

These positions are

$$4I_a \text{ in } 4(e)\ (000,\tfrac{1}{2}\tfrac{1}{2}0) \pm (0y\tfrac{1}{4}).$$

$$8I_b \text{ and } 8I_c \text{ in } 8(f)\ (000,\tfrac{1}{2}\tfrac{1}{2}0) \pm (xyz) \pm (x\bar{y}\tfrac{1}{2} + z).$$

Parameters obtained from the Patterson are listed under column *P* of Table I. No hint of nitrogen or carbon positions was obtained on these or subsequent projections.

Using the Patterson parameters structure factors

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(1) (a) Contribution No. 123 of the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. Work performed in the Ames Laboratory of the Atomic Energy Commission. (b) For detailed material supplementary to this article order Document 3262 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) R. Wyckoff, THIS JOURNAL, **42**, 1100 (1920).

(3) R. C. L. Mooney, (a) *Z. Krist.*, **90**, 143 (1935); (b) *ibid.*, **98**, 324 (1937); (c) *ibid.*, **98**, 377 (1938); (d) *ibid.*, **100**, 519 (1939).

(4) L. C. Pauling, "The Nature of the Chemical Bond," Second Ed., Cornell Univ. Press., Ithaca, N. Y., 1945, p. 111.

(5) Covalent radii as given by Pauling, *ibid.*, p. 179.

(6) A. Geuther, *Ann. Chem.*, **240**, 66 (1887).

were calculated and Fourier projections upon (010), (001) and (100) planes were made using approximately 30 terms with unambiguous signs in each projection. The centers of the peaks were located by drawing contour lines, yielding the parameters of column 1, Table II. With these parameters structure factors were calculated for all observed reflections and Fourier projections were again made. This time all observed terms were used with the sign determined by the calculated structure factors. Synthetic Fouriers were also made with the calculated structure factors. The centers of the peaks were located on both calculated and observed Fouriers by fitting a Gaussian curve to the nine electron density values around the peaks.[7] The difference between parameters found on the synthetic Fouriers and those used to obtain calculated F values were used to correct the observed Fourier parameters, yielding the set shown in column 2, Table II. Structure factors were again calculated using these parameters and the previous Fouriers were checked for terms with incorrect signs. An additional set of Fourier projections was made using only the terms whose signs were changed. Twice the electron density values of these projections were added to the previous Fouriers, and the centers of the peaks were again located.[7] The resulting final set of parameters, column 3, Table II, again includes the parameter shifts indicated by the synthetic Fouriers.

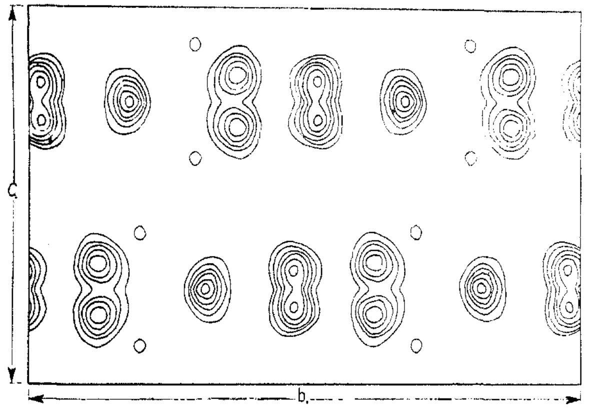

Fig. 1.—Fourier projection along the a_0-axis onto the plane (100).

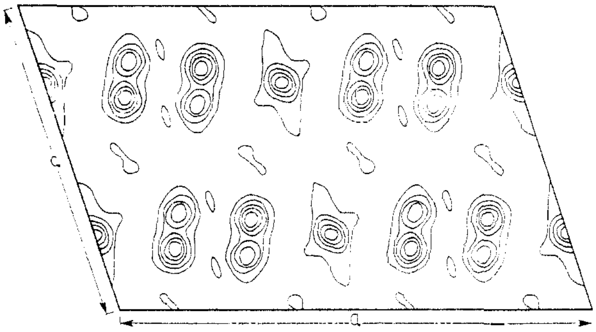

Fig. 2.—Fourier projection onto the plane (010).

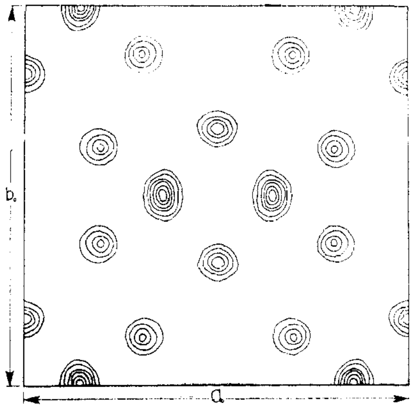

Fig. 3.—Fourier projection along the c_0-axis onto the plane (001).

TABLE II

REFINEMENTS OF IODINE PARAMETERS

	P	1	2	3
y_a	0.183	0.175	0.178	0.178
x_b	.155	.162	.158	.159
y_b	.020	.020	.021	.021
z_b	.205	.203	.198	.199
x_c	.192	.190	.188	.189
y_c	.357	.370	.372	.370
z_c	.320	.320	.322	.322

Column *P*, parameters from Patterson. Columns 1, 2 and 3, parameters from first, second and third Fourier refinements.

Final Fouriers are shown in Figs. 1, 2 and 3. Observed and calculated structure factors have been compared for all observed reflections.[8] The calculated values have been multiplied by a temperature factor, exp $-3.16(\sin\theta/\lambda)^2$. The factor $R = \frac{\Sigma||F_{obsd.}| - |F_{calcd.}||}{\Sigma|F_{obsd.}|}$ has the value 0.18, 0.24, 0.21 and 0.20, for the observed (*0kl*), (*h0l*), (*hk0*) and (*hhl*) reflections, respectively.

Accuracy of the Structure.—The value of R, above, though indicating that this structure is comparable in accuracy with other structures derived from two-dimensional Fourier methods, does not lend itself to quantitative estimation of the accuracy with which parameters have been determined. Booth has shown that ${}_nR_2 = \frac{\Sigma(|F_{obsd.}|-|F_{calcd.}|)^2}{\Sigma F_{obsd.}^2}$, where n is the number of dimensions included in the summation, can be interpreted in terms of a r.m.s. error.[9] For our structure, ${}_2R_2 = 0.036\text{–}0.040$ for the various two dimensional data when the unobserved (zero) reflections are included. If Booth's assumptions are sufficiently well satisfied by this structure (atoms of equal weight, in general positions, etc.) then our r.m.s. error is about 0.03–0.04 Å.

Perhaps a more reliable guide to the errors is that developed by Cruickshank.[10] The standard errors, σ, by this method are $\sigma(y_b) = 0.05$, $\sigma(y_a) = 0.04$, $\sigma(y_c) = 0.04$. On this basis errors in bond distances reported from one Fourier should have standard errors of about $\sqrt{2} \times 0.04 = 0.06$ Å. It

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[7] G. B. Carpenter and J. Donohue, THIS JOURNAL, 72, 2315 (1950).

[8] Tables of observed and calculated intensities are available through the American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C.

[9] A. D. Booth, "Fourier Technique in X-Ray Organic Structure Analysis," Univ. Press, Cambridge (1948), p. 102.

[10] D. W. J. Cruickshank, *Acta Cryst.*, 2, 651 (1949).

is to be noted that our parameters were usually derivable independently from two or more projections, so the above estimate of the standard error should not be too small.

Finally, since we were interested in discovering whether two I–I distances found to be 2.93 and 3.14 Å., respectively, were significantly different, we varied the parameters of the central atom to make these two distances equal, and recalculated R for ($hk0$) data. The value of R increased from 0.21 to 0.28 upon this variation in parameter. This is a very large increase in R indicating that variations of this magnitude materially lowered the agreement between observed and calculated structure factors.

From all of these estimates of errors, we conclude that in the distances reported below, I–I distances of 2.93 Å. are really significantly lower than those reported as 3.14 Å.

Discussion

The structure, Fig. 4, consists of nearly square nets of iodines, planar within ±0.64 Å., separated by about 4.3 Å., and parallel to (001). The nets are so arranged as to leave large holes for the tetramethylammonium ions. The shape and position of the holes define closely the location of carbon and nitrogen, Fig. 4. Most room is achieved if nitrogen is in 4(e) with y = 0.645, and if C–N–C planes are tilted 45° with respect to the iodine net (or (001)). Carbons occupy two general sets of positions, and, assuming C–N = 1.5 Å., carbon parameters for the above arrangement are $x_1 = -0.044$, $y_1 = 0.581$, $z_1 = 0.352$, $x_2 = 0.086$, $y_2 = 0.709$, $z_2 = 0.352$. All C–I distances are 4.2 Å. or greater, slightly larger than required by van der Waals radii, and consequently rotation of the cation about the twofold axis and displacement along it by several tenths of an Å. still lead to satisfactory positions, though the cation hole is too small for free rotation. It is satisfying to note that deviations of the iodine nets from planarity are just such as to allow more room for methyl groups in the postulated arrangement.

Iodine–iodine distances within one net vary enough to justify singling out V-shaped I_5^- ions with I–I distances of 2.93 and 3.14 Å., larger than the I–I distance in I_2, 2.67 Å., but considerably smaller than the next I–I distance (3.55 Å.) within the net. Clearly the I_5^- ion bears no relation to the square ICl_4^- ion found by Mooney.

The V-shaped I_5^- ion is planar within 0.12 Å. The angle I_b–I_a–I_b' is 94° 0′, and the arms are linear within 4°. It may be described roughly as an iodide to which two I_2 molecules are attached. In this interpretation the I_2 distance is 2.93 Å. and the I^-–I distance is 3.14 Å. It is noteworthy that Mooney's I_3^- ion may be similarly interpreted with I–I = 2.82 Å., I^-–I = 3.10 Å.

Though more accurate distances would be desirable, there is no doubt that in I_3^- and I_5^- all distances are appreciably greater than the I_2 distance, and in the I_5^- ion it is reasonably certain that two different distances are involved. In both cases a suggestion of an I_2 molecule remains. Consequently, we suggest that these polyiodide ions result from the interaction of an iodide ion with highly polarizable I_2 molecules. The interaction seems to be strong enough to lead to a small contribution of covalent bonding between I^- and the nearest iodines of the I_2 molecule. Contributing forms would be, for I_5^-; and for I_3^-:

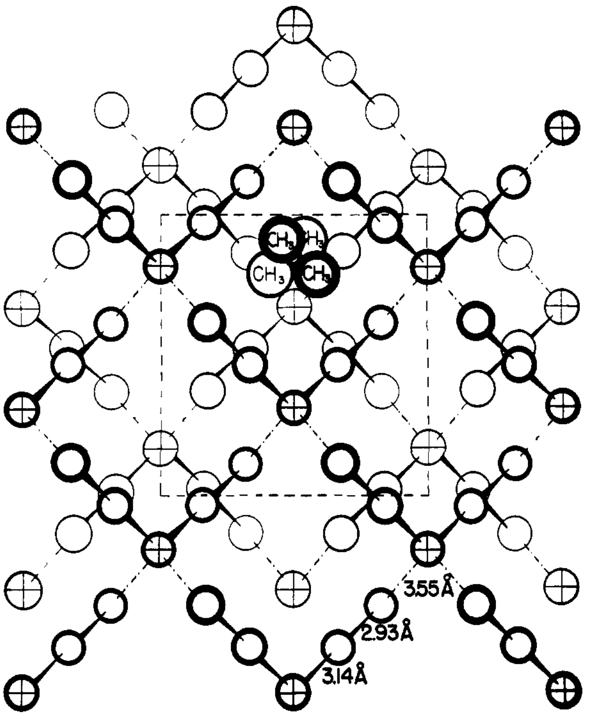
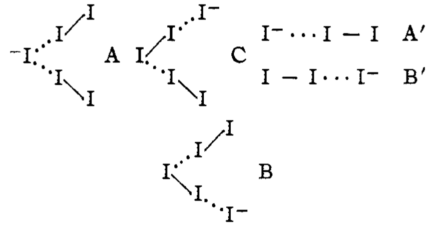


Fig. 4.—Structure of tetramethylammonium pentaiodide. As far as the iodine positions are concerned, this is a resolution into two nets of the oblique projection in Fig. 3. Nets are stacked so as to leave large holes for the cation. Only one is shown, upper center, though every hole is filled. As viewed here, looking down the c_0-axis, the net above those shown would coincide with the bottom net. The dashed line outlines the unit cell.



These forms do not require that iodine violate the octet rule, or use d-orbitals above the valence shell for bond orbitals. Contribution of the forms B and C in I_5^- and B′ in I_3^- will lengthen the I_2 bond while decreasing the I^-–I distances.

A simple molecular orbital argument can be given to show that this type of resonance is sensible without the use of d-orbitals above the valence shell. In the case of I_3^- we must deal with four electrons and three iodine orbitals (which we can regard as p-orbitals). Each iodine will possess, in addition, six electrons in the remaining three s and p orbitals. For a linear case, with equal Coulomb integrals for all atoms, the secular equation for the energy from linear combinations of the three atomic orbitals is

$$\begin{vmatrix} q-W & \beta & 0 \\ \beta & q-W & \beta \\ 0 & \beta & q-W \end{vmatrix} = 0$$

The three roots are $W = q$, $W = q \pm \sqrt{2}\beta$. Four electrons will be put in the two lowest M.O.'s, with total energy, $W = 4q + 2\sqrt{2}\beta$, *versus* an energy of $4q + 2\beta$ for the isolated structure, $\mathrm{I^- \cdots I{-}I}$ and a resonance energy of 0.828 β for resonance of A′ and B′, if β is equal in the two cases. Since distances change materially this is not so, and the true stabilization is doubtless less than given by this crude calculation.

In the case of isolated I_3^- ions, contributing forms A′ and B′ would be identical, and a symmetric ion would result unless the asymmetric structure were more stable than the symmetric by more than the resonance energy of the symmetric structure. Since in I_3^- and I_5^-, the asymmetric structure is severely distorted toward the symmetric, resonance of the type described appears to be important. The I_3^- ion of Mooney is asymmetric undoubtedly because in the crystal the ammonium ion lies nearer one end of the I_3^- ion than the other, increasing the contribution of the resonance form with the negative charge near the cation. This interpretation suggests that small cations would approach the iodide ion so closely as to make the I_2–I^- interactions more nearly dipolar than ionic and at the same time lower the resonance energy, while larger positive ions would tend to allow large ionic interactions and more resonance stabilization. It would seem likely that I–I distances would vary somewhat with the size of the positive ion, and with a sufficiently large positive ion it is possible that the I_3^- ion would become symmetrical. Study of triiodides with cations larger than ammonium would obviously be valuable.

The interpretation offered here suggests each arm of the I_5^- ion should be like the essentially linear I_3^- ion. Consequently the I_5^- ion should be planar. If, as we suggest, resonating forms of each arm of I_5^- use a *p*-orbital of I^-, then the expected bond angle between the arms is 90°, in good agreement with the experimental value.

It is surprising to find such long I_2 distances in I_3^- and I_5^- ions. Applying Pauling's rule,[11] the calculated sum of the bond numbers for the bonds in I_3^- is 0.80, while in I_5^- it is 1.05. These sums should not be less than one for I_3^- and two for I_5^- if Pauling's rule is applicable. It appears that in this case distances increase more rapidly with decrease in bond number than predicted by Pauling's rule. This may be due in part to the negative charge carried by the ion, but it seems doubtful if this is the whole explanation.

The proposed binding in the polyiodides resembles the proposal made for the polyiodine chains in iodine-polymer complexes,[12] where iodine molecules are polarized by the dipoles of the polymer chains, and in the subsequent interaction of the linear array of I_2 molecules, resonance of the bond to positions between the I_2 molecules makes some contribution. It is noteworthy that the average I–I distance is 3.1 Å. in these complexes,[13] just equal to the longer I–I distances found for I_3^- and I_5^-. Whether "polyiodine" consists of chains with longer and shorter I–I distances, due to unequal contributions of forms

$$\mathrm{I - I \cdots I - I \cdots I - I}$$
$$\mathrm{- I \cdots I - I \cdots I - I \cdots I -}$$

as suggested by one of us[14] or whether all distances have become equal to 3.1 Å., as favored by West,[12] has not been settled experimentally. However, the objection to a "polyiodine" chain with all distances equal to 3.1 Å. was based on Pauling's rule, and is now almost eliminated. Since the longer, 3.1 Å., bonds in I_3^- and I_5^- should have bond numbers less than one-half, it seems likely that in an equally spaced polyiodine, I–I distances should be less than 3.1 Å., but perhaps as great as 3.0 Å. In an alternating chain, distances may differ by as little as 0.2 Å.

It is to be noted that our proposal for the nature of the bonding in I_3^- and I_5^- applies only to polyiodides. The usual explanation involving the use of iodine *d*-orbitals above the valence shell in ICl_2^- and ICl_4^- is undoubtedly correct, and the difference in behavior of iodide with iodine and with the lighter halogens is probably to be ascribed to the reluctance of iodine to use these less stable orbitals for bonding except with the more active halogens.

It is quite interesting to note that the short van der Waals distances within one net of this structure (3.55 Å.) are almost precisely equal to the short van der Waals distances in I_2 (3.54 Å.),[15] which occur within the planes containing the I_2 molecules. In both cases van der Waals distances between planes are over 4 Å. It seems possible that the very high polarizability of I_2 and I_5^- along the bonds relative to normal to them, leads to a tendency for iodine and polyiodides to form planes within which van der Waals distances are especially short.

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[11] L. Pauling, THIS JOURNAL, **69**, 542 (1947).

[12] R. S. Stein and R. E. Rundle, *J. Chem. Phys.*, **16**, 195 (1948).

[13] C. D. West, *ibid.*, **15**, 689 (1947).

[14] R. Rundle, *ibid.*, **15**, 880 (1947).

[15] M. Straumanis and J. Sauka, *Z. physik. Chem.*, **53B**, 320 (1943).