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STRUCTURE AND CHEMISTRY OF
POLYIODIDE COMPOUNDS

by

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Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

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I. INTRODUCTION

The chemical industries have been making remarkable technological advancements at an ever increasing rate. These advancements have provided people with a steadily lengthening life expectancy and have supplied them with a tremendous number of products which make their living easier and more enjoyable. It has been largely through an understanding of the nature of matter by research personnel that these many technological advancements of industry have been possible.

In order to insure the continuance of advancements a more and more accurate understanding of matter is essential. In man's comprehension of the nature of matter certainly of prime importance is his understanding of the bonding in chemical compounds. The work contained here is an attempt to further this understanding, in particular the understanding of the bonding in the polyiodide compounds. Some concepts of the nature of these bonds can be obtained from an X-ray crystal structure study, which is the nature of the work contained here. It is hoped that information obtained will be of some help in man's attempt to acquire an integrated conception of the nature of matter.

II. POLYHALOGEN COMPOUNDS

A. Interhalogen Compounds

At least eleven interhalogen compounds are known. They may all be represented by AB_n with $n = 1, 3, 5$ or 7. In all cases A is the heavier of the two halogens. In the only compounds known with n larger than three, B is fluorine; also, when n is one or three, the more stable compounds are those with A and B nearly the same weight. This may be partly due to steric effects; however, the nature of the A-B bond must have an important bearing.

About half of these compounds are gases at room temperature while the remaining compounds have relatively low boiling points. Several of these compounds have been studied by electron diffraction. From the interatomic distances they appear to have the lighter halogen covalently bonded to the heavier central atom. The results of the electron diffraction studies are shown in Table 1. The value of ΣR_1 is the sum of the covalent radii of the respective atoms as given by Pauling (1, p.179). The molecules of ClF_3 have the shape of a trigonal pyramid with the F-Cl-F angle of 86.5°.

Table 1

Results of Structure Study

Compound	Bond	Length	ΣR_1(1,p.179)	Reference
ClF	Cl-F	1.63 Å	1.63 Å	(2)
ICl	I-Cl	2.32	2.34	(3)
ClF_3	Cl-F	1.69	1.63	(2)

B. Polyhalide Compounds

Polyhalide compounds of which tetramethylammonium pentaiodide and enneaiodide are examples have been known for well over a hundred years (4). In solution there is evidence for X_3^-, X_5^- (5), I_7^- and I_9^- (6) where X may contain as many as three different halogens within one ion. Many cations have been found to form well crystallized salts with these anions. Compounds of the type MX_n with n = 3, 5, 7 and 9 are especially numerous when X is exclusively iodine. A. Geuther (7) has studied optically over fifty of these compounds. There are several compounds of the type MX_4 of which CsI_4 is an example. These, however, are thought to be double salts of the type $CsI_3 \cdot CsI_5$.

With any one anion the ease of crystallization and the stability of the solid salt depend largely upon the nature of the cation present. The larger the cation present the more stable the salt; in fact, the higher polyiodides crystallize only if the cation is as large or larger than the tetramethylammonium cation. Polyhalide compounds with organic bases are especially numerous. There are relatively few with inorganic cations which are almost exclusively confined to the alkali metals. Lithium apparently forms no polyhalide compounds while sodium forms only solvated ones. Though stability is closely connected with the size of the cation, symmetry seems to have an effect in the substituted ammoniums (8). The order of stability is $N(CH_3)_4 > NH_2(CH_3)_2 > NH_3(CH_3) > NH(CH_3)_3 > NH_4$.

It appears that the stability of the polyhalides is a function of the heaviest halogen present. Compounds with at least one iodine are much more stable than those without it. The stability of the trihalide ion seems to depend on two additional factors - the nearness of the weight of the two lighter atoms to the heavier one and the nearness of the weight of the lighter atoms to each other. The order of stability is $I_3^- > IBr_2^- > ICl_2^- > IBrCl^- > Br_3^- > I_2Br^- > I_2Cl^- > Br_2Cl^-$ (9).

Polyhalide compounds are quite different from interhalogen compounds. Higher members of AB_n form only when A is iodine and B is fluorine whereas higher members of MX_n

form only when X is exclusively iodine. There may be something unique about the bonding in the high polyiodides since the corresponding interhalogen compounds do not form.

The results of X-ray diffraction studies of polyhalide compounds are listed in Table 2. The compounds CsI_3, KI_3, $CsIBr_2$, $CsICl_2$, CsClIBr and $N(CH_3)_4I_3$ (14)(15)(16) have received more or less complete structure studies but are probably less accurate than the values listed in the table.

Table 2

Results of Structure Studies

Compound	Bond	Length	ΣR_1(1, p.179)	Reference
$N(CH_3)_4ICl_2$	I-Cl	2.34 Å	2.32 Å	(10)
NH_4IClBr	I-Cl	2.38	2.32	(11)
	I-Br	2.50	2.47	
$KICl_4$	I-Cl	2.34	2.32	(12)
NH_4I_3	I-I	2.82	2.67	(13)
	I-I	3.10	2.67	

The polyhalides have generally been assumed to be covalently bonded and the structural studies support this with the exception of ammonium triiodide. The bond lengths are quite close to what one would expect for covalent bonds and the configuration is what one would expect.

The electronic structure of ICl_2^- is probably $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot\,\cdot\cdot}{\mathrm{I}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$. Iodine has two 5d electrons used for bonding. The directions of the bonds are those expected for sp^3d hybridized bonds, namely toward the corners of a trigonal bipyramid. The configuration of ICl_2^- is linear and symmetrical. The three unshared electrons may be interpreted to be in a plane (1, p.111).

The $IClBr^-$ ion is linear and probably has the same electronic structure as ICl_2^-.

The ICl_4^- ion is an example of sp^3d^2 bonding. The bond directions expected are to the corners of a regular octahedron. Iodine is in the middle of a coplanar square of chlorine atoms. Apparently there are two pairs of unshared electrons on opposite sides of iodine (1, p.111).

The reported structure of NH_4I_3 is in general disagreement with these interpretations. This structure determination was done relatively early in the development of X-ray technique and many of the more precise modern methods were not used. There is probably some reason for questioning the accuracy of this determination.

The reported triiodide ion is unusual in two ways. The ion is asymmetrical and it has unusually long iodine-iodine distances. The work of West (18) in which iodine was found to form chains of atoms with a repeat distance of about 3.1 Å in the starch-iodine addition compounds makes the long iodine-iodine distance seem somewhat more reasonable.

The structure determination of tetramethylammonium pentaiodide was undertaken in an attempt to explain the anomalous reported triiodide structure and to obtain a better understanding of the iodine-iodine interaction in polyiodide compounds. It was also hoped that an explanation could be obtained for some of the unconnected facts listed above concerning the chemistry of these compounds.

III. STRUCTURE OF TETRAMETHYLAMMONIUM PENTAIODIDE

A. Preparation of the Compound

Tetramethylammonium pentaiodide can be prepared by the addition of iodine to tetramethylammonium iodide in an alcohol solution. A. Geuther (7) prepared this compound by dissolving tetramethylammonium iodide and iodine in the molar ratio of one to two respectively in boiling iodine-alcohol solution which was previously saturated with iodine at a lower temperature. The solution was then slowly cooled to the lower temperature with the precipitation of tetramethylammonium pentaiodide. It was found, however, that better crystals were obtained if an excess of iodine was used. It was also found that the nature of the crystals changed relatively slowly over a wide range of excess iodine.

The best crystalline product was obtained by adding a two- to three-fold excess of iodine to tetramethylammonium iodide in boiling alcohol which contained no additional iodine. The solution was then cooled in two concentric Dewar flasks. The outer flask contained hot water and the flask of alcohol solution. When placed in a room whose temperature was 0° the alcohol solution required approximately forty-eight hours to drop to 5°. The mother liquor was decanted off the crystals which were then shaken on filter paper until most of the mother liquor was absorbed. The crystals were then stored in a sealed container.

B. Identification of Tetramethylammonium Pentaiodide

Tetramethylammonium pentaiodide is an iodine colored crystalline compound which loses iodine when exposed to air. Within a half hour the crystals no longer reflect sufficient light to permit study by an optical goniometer. If placed in a sealed container they remain shiny indefinitely. Analysis of samples of the compound by titrating the free iodine with sodium thiosulfate gave erratic and low results. This was attributed to either the loss of iodine in handling the samples or the incomplete removal of mother liquor from the crystalline product. The analyses of three samples were 69.76%, 67.72% and 67.23% in comparison to a theoretical value of 71.58%.

Lüdecke (19) studied tetramethylammonium pentaiodide optically and reported it to be monoclinic with $\beta = 72^\circ\ 20'$ (or $107^\circ\ 40'$) and axial ratios of 0.9866:1:0.6553. By means of X-rays tetramethylammonium pentaiodide was found to be monoclinic with $\beta = 107^\circ\ 50'$ and axial ratios 0.982:1:0.655. The observed density of individual crystals determined by means of floatation in a mixture of methyl iodide and methylene iodide was found to be between 2.98 and 3.04 g./cc. The calculated density for $4N(CH_3)_4I_5$ per unit cell is 3.06.

C. Determination of the Structure

1. Determination of the space group

Individual crystals of tetramethylammonium pentaiodide were sealed in a thin-walled glass capillary. The crystal class was determined by means of X-ray technique. The crystals were found to possess only a 2-fold axis of symmetry and a mirror plane perpendicular to it and were therefore monoclinic. When indexed consistently with the monoclinic convention

$$a_o = 13.34 \text{ Å}$$
$$b_o = 13.59 \qquad \beta = 107^\circ \, 50'$$
$$c_o = 8.90.$$

General reflections were observed only when $h + k = 2n$ and $(h0\ell)$ reflections were observed only when h and $\ell = 2n$. These facts required the space group to be C2/c or the noncentrosymmetric group, Cc. Since in many cases there is no reliable means for determining whether a crystal is centrosymmetric or not, work was continued assuming the crystal to be centrosymmetric, since work with this space group is the easier of the two. In the course of the structure determination no inconsistencies were found in this assumption, therefore the space group is C2/c. The point positions in this space group are listed in Table 3.

2. Collection of intensity data

A long crystal about 0.005 cm. on a side was selected and sealed in a thin-walled glass capillary. Multiple film Weissenberg data were recorded about the 2-fold axis with Cu Kα radiation. The equator and seven layer lines were photographed. The reflections on these films were visually estimated and corrected with the appropriate Lorentz-polarization corrections. Data of the type (0kℓ) were used to

Table 3

Point Positions in the C2/c Space Group

$(000;\ \frac{1}{2}\frac{1}{2}0)+$		
4:	(a)	$000;\ 00\frac{1}{2}$
	(b)	$0\frac{1}{2}0;\ 0\frac{1}{2}\frac{1}{2}$
	(c)	$\frac{1}{4}\frac{1}{4}0;\ \frac{3}{4}\frac{1}{4}\frac{1}{2}$
	(d)	$\frac{1}{4}\frac{1}{4}\frac{1}{2};\ \frac{1}{4}\frac{1}{4}0$
	(e)	$0y\frac{1}{4};\ 0\bar{y}\frac{1}{4}$
8:	(f)	$xyz;\ \bar{x}\ \bar{y}\ \bar{z};\ \bar{x},y,\frac{1}{2}-z;\ x,\bar{y},\frac{1}{2}+z$

place $(h0\ell)$, $(h2\ell)$, $(h4\ell)$ and $(h6\ell)$ on the same arbitrary scale since each set of data had been visually estimated relative to the strongest reflection present in the film set. Since no reflections were common to both $(0k\ell)$ and $(hk\ell)$ data when k is 2n + 1, $(1k\ell)$ data were used to scale $(h1\ell)$, $(h3\ell)$, $(h5\ell)$ and $(h7\ell)$. Finally, $(hh\ell)$ data were used to scale $(0k\ell)$ and $(1k\ell)$. In this manner the eight sets of films taken about b_o were put upon the same relative intensity scale.

3. Projections

Patterson projections (20) were made down a_o, b_o and c_o. Several months were spent attempting to interpret these projections. No suitable interpretations were obtained; consequently, it was concluded that H(x0z) (21) should be made. This projection required the use of the three dimensional data.

The H(x0z) projection had only seven peaks in the entire unit cell. This projection was studied in considerable detail; however, still no suitable structure was obtained. The general reliability of all the data was questionable since it contained only about eight orders of reflections and since so many cross correlations were used to scale the three dimensional data. The inaccurate data were evidenced by the fluctuations of the background values in the H(xOz) projection. It was finally decided to collect new data with a larger crystal of the order of 0.015 cm. on an edge since the larger crystals were known to show reflection of as high as twelve orders.

New data of the type (hk0), (h0ℓ), (0kℓ) and (hhℓ) was recorded with a precession camera using Mo Kα radiation. The use of the shorter wave length Molybdenum radiation helped to offset the higher absorption of the larger crystal. Since the precession camera does not lend itself to multiple film technique, the method of timed exposures was used. With this method a series of eight films were usually taken starting with about a ten minute exposure and doubling the length of each successive exposure. The films were collected and developed simultaneously as usual. With this lower film to film intensity ratio, intensities could be estimated visually more quickly and accurately. The intensities on the four sets of film were visually estimated and corrected with circularly symmetrical Lorentz-polarization corrections factors. Over three hundred independent reflections were recorded in these four zones.

New Patterson projections were made with these new data. The projections down a_o, b_o and c_o are shown in Figures 1, 2 and 3. After a period of study all Patterson projections were interpreted roughly by means of the sets of parameters listed under one in Table 4.

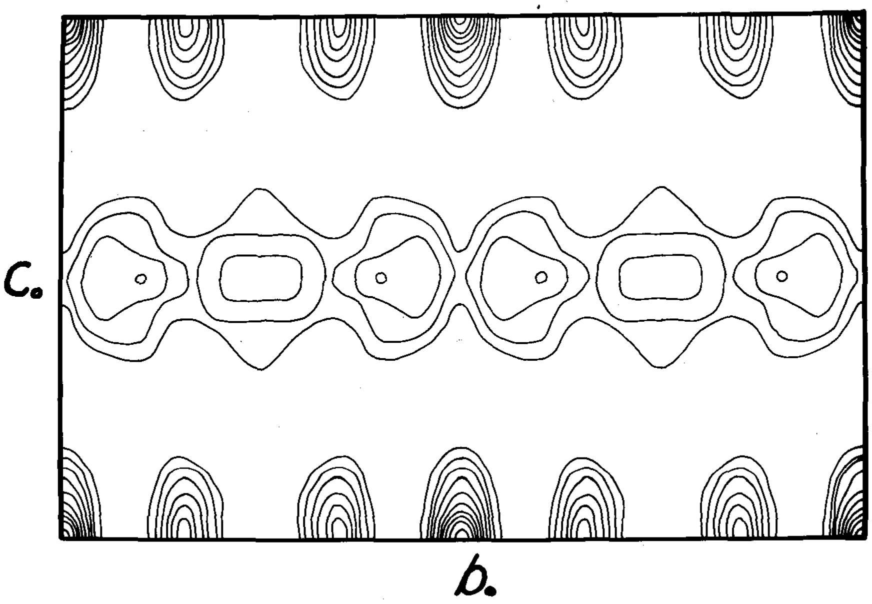

Figure 1 Patterson projection down a_o

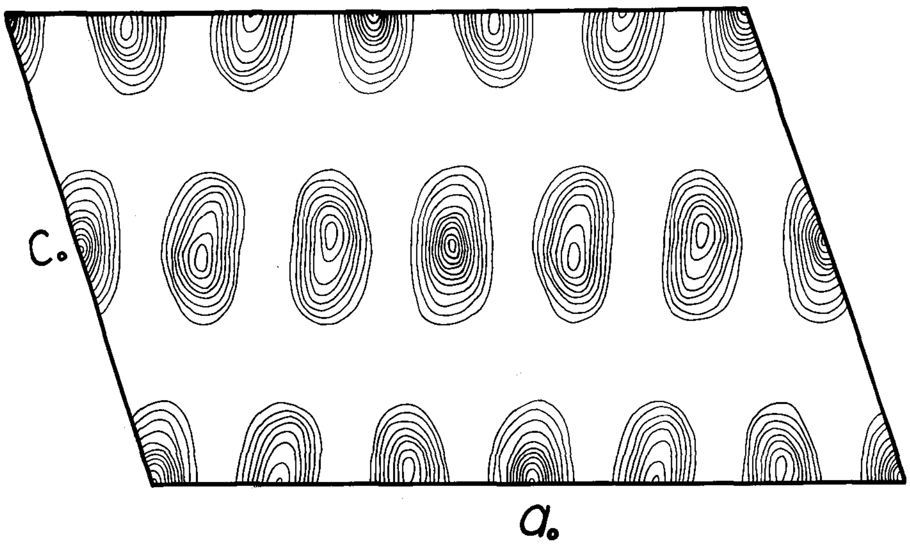

Figure 2 Patterson projection down b_0

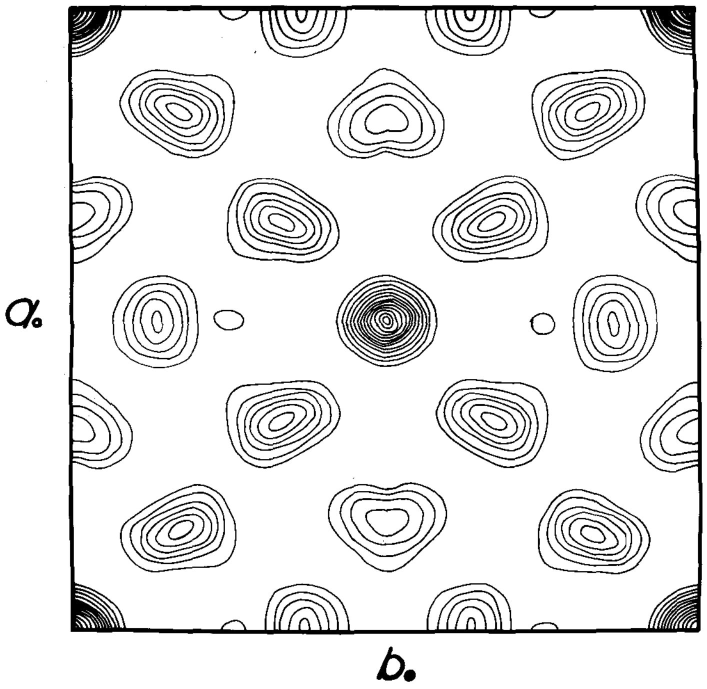

Figure 3 Patterson projection down c_o

There is one 4-fold set of atoms on the 2-fold axis, 4(a), and two general 8-fold sets, 8(f). The parameter for the 4-fold set is listed under y_a and the parameters of the two general sets are listed under $(x_b y_b z_b)$ and $(x_c y_c z_c)$.

Table 4

Refinements of Iodine Parameters

	Parameters			
	1	2	3	4
y_a	0.183	0.175	0.178	0.178
x_b	0.155	0.162	0.158	0.159
y_b	0.020	0.020	0.021	0.021
z_b	0.205	0.203	0.198	0.199
x_c	0.192	0.190	0.188	0.189
y_c	0.357	0.370	0.372	0.370
z_c	0.320	0.320	0.322	0.322

4. Refinement of parameters

With parameters obtained from the Pattersons, intensities were calculated and approximately thirty terms with unambiguous signs were used to make electron density projections about a_o, b_o and c_o. These projections were plotted to scale and the centers of the peaks located by means of drawing contour lines about the peaks. The new parameter values obtained are listed in Table 4 under two.

With these refined parameters intensities were again calculated and all the reflections were used to make new electron density projections with the sign determined by the intensity calculations. These projections are shown in Figures 4, 5 and 6. The centers of the peaks were then located by fitting Gaussion curves (22) to nine electron density values around the center of the peaks. Backshift corrections obtained from synthetic electron density projections were applied to these parameters. The resulting parameters are listed under three in Table 4.

Again the intensities were recalculated using the backshift corrected parameters and the electron density projections were checked to determine whether any error had been made in the sign. Several errors were observed for weaker reflections. The weaker reflections whose signs had changed were then used to make correcting projections. Twice the electron density values obtained from these projections were added to the second set of electron density projections and the centers of the peaks were again located by fitting Gaussion curves to the electron density values. The backshift corrections were again applied. The resulting final parameters are listed under four in Table 4. Observed and calculated

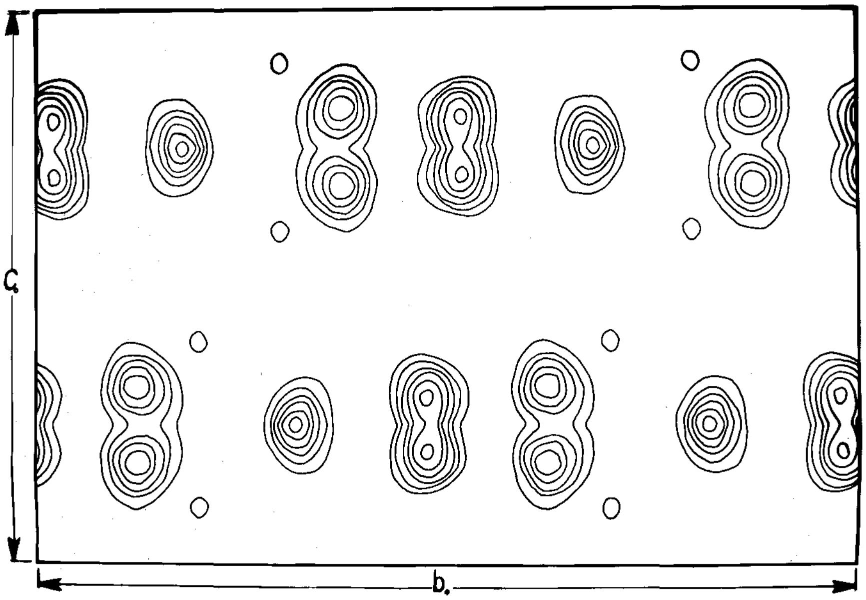

Figure 4 Electron density projection down a_o

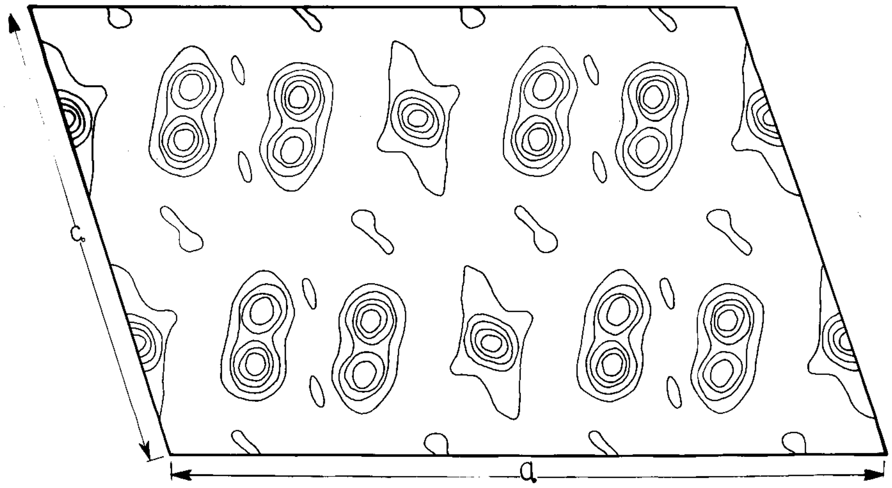

Figure 5 Electron density projection down b_o

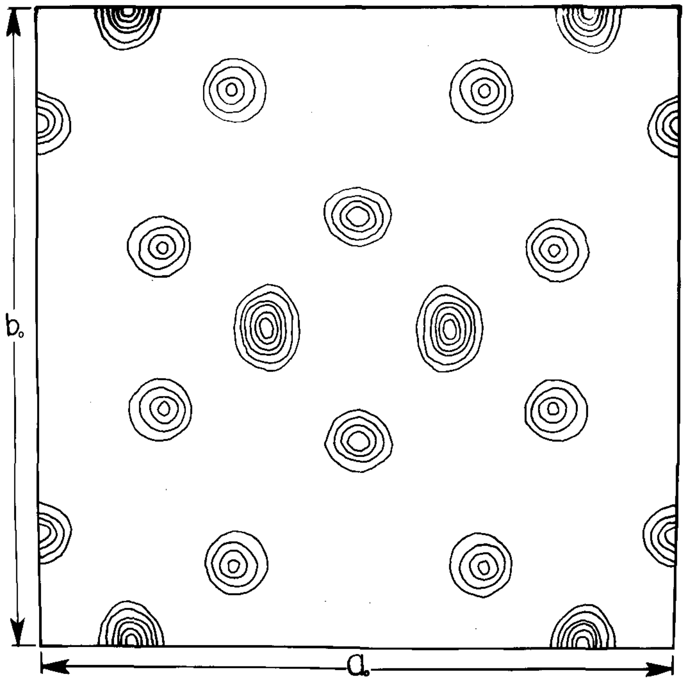

Figure 6 Electron density projection down c_o

$F_{hk\ell}$ made with the final parameters are tabulated in Table 5. An empirical temperature factor of exp $-3.16(\sin\theta/\lambda)^2$ has been applied to the calculated F's.

D. Description of the Structure

Figures 7, 8 and 9 represent the structure of tetramethylammonium pentaiodide. Figure 7 shows that the iodine atoms generally lie in planes. The deviation from a plane is only ± 0.64 Å. The planes are about 4.3 Å apart. Within one plane the iodine atoms form square nets as shown in Figure 8. Within these nets I_5^- anions are separated from the rest of the net by 3.55 Å while the distances within the ion are 2.93 and 3.14 Å. The I_5^- anion is V-shaped with an angle of 94° at the apex. The arms of the V are linear within 4°.

Since the diffraction of X-rays by crystals is due to the electrons and since less than 14 per cent of the electrons in tetramethylammonium pentaiodide are contained in the large positive ion essentially no evidence for this ion is ever observed in the electron density projections. There are, however, large voids within the planes of the iodines which must contain the positive ions. If the nitrogen of the $N(CH_3)_4^+$ cation is placed in the 4-fold set on the 2-fold axis with $y = 0.645$ the carbons may remain over 4.2 Å away from

Table 5

Observed and Calculated Structure Factors

Indices	$F_{obsd.}$	$F_{calcd.}$	Indices	$F_{obsd.}$	$F_{calcd.}$
	(0k)		4	18	15
			5	6	-17
(00ℓ)			6	--	-1
2	87	-87	7	15	16
4	19	17	8	--	-3
6	15	16	9	10	-9
8	15	-16			
10	12	5	(08ℓ)		
			0	24	28
(02ℓ)			1	31	22
0	27	30	2	13	-14
1	8	-13	3	16	-13
2	24	-19	4	11	-10
3	10	-12	5	--	0
4	--	-1	6	17	21
5	19	26	7	--	0
6	13	12	8	14	-15
7	15	-19			
8	14	-13	(0·10·ℓ)		
9	--	7	0	5	1
10	5	9	1	11	-9
			2	7	-2
(04ℓ)			3	--	4
0	14	-11	4	--	4
1	4	4	5	--	1
2	--	2	6	--	3
3	7	6			
4	10	10	(0·12·ℓ)		
5	11	-14	0	--	-10
6	7	-9	1	22	28
7	9	2	2	--	4
8	--	0	3	15	-13
9	5	-9	4	5	7
			5	--	1
(06ℓ)			6	6	-10
0	51	47			
1	66	60	(0·14·ℓ)		
2	41	-36	0	7	-4
3	23	-23	1	20	18

Table 5 (Continued)

Indices	$F_{\text{obsd.}}$	$F_{\text{calcd.}}$
2	5	5
3	8	-8
4	5	-6
5	5	-5
	$(h0\ell)$	
(00ℓ)		
2	87	-87
4	19	17
6	15	16
8	15	-16
10	12	5
(20ℓ)		
10	7	-13
8	21	29
6	32	-39
4	24	25
2	10	4
0	26	-26
$\bar{2}$	14	8
$\bar{4}$	7	16
$\bar{6}$	15	-20
$\bar{8}$	8	12
$\overline{10}$	6	-4
(40ℓ)		
10	--	2
8	--	3
6	--	-8
4	8	16
2	13	26
0	--	-1
$\bar{2}$	6	6
$\bar{4}$	4	5
$\bar{6}$	21	-21
$\bar{8}$	22	31
$\overline{10}$	12	-21
(60ℓ)		
8	6	-5
6	10	11
4	7	-6
2	28	-23
0	82	75
$\bar{2}$	99	87
$\bar{4}$	57	49
$\bar{6}$	10	-5
$\bar{8}$	13	-15
$\overline{10}$	12	12
(80ℓ)		
8	10	14
6	16	-26
4	25	28
2	13	-11
0	16	-14
$\bar{2}$	37	-52
$\bar{4}$	16	-6
$\bar{6}$	6	-11
$\bar{8}$	11	14
$\overline{10}$	8	-9
$(10\cdot0\cdot\ell)$		
6	--	3
4	6	3
2	--	-9
0	8	10
$\bar{2}$	14	-4
$\bar{4}$	10	1
$\bar{6}$	10	-7
$\bar{8}$	11	14
$\overline{10}$	8	-14
$(12\cdot0\cdot\ell)$		
4	--	-10
2	--	1
0	15	18
$\bar{2}$	31	-35
$\bar{4}$	32	34
$\bar{6}$	17	-17
$\bar{8}$	--	-16
$\overline{10}$	8	8
$(14\cdot0\cdot\ell)$		
2	10	-13

Table 5 (Continued)

Indices	$F_{obsd.}$	$F_{calcd.}$	Indices	$F_{obsd.}$	$F_{calcd.}$
$\underline{0}$	--	1	12	12	16
$\underline{2}$	7	9	14	6	-9
$\underline{4}$	13	-10	16	--	-1
$\underline{6}$	6	-8			
			(3k0)		
(16·0·ℓ)			1	4	-4
$\underline{0}$	--	4	3	92	89
$\underline{2}$	6	-5	5	35	-30
$\underline{4}$	7	4	7	--	6
$\underline{6}$	7	-3	9	8	-9
			11	4	-6
			13	4	-6
	(hk0)		15	--	8
			17	7	9
(0k0)					
2	27	30	(4k0)		
4	14	-11	0	--	-1
6	51	47	2	46	-39
8	24	28	4	33	26
10	5	1	6	--	3
12	--	-10	8	14	-19
14	7	-4	10	--	-1
16	4	6	12	--	5
18	3	-7	14	3	-4
			16	4	6
(1k0)					
1	23	28	(5k0)		
3	16	9	1	5	4
5	47	43	3	20	13
7	--	1	5	45	36
9	8	-11	7	7	-15
11	13	18	9	15	-16
13	--	-2	11	16	22
15	5	-8	13	4	9
17	--	1			
			(6k0)		
(2k0)			0	82	75
0	26	-26	2	24	16
2	40	-34	4	--	4
4	5	9	6	33	33
6	5	4	8	7	12
8	37	38	10	7	2
10	--	5	12	--	4

Table 5 (Continued)

Indices	$F_{obsd.}$	$F_{calcd.}$	Indices	$F_{obsd.}$	$F_{calcd.}$
14	5	-5	11	5	10
(7k0)			(12·k·0)		
1	41	36	0	15	18
3	5	-6	2	7	6
5	11	18	4	13	8
7	21	17	6	8	11
9	--	0	8	--	2
11	--	3	10	4	3
13	--	-5	12	4	3
(8k0)			(13·k·0)		
0	16	-14	1	14	19
2	10	-11	3	--	10
4	10	16	5	--	5
6	6	5	7	8	11
8	24	-25	9	--	2
10	--	5			
12	8	13	(14·k·0)		
14	--	-8	0	--	1
			2	--	-2
(9k0)			4	--	5
1	13	-9	6	--	4
3	27	-32	8	--	-7
5	9	-8			
7	8	-4	(15·k·0)		
9	8	-8	1	6	-6
11	--	2	3	5	-6
			5	--	1
(10·k·0)			7	--	-5
0	8	10	9	4	-5
2	18	-21			
4	26	26	(16·k·0)		
6	--	2	0	--	4
8	--	-2	2	5	3
10	--	-3	4	6	-2
12	--	-2	6	--	6
(11·k·0)					
1	--	-5		(hhℓ)	
3	--	1			
5	8	12	(00)		
7	--	8	2	87	-87
9	6	-8	4	19	17

Table 5 (Continued)

Indices	$F_{obsd.}$	$F_{calcd.}$	Indices	$F_{obsd.}$	$F_{calcd.}$
6	15	16	6	13	-12
8	15	-16	7	--	1
10	12	5	8	7	5
			9	--	7
(11ℓ)			10	--	0
$\bar{10}$	--	-4			
$\bar{9}$	5	8	(33ℓ)		
$\bar{8}$	5	0	$\bar{10}$	--	8
$\bar{7}$	--	5	$\bar{9}$	9	-9
$\bar{6}$	21	18	$\bar{8}$	13	14
$\bar{5}$	15	-22	$\bar{7}$	11	13
$\bar{4}$	37	-34	$\bar{6}$	--	6
$\bar{3}$	47	44	$\bar{5}$	--	3
$\bar{2}$	27	24	$\bar{4}$	41	-31
$\bar{1}$	40	-52	$\bar{3}$	23	-27
0	23	28	$\bar{2}$	76	77
1	12	25	$\bar{1}$	51	48
2	62	64	0	92	-89
3	--	0	1	35	-34
4	63	58	2	51	46
5	--	-3	3	--	4
6	25	-25	4	--	-3
7	--	-4	5	11	12
8	--	2	6	11	-15
9	--	8	7	9	11
10	5	8	8	11	9
			9	--	4
(22ℓ)			10	--	-1
$\bar{10}$	12	-2			
$\bar{9}$	--	-7	(44ℓ)		
$\bar{8}$	5	-6	$\bar{9}$	--	0
$\bar{7}$	6	-8	$\bar{8}$	7	4
$\bar{6}$	21	23	$\bar{7}$	--	0
$\bar{5}$	15	23	$\bar{6}$	23	-24
$\bar{4}$	49	-43	$\bar{5}$	--	4
$\bar{3}$	9	-16	$\bar{4}$	48	40
$\bar{2}$	61	49	$\bar{3}$	9	-14
$\bar{1}$	42	-25	$\bar{2}$	21	-20
0	44	-34	$\bar{1}$	25	26
1	62	58	0	33	26
2	--	2	1	28	-30
3	47	-46	2	61	53
4	9	13	3	22	24
5	11	18	4	37	-41

Table 5 (Continued)

Indices	$F_{obsd.}$	$F_{calcd.}$	Indices	$F_{obsd.}$	$F_{calcd.}$
5	11	-15	5	11	-12
6	9	14	6	--	1
7	--	7	7	--	1
8	--	5	8	--	-2
9	--	-2	9	--	0
(55ℓ)			(77ℓ)		
$\bar{9}$	--	2	$\bar{8}$	9	-7
$\bar{8}$	--	2	$\bar{7}$	9	-6
$\bar{7}$	11	12	$\bar{6}$	15	16
$\bar{6}$	6	-7	$\bar{5}$	12	10
$\bar{5}$	13	-21	$\bar{4}$	15	-19
$\bar{4}$	21	21	$\bar{3}$	--	-1
$\bar{3}$	--	11	$\bar{2}$	--	4
$\bar{2}$	50	35	$\bar{1}$	21	-20
$\bar{1}$	22	16	0	21	17
0	45	36	1	29	33
1	25	-32	2	18	-24
2	12	16	3	22	-28
3	25	26	4	5	14
4	6	4	5	7	13
5	11	-12	6	--	-2
6	12	11	7	--	-2
7	--	1	8	--	-5
8	7	6			
9	--	0	(88ℓ)		
			$\bar{7}$	--	6
(66ℓ)			$\bar{6}$	5	0
$\bar{9}$	--	2	$\bar{5}$	--	1
$\bar{8}$	--	-1	$\bar{4}$	21	-12
$\bar{7}$	11	12	$\bar{3}$	--	12
$\bar{6}$	5	-6	$\bar{2}$	25	24
$\bar{5}$	13	-21	$\bar{1}$	--	16
$\bar{4}$	21	20	0	24	25
$\bar{3}$	--	11	1	--	5
$\bar{2}$	29	-32	2	5	11
$\bar{1}$	22	15	3	5	9
0	33	33	4	--	3
1	25	-32	5	5	15
2	16	18	6	--	7
3	25	26	7	--	11
4	5	5			

Table 5 (Continued)

Indices	$F_{\text{obsd.}}$	$F_{\text{calcd.}}$
(99ℓ)		
$\bar{7}$	--	-2
$\bar{6}$	--	4
$\bar{5}$	14	13
$\bar{4}$	--	-2
$\bar{3}$	22	-26
$\bar{2}$	--	3
$\bar{1}$	15	25
0	8	-8
1	5	-11
2	12	9
3	--	3
4	12	-8
5	--	7
6	--	3
7	--	4
(10·10·ℓ)		
$\bar{7}$	7	9
$\bar{6}$	--	-4
$\bar{5}$	5	-10
$\bar{4}$	--	3
$\bar{3}$	--	1
$\bar{2}$	--	0
$\bar{1}$	15	13
0	--	-3
1	16	-14
2	--	3
3	11	9
4	--	-1
5	--	-4
6	--	-1
7	--	-2
(11·11·ℓ)		
$\bar{7}$	--	1
$\bar{6}$	5	0
$\bar{5}$	--	-6
$\bar{4}$	12	6
$\bar{3}$	9	10
$\bar{2}$	11	-11
$\bar{1}$	5	-6
0	5	10
1	--	1
2	--	-4
3	4	7
4	--	-8
5	--	-7
6	--	1
7	--	4
(12·12·ℓ)		
$\bar{5}$	5	-11
$\bar{4}$	--	-4
$\bar{3}$	5	16
$\bar{2}$	--	3
$\bar{1}$	5	-12
0	4	3
1	--	3
2	3	-6
3	--	3
4	--	4
5	--	-3
(13·13·ℓ)		
$\bar{4}$	--	0
$\bar{3}$	5	3
$\bar{2}$	--	2
$\bar{1}$	4	-9
0	--	-4
1	--	10
2	--	3
3	--	5
4	--	1

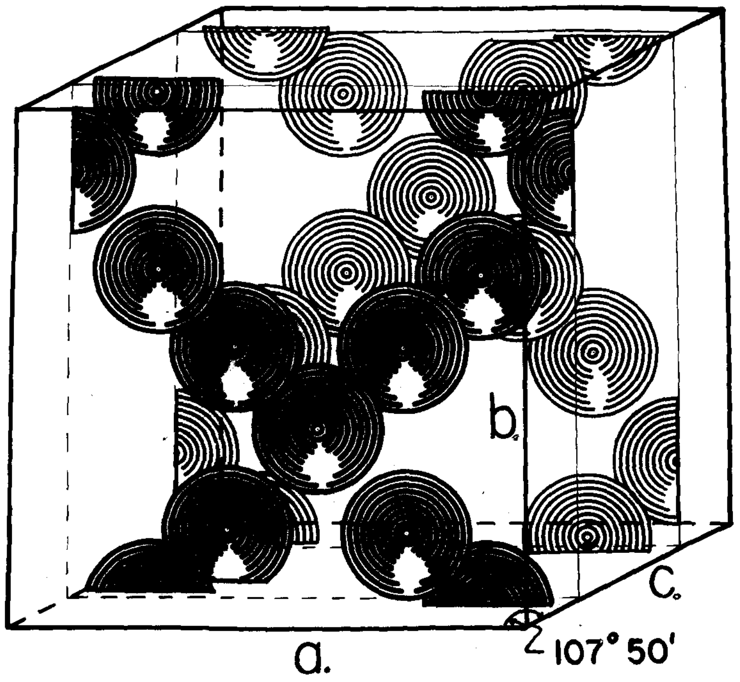

Figure 7 Packing of the pentaiodide ion in the unit cell

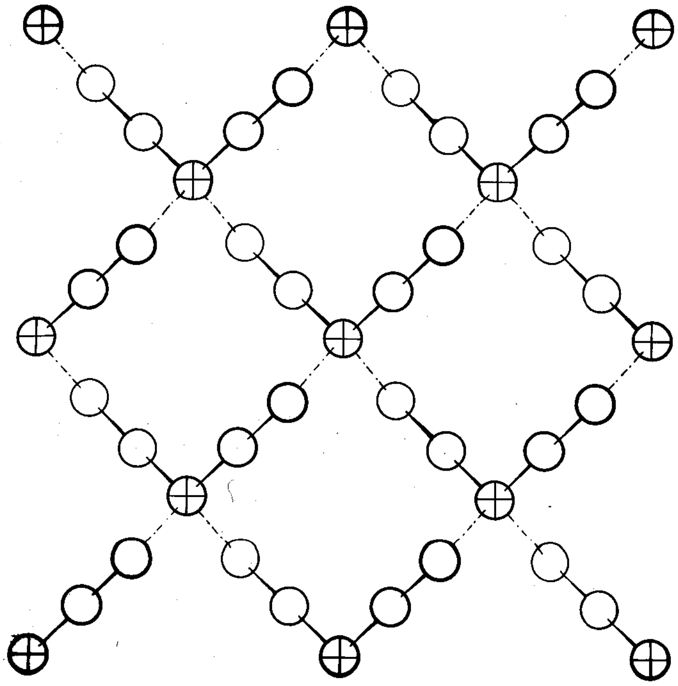

Figure 8 Arrangement of iodine atoms in one net running normal to c_0

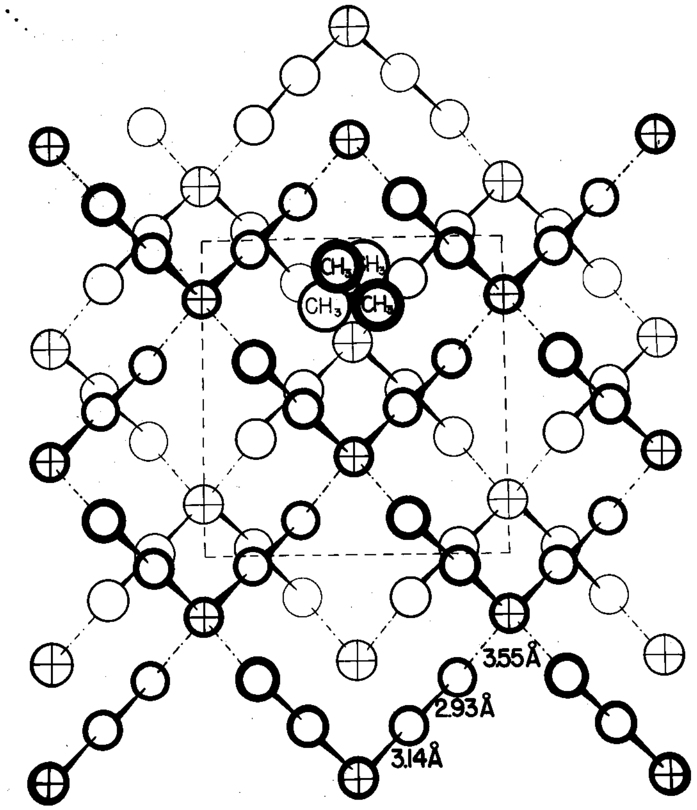

Figure 9 Arrangement of one net with respect to another

iodines and still retain their tetrahedral configuration about nitrogen.

E. Errors

The R factor, $R = \frac{\sum \left| |F_{obsd.}| - |F_{calcd.}| \right|}{\sum |F_{obsd.}|}$, is often used to show quantitatively how closely calculated and observed structure factors agree. In this structure determination R = 0.18, 0.24, 0.21 and 0.20 for all $(0k\ell)$, $(h0\ell)$, $(hk0)$ and $(hh\ell)$ observed reflections respectively.

The values of R, however, have no corresponding interpretation in standard errors and since bond distances are of interest in this structure, a study was made to determine the accuracy of the reported bond distances. Booth (23) has shown that the values of

$${}_2R_2 = \frac{\sum \left(|F_{obsd.}| - |F_{calcd.}| \right)^2}{\sum (F^2_{obsd.})}$$

corresponds to r.m.s. errors. For this structure ${}_2R_2$ = 0.036 - 0.040 for the various two dimensional data when all reflections are included. The r.m.s. errors in the positions of the atoms corresponding to these ${}_2R_2$ values are 0.03 to 0.04 Å.

The method of Cruickshank (24) which gives standard errors (σ) results in $\sigma\bar{y}_a = 0.04$, $\sigma\bar{y}_b = 0.05$ and $\sigma\bar{y}_c =$

0.04 Å. By this method the standard errors in bond distances are $\sqrt{2} \times 0.04 = 0.06$ Å.

Since the primary question is whether the reported distances of 3.14 and 2.93 Å are really different, the R value was recalculated for (hk0) data with these distances made equal. The value was found to rise from 0.21 to 0.28 when this was done. The distances were made equal by moving only the middle iodine atom in the arms of the V-shaped I_5^- ion. Since the plane of this ion is normal to c_o, the (hk0) data should be most sensitive to this change.

The above facts indicate that the errors in this structure determination are sufficiently small that it is reasonable to conclude that the reported distance of 2.93 and 3.14 Å are actually different.

IV. STRUCTURE OF TETRAMETHYLAMMONIUM ENNEAIODIDE

A. Preparation of the Compound

Tetramethylammonium enneaiodide was prepared in a manner similar to that used for the preparation of tetramethylammonium pentaiodide. A two- or three-fold excess of iodine to tetramethylammonium iodide was dissolved in a minimum amount of boiling alcohol by the slow addition of alcohol. Before solution was complete a second liquid phase was observed near the boiling point of alcohol. Alcohol was added until the second liquid phase disappeared. The solution was then allowed to cool slowly and tetramethylammonium enneaiodide separated. The mother liquor was then decanted off and the crystals were shaken on filter paper until most of the remaining mother liquor was absorbed. The crystals were then stored in a sealed container.

B. Identification of the Compound

The color of tetramethylammonium enneaiodide is very dark green, almost black. When exposed to air, iodine is slowly lost. Analyses of samples of this compound prepared in the manner described were erratic and low. A sample of this compound was prepared in the usual manner except the crystalline product was crushed between filter papers to obtain more complete absorption of the mother liquor. When these samples were analyzed for tetramethylammonium iodide by volatilizing the free iodine at about 200° the results were 16.54%, 16.56% and 16.50% as compared to the theoretical value of 16.53%.

Single crystals were observed to sink in methylene iodide which indicated their densities were larger than 3.32 g./cc. A sample of the crystals was observed to have a density of 3.47 g./cc. when determined with a pycnometer using mineral oil. The calculated density for $4N(CH_3)_4I_9$ per unit cell is 3.51 g./cc.

C. Determination of the Structure

1. Determination of the space group

Tetramethylammonium enneaiodide was found to be monoclinic. Reflections of the type $(hk\ell)$ were present in all orders while $(h0\ell)$ reflections appeared only with $\ell = 2n$. The $(0k0)$ reflections appeared only when $k = 2n$. These absences required the space group to be uniquely $P2_1/c$. When indexed in this manner $\beta = 136° 35'$. Since this large monoclinic angle is somewhat inconvenient to work with, the a_o and c_o axes were rechosen to give $\beta = 95° 25'$. When this was done $(h0\ell)$ reflections appear only when $h + \ell = 2n$. All other types of absences remained unchanged. The space group with this choice of axes is $P2_1/n$. These two space groups, $P2_1/c$ and $P2_1/n$, are equivalent involving only a reselection of the a_o and c_o axes. The point position and pertinent information for the space group $P2_1/n$ is listed under Figure 10.

2. Collection of intensity data

From a preliminary look at the complexity of this problem it appeared that there would be twenty-seven parameters needed to locate the thirty-six iodine atoms in the unit cell. With a problem as complex as this it is quite unlikely that the complete structure could be obtained from two dimensional work. It was therefore decided at the beginning of the problem that complete three dimensional data would be obtained immediately without even a preliminary look at the two dimensional Pattersons. Great care was taken to obtain a single crystal of sufficient size in order to obtain reflections of high orders and yet small enough to have reasonable absorption. Many crystals selected were found to be twinned. About thirty crystals were examined by X-rays before one was selected. The $(h0\ell)$ Weissenberg photograph was generally taken in examining the crystals since the twinning appeared there. A long crystal with nearly rectangular cross sections and edges of 0.015 and 0.030 cm. ± 10% was selected.

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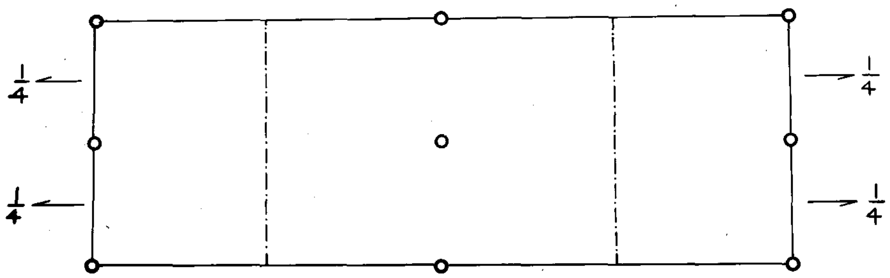


Figure 10 Symmetry operations in the space group $P2_1/n$

<u>Point positions</u>

2: (a) $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2})$
(b) $(00\frac{1}{2}, \frac{1}{2}\frac{1}{2}0)$
(c) $(0\frac{1}{2}0, \frac{1}{2}0\frac{1}{2})$
(d) $(\frac{1}{2}00, 0\frac{1}{2}\frac{1}{2})$
4: (e) $xyz;\ \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z;$
$\bar{x}\bar{y}\bar{z};\ \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z;$

<u>Absences</u>

$(hk\ell)$ all orders present
$(h0\ell)$ only with $h + \ell = 2n$
$(0k0)$ only with $k = 2n$

<u>Structure factor</u>

for $h + k + \ell = 2n$

$A = 4\cos 2\pi(hx + \ell z)\cos 2\pi ky$
$B = 0$

for $h + k + \ell = 2n$

$A = -4\sin 2\pi(hx + \ell z)\sin 2\pi ky$
$B = 0$

$a_o = 11.60$ Å
$b_o = 15.10$
$c_o = 13.18$

$\beta = 95^\circ\ 25'$

This crystal was mounted in a thin walled glass capillary. The direction of the 2-fold screw axis was parallel to the long axis of the crystal.

With a Weissenberg camera intensity data were recorded for the equator and ten layers about the 2-fold screw axis. The films were taken by means of timed exposure and concentric film technique. Careful line-up pictures were taken for the equator and for the higher layers. The equiinclination Weissenberg angle, μ, and the layer line shield settings, s, were carefully recorded for each layer. An additional correction of centering the crystal in the beam had to be made for each layer. This was done by placing a scale on the crystal's horizontal centering screw and marking the appropriate centered positions for each layer. It was then possible to go from one layer line to another without taking line-up pictures or making minor corrections.

Timed exposure series were taken starting with about a three minute photograph on each of the eleven levels. The exposure time was governed by the time taken for the film holder to make one traversal and return, which was slightly over three minutes. The films were coded with an identifying punch mark and were retained for later development. The single complete traversal photographs were followed by series of two, four and eight traversals.

It was decided that longer exposures would be made with concentric films since the weaker reflections would be judged on these darker films and therefore the greater film to film attenuation factor of concentric films would affect only the judging accuracy of the weaker, less significant reflections. A series of photographs using four concentric films was then made with the exposure time of 45 hours and 19 minutes. This exposure time was such that the fourth concentric film received the equivalent of time required for sixteen complete traversals of the film holder assuming 27 per cent attenuation on each of the first three films.

The films were developed in two groups. The first four series were developed together and the sets of four concentric films were developed together. Both groups were developed with fresh developer.

This technique of recording the layers made it possible to estimate all the reflections in comparison to a few reference reflections. No scaling factors were needed between the various layers. The film to film attenuation factor was low for the weaker films which permitted accurate estimations of the important stronger reflections. The film to film attenuation factor for the eight films taken on each layer is 2, 2, 2, 2, 3.7, 3.7, 3.7 starting with the weakest film.

The intensities on the $(h0\ell)$ set of films were estimated visually and corrected with the appropriate Lorentz-polarization corrections. It was apparent from the appearance of the film that there was a large absorption correction needed. An analytic expression for this correction is very difficult to obtain for a rectangular crystal and may also be inaccurate since it would be based upon a crystal which possessed no flaws. The tetramethylammonium enneaiodide crystals were often found to contain visible flaws. An emprical absorption correction was therefore made by comparison of corrected intensities from the precession and Weissenberg cameras. With the precession camera $(h0\ell)$ data was obtained with Mo K_α radiation and with a smaller crystal. These data were visually estimated twice and then averaged and corrected. The precession $(h0\ell)$ data were then compared with the Weissenberg $(h0\ell)$ data to obtain the correcting factors. These absorption corrections were plotted on a grid which could be superimposed upon the Weissenberg films. All the Weissenberg layers were corrected by these same empirical absorption corrections.

After estimating $(h0\ell)$, $(h1\ell)$ and $(h2\ell)$ it appeared that, even with the empirical absorption correction, an error of the order of half the observed intensity may still be present in the estimated intensities. Because of this large error, it was decided to make the Patterson projection about the principle axes using precession data.

3. Patterson projections and interpretation

Intensity data of the type (h0ℓ), (hk0), (0kℓ), (hkh) and (hk$\bar{h}$) were obtained with the precession camera and Mo Kα radiation. These were visually estimated and corrected with circularly symmetrical Lorentz-polarization corrections. Patterson projections were made with these data. They are shown in Figures 11, 12, 13, 14 and 15.

After the Patterson projections were made, a preliminary examination indicated that the projection onto (010) might possibly be interpreted without additional information. This projection indicates all iodine atoms must project into lines running in the direction of $a_o + c_o$. These lines must be spaced approximately 3 Å apart. The next most significant observation from this Patterson is that there must be a large number of atoms approximately $(a_o+c_o)/4$ apart in each line since the largest peak present, except for the origin, is at $x = \frac{1}{4}$ and $z = \frac{1}{4}$. These two restrictions above permit only a few possible major structures. There are only two possible sets of lines upon which atoms may be placed and still maintain the 3 Å separation. A large percentage of the atoms must be placed within any one line in one of only two manners such that there is a large number of atoms $(a_o+c_o)/4$ apart as one goes up the line of atoms. It must be true that many atoms are positioned such that their projection upon (010) coincides for there are far less individual peaks in this

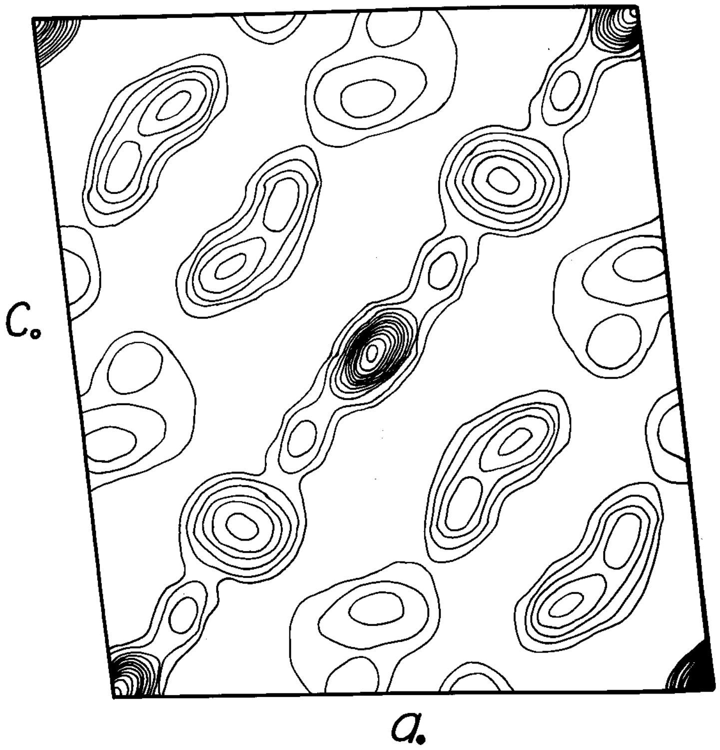


Figure 11 Patterson projection upon (010)

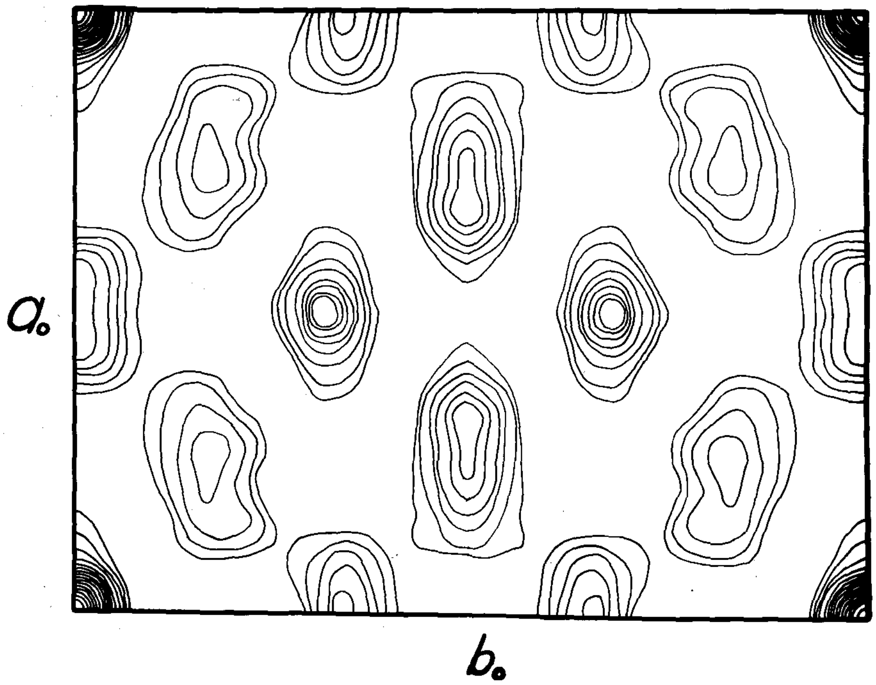


Figure 12 Patterson projection down c_o

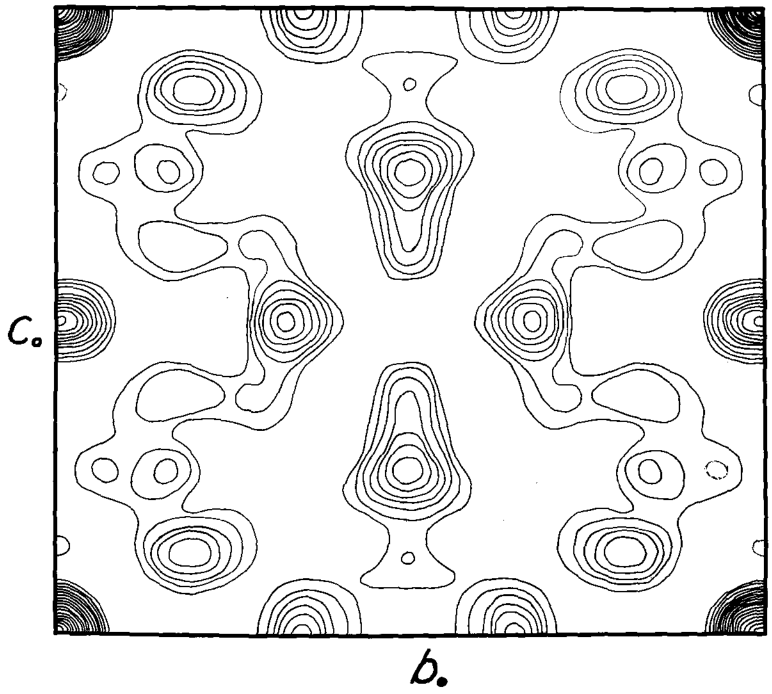


Figure 13 Patterson projection down a_o

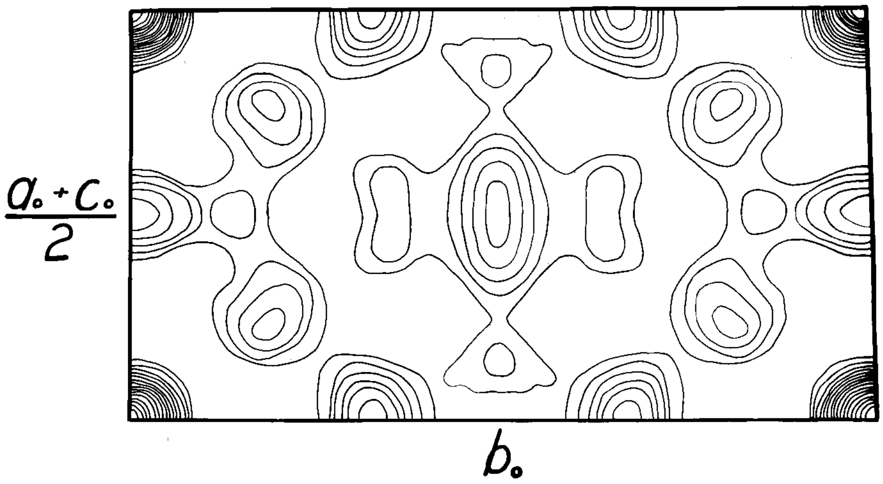


Figure 14 Patterson projection down a_o-c_o

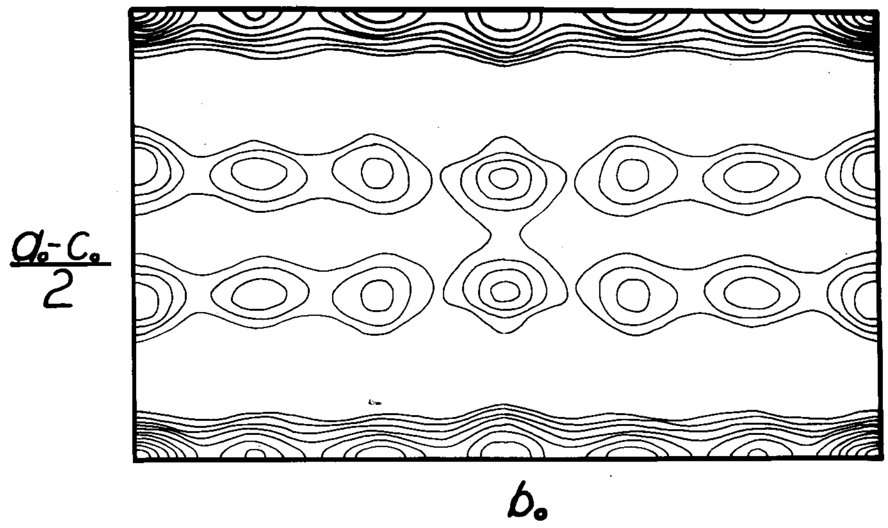


Figure 15 Patterson projection down $a_o + c_o$

projection than the 1260 separate possible peaks.

Several possible arrangements of atoms in lines spaced 3 Å apart were postulated. Intensities were calculated for about thirty of the strongest observed reflections in the $(h0\ell)$ data. Observed reflections whose calculated intensities were large were used to make trial electron density projections with the signs determined by the calculated intensities. Seven of these projections were made with different arrangements of the atoms. Apparently none of these were correct as evidenced by the poorly defined peaks and in some cases the complete absence of peaks where atoms had been postulated. Several conclusions were reached after the seven projections were studied together. There were two regions, $x = 33/60$, $z = 5/60$ and $x = 42/60$, $z = 10/60$, which always had a peak of some type whether atoms had been placed there or not in the postulated trial structure. When this was noticed a trial structure was postulated with atoms at these two sites and also at $x = 5/60$, $z = 10/60$ and $x = 10/60$, $z = 5/60$. The electron density projections of this trial structure had nicely defined peaks close to where the atoms had been postulated and also there were almost no extraneous peaks. A refinement of this trial structure was made using forty-six reflections with unambiguous signs as determined by calculated intensities from parameters obtained from the first trial electron density projections.

The resulting projection had very nicely defined peaks and appeared to be the correct interpretation of the Patterson. Parameters were then obtained from this projection and the R correlation factor was calculated and found to be 0.32. This value was obtained by placing two atoms at the center of three of the four different peaks and three atoms at the center of the fourth peak. The peaks were elongated in the direction of (a_0+c_0) which indicated the atoms did not project exactly upon each other.

A new set of parameters were then taken by spreading out the several atoms projecting into each peak by approximately one-sixtieth. When the $(h0\ell)$ reflections were calculated with these parameters R was 0.29. An additional refinement was then possible with these calculated intensities. This refinement contained sixty-seven of the seventy-eight possible reflections appearing in $(h0\ell)$ data. The peak heights on this projections, Figure 16, are almost exactly the proper height for three atoms in one peak and two in the remaining. An additional R value has not been determined with parameters obtained from this projection. Presumably the value would drop somewhere below 0.28. The x and z parameters obtained by fitting a parabola to the electron density values around the peaks are

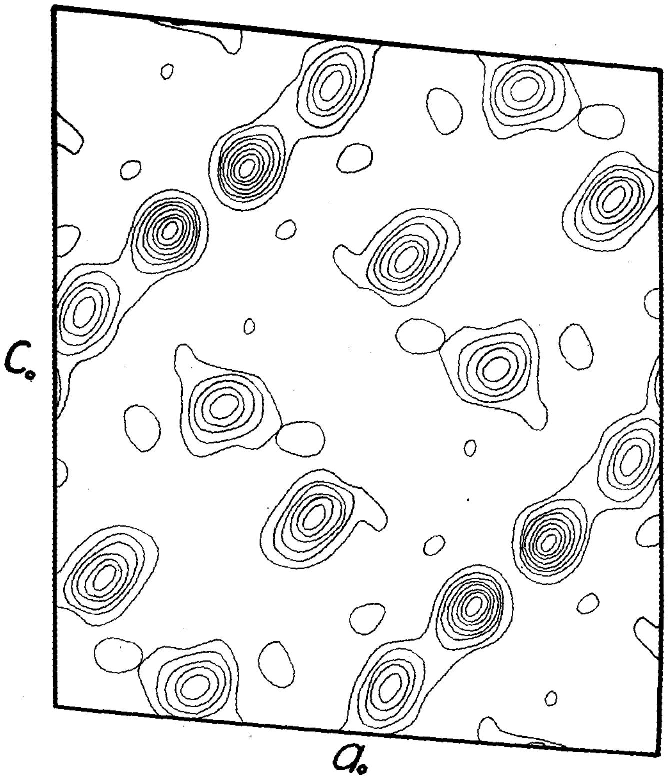


Figure 16 Electron density projection upon (010)

$x_1 = 0.070$	y_1, y_2	$z_1 = 0.189$
$x_2 = 0.220$	y_3, y_4	$z_2 = 0.044$
$x_3 = 0.539$	y_5, y_6	$z_3 = 0.065$
$x_4 = 0.667$	y_7, y_8, y_9	$z_4 = 0.194$.

The y_i are values of the y parameters which must be associated with the x and z values but are still unknown.

4. Discussion of y parameters

At the present state of this problem it seems reasonable to assume that the interpretation of the Patterson projection onto (010) is correct since R is quite low. Given x and z parameters it should be possible to determine the remaining y parameters with two dimensional data and thus interpret the complete structure of the compound.

Several observations about the y parameters can be made from a study of the Patterson projections shown in Figures 12, 13, 14 and 15. One observation is that the iodine atoms lie in planes running normal to b_o and 10/60 b_o apart since all the peaks on the Pattersons fall on y values of 0, 10/60 b_o, 20/60 b_o etc.

There are two sets of values which y parameters may have and produce planes of atoms 10/60 b_o apart. These values are $y_i = 0$, 10/60, 20/60, 30/60, 40/60, 50/60 or $y_i = 5/60$, 15/60, 25/60, 35/60, 45/60 and 55/60. These are the only possible sets of y parameters which will maintain planes of atoms 10/60 b_o apart since the point positions of $P2_1/n$ generate atoms at y, $\frac{1}{2}$-y, $\frac{1}{2}$+y, and -y. Probably all y parameters are in one set or all are in the other set since there is no indication on any projection of a peak with y = 5/60 b_o.

The (032), (230) and the (232) reflections are the strongest reflections present in the (0kℓ), (hk0) and (hkh) data respectively. In all three of these cases the structure factor for these reflections involve the products of the trigonometric sine functions. The $\sin 2\pi 3y_1$ is common to all these products. If the first set of y parameters listed above are chosen, $\sin 2\pi 3y_1$ is always zero, whereas if the second set is chosen $\sin 2\pi 3y_1$ is always ± 1. Since the strongest reflections involve the product of $\sin 2\pi 3y_1$ it must have a large value, therefore y_1 must be 5/60, 15/60, 25/60, 35/60, 45/60 or 55/60.

The electron density projection upon (010), Figure 16, indicates there are many atoms whose projection coincide. This means that on Patterson projections down a line normal to b_o there should be peaks upon the b_o axis which involve the spacing of the atoms in the b_o direction. From a study of the Patterson projection down a_o-c_o, Figure 13; c_o, Figure 14; and down a_o, Figure 15, one can conclude that the separations in the b_o direction of atoms with similar x's and z's is 20/60 b_o or 40/60 b_o, since there are peaks only at these values on the b_o axis.

The above conclusions require the y_i values to be one of six, 5/60, 15/60, etc. and that if one of these values is assigned to an atom with given x and z values then the y_i parameter of the other atom with the same x and z values must be either 20/60 or 40/60 larger. Also in the particular case of x_4 and z_4 if y_7 is chosen for one atom the two other atoms with x_4 and z_4 must have y parameter values of $y_8 = y_7 + 20/60$ and $y_9 = y_7 + 40/60$.

In the electron density projection upon (010), Figure 16, the distance from the peak of x_3 z_3 to the peak of x_4 z_4 is only 2 Å. This means that if y_5 or y_6 have the same value as y_7, y_8 or y_9 then there is an iodine-iodine distance of 2 Å which is impossible since the iodine-iodine distance in free iodine is 2.67 Å. The value of y_5 and y_6 must then be different from the value of y_7, y_8 and y_9.

The distance from the peak at x_1 z_1 to x_2 z_2 in the electron density projection onto (010) is about 2.8 Å, while the distance from x_2 z_2 peak to any other peak is 3.5 Å or larger. It is reasonable to assume that all (except possibly one) iodine atoms are bonded to other iodine atoms by bonds of length 2.9 ± 0.2 Å. This means that iodine with x_1 and z_1 are probably bonded to others with x_2 and z_2. If this is true then $y_1 = y_3$ and $y_2 = y_4$.

With the above restrictions on the values of y there are only eight different structures that can be made with the various permitted y values. If y_7 is chosen equal to 5/60 then y_8 must be 25/60 and y_9 must be 45/60. One other choice of y_7, y_8 or y_9 can be made but it is identical involving only a shift of the origin from the center of symmetry at (000) to $(0\frac{1}{2}0)$. The eight different structures arise from two possible choices of the y_i values associated with each of $x_1\ z_1$, $x_2\ z_2$ and $x_3\ z_3$, thus giving 2^3 different structures.

The values of $y_i = 5/60$, 15/60, etc. are certainly not exact. By the shape of the peaks on the various Patterson projections it seems reasonable that the y values may be of the order of 2/60 b_o from these idealized values. It should be possible to postulate a trial structure and make electron density projections and thus refine y values. Approximately twenty of these trial structures were postulated and projections were made, however, no useable results were obtained.

Since the method of making electron density projections from trial structures failed to give results, it was thought that the calculation of R correlation factors for the eight possible trials might be useful in determining which of the eight possible rough structures is closest to the true structure. The R correlation factors were calculated for these eight structures using twenty-five (hkh) reflections. Figure

17 shows the values of R for each trial structure plotted with various scaled observed structure factors. The parameters used for each trial structure are listed in Table 6. Two fairly closely related structures, T_5 and T_7, give an appreciably lower R value than the other six. Probably one of these two structures is a fair approximation of the true structure; however, from the value of $R = .475$ it appears that the approximation is not very close to the true structure. The rough structures seem to be so far from the true structure that the technique of making projections from trial structures does not lead to a refinement. A trial structure must be postulated which more closely resembles the true structure in order to proceed with further refinement. The Patterson projections give little or no help in this connection. Since three dimensional projections had not been made it was thought possibly new information would be obtained in this manner.

Visual estimation of the data recorded about b_0 with the Weissenberg camera was completed and two three dimensional projections were made. These were the $H(x0z)$ and $H(x\frac{1}{2}z)$. The data from which these projections were made are quite inaccurate since the absorption errors are large. The projections, however, do give some information concerning the two postulated trial structures which give low R factors. From $H(x0z)$ it appears that T_5 is probably nearest

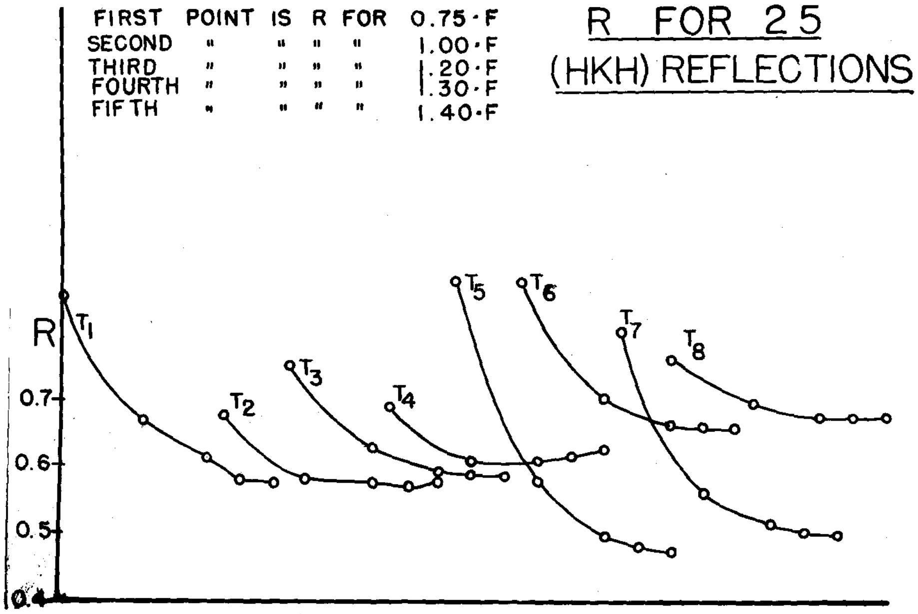


Figure 17 R for 25 (hkh) reflections

Table 6

Parameters of the Eight Possible Structures

Trial Number	$x_1=0.070$ $z_1=0.189$	$x_2=0.220$ $z_2=0.044$	$x_3=0.539$ $z_3=0.065$	$x_4=0.667$ $z_4=0.194$
T_1	$y=0.083$ 0.417	$y=0.083$ 0.417	$y=0.250$ 0.583	$y=0.083$ 0.417 0.750
T_2	0.083 0.750	0.083 0.750	0.250 0.583	0.083 0.417 0.750
T_3	0.583 0.917	0.583 0.917	0.250 0.583	0.083 0.417 0.750
T_4	0.250 0.917	0.250 0.917	0.250 0.583	0.083 0.417 0.750
T_5	0.083 0.417	0.083 0.417	0.583 0.917	0.083 0.417 0.750
T_6	0.083 0.750	0.083 0.750	0.583 0.917	0.083 0.417 0.750
T_7	0.583 0.917	0.583 0.917	0.583 0.917	0.083 0.417 0.750
T_8	0.250 0.917	0.250 0.917	0.583 0.917	0.083 0.417 0.750

the true structure. The observed structure factors obtained from the Weissenberg camera together with those obtained from the precession camera are listed in Table 6.

D. Suggested Methods of Solution

It is difficult to understand exactly why it has been impossible to obtain accurate y parameters. The reason must necessarily be either an error has been made and the present description of the structure is incorrect or the present description is correct but still sufficiently far from the true structure that refinement has been impossible. In attempting to proceed further with this structure determination it is suggested that the entire work so far completed should be examined for errors.

If an error has been made it seems most likely that it would be in the electron density projection upon (010). This should therefore be very carefully examined. A suggested method for testing whether or not this projection is correct is to proceed with the refinement of the x and z parameters. The next step in this refinement is the recalculation of intensities from the parameters obtained from the latest projection upon (010), Figure 16. A new projection upon (010) should then be made adding as many new terms as possible. The procedure should be repeated until the minimum R value is obtained. If the R factor does not drop to 0.20-0.25 for the final refinement then the electron density projection upon (010) may contain an error. A new interpretation of the Patterson down b_o should then be sought. The present interpretation must necessarily be correct or be closely similar to the correct interpretation since the R value of 0.28 is already quite low.

If the electron density projection upon (010) is found to be correct and if no other errors are found which suggest methods of attack, one must assume that the present description of the structure is essentially correct but still too inaccurate to permit refinement. If this is the case the approximately twenty electron density projections of trial structures could be re-examined to see if any suggested directions of refinement have been overlooked. If no new information is obtained from the trial structure technique then a new method of refinement must be found. One refinement technique which could be applied is a variation treatment of y parameters similar to that performed on the eight trial structures. For example this refinement could be made by using minor shifts of the y parameters from those given in Table 6 for T_5 and T_7. If one of these structures is near the real structure then this variation treatment may make R drop sufficiently such that projection technique could be used to complete the refinement.

Table 7

Observed Structure Factors Squared

Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$
Weissenberg data		7	11	1	2
				3	2
(h0ℓ)		(h04)			
		-10	25	(h08)	
(h00)		-8	2	-10	2
2	4	-6	13	-8	11
4	11	-4	45	-6	3
6	8	-2	184	-4	17
8	42	0	10	-2	3
		2	24	0	146
(h01)		4	6	2	0
-7	102	6	0	4	0
-5	26	8	21	6	2
-3	2				
-1	--	(h05)		(h09)	
1	0	-7	78	-7	45
3	84	-5	177	-5	15
5	61	-3	0	-3	25
7	33	-1	220	-1	0
9	4	1	4	1	0
11	11	3	224	3	6
		5	13		
(h02)				(h·0·10)	
-10	15	(h06)		-8	19
-8	16	-8	7	-6	0
-6	41	-6	104	-4	18
-4	189	-4	82	-2	0
-2	240	-2	110	0	0
0	3	0	16	2	12
2	492	2	100		
4	52	4	7	(h·0·11)	
6	74	6	9	-5	11
8	4	8	0	-3	15
		10	3		
(h03)				(h·0·12)	
-5	21	(h07)		-10	2
-3	810	-9	10	-8	0
-1	16	-7	14	-6	7
1	143	-5	137	-4	0
3	3	-3	0	-2	10
5	186	-1	2		

Table 7 (Continued)

Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$
(01ℓ)		-7	0	(41ℓ)	
1	--	-6	0	-13	8
2	21	-5	2	-12	5
3	3	-4	40	-11	0
4	0	-3	0	-10	0
5	34	-2	0	-9	0
6	69	-1	0	-8	13
7	52	0	10	-7	0
8	84	1	0	-6	0
9	0	2	8	-5	0
10	0	3	4	-4	0
11	19	4	6	-3	9
		5	2	-2	17
(11ℓ)		6	75	-1	21
-12	8	7	12	0	31
-11	0	8	0	1	9
-10	13	9	43	2	15
-9	50	10	1	3	85
-8	0			4	154
-7	12	(31ℓ)		5	33
-6	0	-11	42	6	6
-5	5	-10	5	7	1
-4	0	-9	14	8	1
-3	2	-8	12	9	4
-2	0	-7	0	10	0
-1	0	-6	2	11	0
0	0	-5	27	12	3
1	0	-4	0		
2	0	-3	40	(51ℓ)	
3	2	-2	8	-13	3
4	0	-1	7	-12	0
5	4	0	0	-11	3
6	44	1	9	-10	4
7	115	2	12	-9	3
8	0	3	27	-8	12
9	5	4	122	-7	0
10	4	5	27	-6	0
11	0	6	9	-5	22
12	1	7	1	-4	18
		8	13	-3	19
(21ℓ)		9	1	-2	7
-10	27	10	1	-1	10
-9	3	11	0	0	41
-8	3	12	1	1	3

Table 7 (Continued)

Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$
2	0	3	1	-3	1
3	18	4	5	-2	4
4	5			0	4
6	15	(91ℓ)		1	10
7	17	-11	2	2	38
11	1	-10	5	3	60
		-8	6	4	6
(61ℓ)		-6	3	8	2
-14	3	-5	13	9	14
-12	1	-3	2	10	49
-11	1	2	12		
-10	1	5	4	(32ℓ)	
-8	7	6	4	-9	24
-7	6			-7	23
-6	42	(10·1ℓ)		-6	11
-5	18	-5	3	-5	6
-2	53	-3	5	-4	11
1	22			-3	19
2	5			-2	12
3	9	(02ℓ)		0	21
4	7	3	3	2	28
5	26	4	23	4	5
7	1	5	2	6	23
9	4	6	3	9	1
10	1	8	21	12	1
		9	7		
(71ℓ)				(42ℓ)	
-4	2	(12ℓ)		-8	31
-3	9	-6	5	-7	11
-2	16	-5	196	-6	6
-1	5	-4	100	-4	27
0	30	2	115	-3	7
1	32	3	48	-2	11
2	11	4	54	-1	35
5	2	5	11	0	16
6	2	6	30	1	11
8	1	7	29	2	9
9	4	11	7	3	3
				4	51
(81ℓ)		(22ℓ)		5	4
-8	12	-9	10	6	7
-7	7	-8	26	7	12
-5	9	-5	76	8	17
-3	18	-4	26	11	4

Table 7 (Continued)

Indices	$F^2_{obsd.}$
(52ℓ)	
-11	14
-9	4
-8	4
-7	12
-6	4
-4	6
-3	19
-2	84
-1	58
0	65
2	12
3	21
4	5
6	23
7	8
8	3
(62ℓ)	
-12	6
-11	2
-10	6
-9	2
-8	5
-7	14
-5	18
-3	1
-1	39
0	13
1	16
2	5
3	51
4	7
6	4
7	1
9	1
(72ℓ)	
-11	3
-9	7
-6	12
-5	3
-3	10
-1	3
1	16
2	13
3	4
4	7
5	15
8	2
(82ℓ)	
-6	9
-5	11
-3	16
-1	3
3	7
4	2
5	7
(92ℓ)	
-8	37
-4	13
-3	3
-2	7
-1	4
0	19
1	2
3	5
4	3
(10·2ℓ)	
-10	4
-1	6
2	5
(12·2·$\bar{3}$)	4
(03ℓ)	
2	490
3	17
4	315
5	27
8	168
(13ℓ)	
-7	12
-6	47
-5	87
-4	92
-3	69
1	110
3	179
4	7
6	6
9	22
10	8
(23ℓ)	
-8	27
-6	261
-5	33
-4	140
-2	1
-1	2
0	375
1	17
2	558
3	62
4	41
8	3
9	3
10	2
(33ℓ)	
-11	10
-9	44
-7	13
-6	15
-5	62
-3	25
-2	9
-1	120
1	60
2	20
3	177
5	10
6	4
7	1
8	4
9	1

Table 7 (Continued)

Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$
10	2	2	30	(04ℓ)	
		3	6	2	14
(43ℓ)		4	1	3	12
-9	8	5	1	4	12
-7	58	7	5	5	16
-5	9			6	20
-4	42	(73ℓ)		7	7
0	70	-10	8	8	44
1	3	-8	3		
2	22	-7	30	(14ℓ)	
3	5	-5	20	-8	8
4	28	-3	23	-6	10
5	1	-1	6	-5	80
6	2	1	8	-3	57
7	8	3	8	-1	28
8	2	5	10	2	4
9	8	6	8	3	3
		8	2	4	25
(53ℓ)				5	7
-11	7	(83ℓ)		6	50
-9	8	-12	6		
-8	18	-11	5	(24ℓ)	
-7	8	-9	3	-9	41
-6	10	-7	2	-7	7
-4	5	-6	13	-5	17
-3	150	-4	29	-3	11
-2	3	0	6	-1	3
-1	243	4	12	0	15
0	22	5	4	2	23
3	4	6	4	3	6
4	4			5	8
5	10	(93ℓ)		6	5
6	3	-3	5	9	23
7	25	0	4	10	22
8	6	8	2	11	4
9	4	10	1		
				(34ℓ)	
(63ℓ)		(10·3ℓ)		-7	13
-12	3	-10	3	-6	4
-9	7	-8	9	-5	8
-8	3	-6	2	-4	12
-6	22	0	5	-3	10
-4	19	2	7	-1	2
-1	2	3	2	0	2

Table 7 (Continued)

Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$
2	8	0	18	(25ℓ)	
3	71	2	7	-8	16
4	15	3	5	-7	14
5	24	4	5	-6	25
6	2	6	5	-5	12
8	1	7	4	-3	26
9	4	8	1	-2	1
		9	5	-1	8
(44ℓ)				0	49
-8	19	(74ℓ)		1	10
-7	3	-6	2	3	9
-6	2	-5	13	4	18
-5	2	-3	3	6	19
-4	1	-2	20	7	39
-2	59	0	21		
-1	2	3	15	(35ℓ)	
0	11	4	1	-7	3
1	27	8	3	-5	48
2	3			-4	19
3	84	(84ℓ)		-2	35
4	10	-5	2	-1	6
5	1	-4	14	2	1
6	24	3	1	3	1
7	4	5	7	4	57
8	4			5	1
11	4	(05ℓ)		6	7
		1	39	7	2
(54ℓ)		2	78	8	1
-8	15	4	4		
-7	3	7	28	(45ℓ)	
-2	10	8	9	-7	18
-1	3			-6	5
0	3	(15ℓ)		-5	2
2	4	-8	25	-4	13
3	4	-7	38	-3	44
4	5	-4	43	-2	7
6	6	-3	43	1	47
7	4	-2	13	2	39
8	5	0	13	3	23
		1	2	4	3
(64ℓ)		4	46	5	7
-8	3	5	40	6	6
-7	15	6	22	8	1
-2	14			9	2

Table 7 (Continued)

Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$
10	2	(95ℓ)		(36ℓ)	
		3	1	-10	18
(55ℓ)		4	1	-5	4
-9	17			-3	27
-8	3	(10·5·3)	1	-2	3
-7	1			-1	31
-4	4			0	9
-3	9	(06ℓ)		2	6
0	22	2	52	3	1
1	4	3	8	4	7
2	6	7	28	5	17
5	6	8	33	6	15
		9	19	7	7
(65ℓ)					
-8	6	(16ℓ)		(46ℓ)	
-5	20	-8	17	-6	16
-2	9	-6	16	1	15
-1	4	-5	46	2	14
1	14	-3	28	5	15
3	11	0	7		
5	1	1	31	(56ℓ)	
6	4	2	2	-7	43
		3	12	-6	9
(75ℓ)		5	31	-5	6
-7	14	6	18	-4	7
-6	19	8	29	-3	31
-2	29			-1	19
-1	11	(26ℓ)		0	19
0	16	-9	21	1	40
1	5	-7	16	2	3
2	7	-6	28	3	13
3	4	-5	6	4	9
4	1	-4	101	5	21
5	1	-3	22		
6	3	-2	2	(66ℓ)	
7	1	-1	6	-5	7
		0	36	-4	4
(85ℓ)		2	50	-3	5
-8	16	3	17	0	5
2	2	4	23	2	3
4	3	6	8	3	5
5	2	7	10	4	4
		8	16	7	2
		10	1		

Table 7 (Continued)

Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$	Indices	$F^2_{obsd.}$
(76ℓ)		5	12	-3	4
-9	10	6	2	-2	108
-3	4	8	2	0	3
-1	17			2	16
2	3	(47ℓ)		4	7
6	1	-6	3	5	16
		-4	3	6	15
(86ℓ)		-3	2	7	6
-6	8	-2	13		
2	9	3	1	(28ℓ)	
5	8	4	1	-8	8
		7	1	-7	8
(964)	2	9	3	-6	14
				-5	24
		(57ℓ)		-3	2
(07ℓ)		-7	6	-1	55
1	5	-5	4	1	10
2	11	-4	17	2	11
4	14	-1	31	3	9
		1	4	4	19
(17ℓ)		2	7	7	1
-7	7	3	4	8	4
-5	11	6	2	9	1
-3	21	7	6		
1	20			(38ℓ)	
4	3	(67ℓ)		-5	2
		-6	18	-4	14
(27ℓ)		-5	4	-3	6
-4	44	0	10	-2	16
-1	18	2	23	0	4
0	21	5	8	3	21
2	40			4	18
4	6	(874)	5	6	1
				7	1
(37ℓ)		(972)	3	9	1
-6	2				
-5	2			(48ℓ)	
-3	11	(08ℓ)		-9	6
-2	7	1	43	-5	57
-1	3	6	33	-3	2
1	8	7	15	-1	3
2	1				
3	4	(18ℓ)			
4	3	-4	14		

Table 7 (Continued)

Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$
2	5	(19ℓ)		(69ℓ)	
3	28	-6	13	0	5
		-4	18	3	4
(58ℓ)		-3	7		
-8	6	0	12	(792)	4
-5	5	3	3		
-4	5	5	8		
-3	2	6	5	(0·10ℓ)	
-2	4			3	17
-1	4	(29ℓ)		4	4
0	4	-3	5	6	12
4	1	-2	2		
6	1	-1	5	(1·10ℓ)	
9	1	0	17	1	2
		2	8	2	2
(68ℓ)		3	12	3	11
-9	3			4	4
-8	5	(39ℓ)			
-7	3	-5	20	(2·10ℓ)	
-6	2	-4	14	-7	3
-5	8	-3	1	2	1
-3	3	-2	17	5	3
-1	5	-1	5		
2	1	0	2	(3·10ℓ)	
3	4	2	7	-6	2
4	6	3	28	0	7
6	1	6	5	3	4
8	1			5	2
		(49ℓ)			
(78ℓ)		-7	7	(4·10ℓ)	
-8	11	-4	1	-6	3
0	5	-3	7	0	10
2	2	-1	6	1	2
4	2	0	3		
7	1	2	8		
		4	6		
		5	3		
(09ℓ)					
1	35	(59ℓ)			
2	49	-1	4		
5	5	1	4		
6	14	4	4		

Table 7 (Continued)

Indices	$F^2_{obsd.}$
Precession data	
(00ℓ)	
2	9
4	13
6	20
8	224
10	5
12	2
(01ℓ)	
1	--
2	58
3	19
5	62
6	76
7	72
8	88
11	12
14	2
(02ℓ)	
0	152
3	163
4	44
5	2
6	58
8	18
9	7
12	2
13	2
(03ℓ)	
1	14
2	717
3	17
4	392
5	41
6	295
8	2
11	4
14	4
(04ℓ)	
0	204
2	21
3	17
4	17
5	18
6	20
7	5
8	34
12	2
(05ℓ)	
1	276
2	160
4	2
7	52
8	9
10	2
(06ℓ)	
0	432
2	119
3	20
6	2
7	2
8	59
9	25
10	8
(07ℓ)	
1	10
2	15
4	13
7	11
8	2
9	4
10	6
(08ℓ)	
0	23
1	10
4	3
5	2
6	53
10	2
(09ℓ)	
1	52
2	48
5	7
6	37
8	2
9	8
10	8
(0•10ℓ)	
0	7
3	20
4	2
5	2
6	8
8	4
10	2
(0•11ℓ)	
1	4
2	4
3	11
5	6
(0•12ℓ)	
2	2
4	2
8	2
(0•13ℓ)	
2	2
4	2
6	4
8	2
9	1
(0•14ℓ)	
0	2
1	10
2	2
3	2

Table 7 (Continued)

Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$	Indices	$F^2_{\text{obsd.}}$
(hk0)		(4k0)		(8k0)	
		0	24	0	96
(0k0)		1	49	3	24
2	196	2	46	6	6
4	232	3	150	7	11
6	565	4	38		
8	45	5	2	(9k0)	
10	10	6	2	1	2
14	4	7	2	2	55
		8	8	4	2
(1k0)		9	10	5	9
0	--	10	26	6	2
5	295	11	2	8	8
6	34				
7	11	(5k0)		(10·k·0)	
8	28	1	96	3	16
9	38	2	162	4	7
11	2	3	48		
12	4	4	15		
14	8	5	67	(hkh)	
		6	38		
(2k0)		8	22	(0k0)	
0	23	9	4	2	--
1	30	12	5	4	400
2	31			6	890
3	954	(6k0)		8	62
4	55	0	17	10	16
5	18	2	26		
6	118	3	4	(1k1)	
7	46	4	48	0	--
9	46	6	12	1	--
11	8	7	20	2	0
12	2	9	10	3	705
		10	7	4	218
(3k0)		11	3	5	28
1	15			6	78
2	130	(7k0)		7	208
4	5	1	53	9	2
6	35	2	2	10	8
8	19	3	2	11	6
9	10	4	55		
10	18	5	36	(2k2)	
11	45	7	2	0	860
		8	17	1	13

Table 7 (Continued)

Indices	$F^2_{obsd.}$
3	1125
4	62
6	198
7	137
8	24
9	12
10	4
11	2
$(3k3)$	
0	18
1	42
3	322
4	122
5	5
6	2
7	8
8	27
9	72
10	18
$(4k4)$	
0	14
1	294
2	65
3	54
4	20
5	11
7	2
8	32
9	18
10	8
$(5k5)$	
0	32
3	27
5	64
6	64
9	6
10	9
$(6k6)$	
0	30
2	8
3	2
4	14
5	14
$(hk\bar{h})$	
$(0k0)$	
2	42
4	45
6	124
8	6
10	1
$(1k\bar{1})$	
0	75
1	--
2	32
3	1
6	1
$(2k\bar{2})$	
0	330
2	19
3	2
5	1
6	2
9	1
11	2
$(3k\bar{3})$	
0	375
1	47
2	22
3	49
4	20
6	71
7	15
8	7
$(4k\bar{4})$	
0	5
2	21
3	38
5	12
7	2
9	2
$(5k\bar{5})$	
0	47
1	6
6	2
$(6k\bar{6})$	
0	29
1	30
3	8
7	18
$(7k\bar{7})$	
0	2
3	28
5	8
$(8k\bar{8})$	
0	4
1	4

V. DISCUSSION

From a study of the iodine-iodine distances in tetramethylammonium pentaiodide, Figure 8, one notes that groups of five iodine atoms may be separated out from other groups by 3.55 Å while the distances within one group are only 2.93 and 3.14 Å. It seems reasonable to think of these groups of five atoms as the pentaiodide anion. The nature of the bonds in this V-shaped anion is certainly quite different from the sp^3d^2 bonds observed in the coplanar square ICl_4^-. The bonding of the apex iodine must also be different from the sp^3d bonding observed in ICl_2^-, for the bond distances are 0.37 Å larger than those expected for this type bonding.

The unequal spacing in the arms of the pentaiodide anion suggests that the bonding between the end two iodine atoms is stronger than the bonding between the apex iodine and the adjacent atoms. This leads one to think of the pentaiodide anion as being made of two iodine molecules bonded more or less weakly to an iodide ion. It may also be noted that the linear, asymmetric triiodide anion reported by Mooney may be considered to be one iodine molecule similarly bonded to an iodide ion.

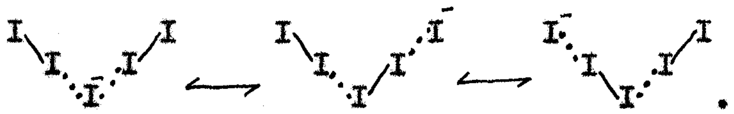
When the nature of an unusual chemical bond is found to be intermediate between the nature of two ordinary bonds then this unusual bond can often be described as a resonance between the two ordinary bonds. The exceptionally long iodine-iodine bond, 3.1 Å, found in ammonium triiodide and this pentaiodide structure might reasonably be considered to be a resonance between the ordinary covalent iodine-iodine bond and some longer interaction. The nature of the longer bond is probably ion-induced dipole interaction since the iodine molecule is quite polarizable due to its large size and to the fact that the electrons are not extremely tightly held in iodine.

The triiodide anion can be pictorially represented by a resonance hybrid of the following structures

$$\overset{-}{I}\cdots I - I \longleftrightarrow I - I \cdots I^{-}.$$

In order to show that it is reasonable to think of a resonance of this type, one can show by molecular orbital treatment (17) that resonance stabilization is expected. Four electrons must be placed in two molecular orbitals. Three molecular orbitals are formed from linear combinations of the atomic orbitals of each iodine. These atomic orbitals can be considered to be the p-orbitals of the valence shell. If the Coulombic integrals are assumed to be equal and if exchange integrals, β, for adjacent atoms are assumed equal the resonance stabilization for the resonating structure is $2(\sqrt{2} - 1)\beta$ over that of either individual contributing structures. This value is only a rough approximation of the resonance energy of the triiodide anion in ammonium triiodide since the anion is not symmetrical and the Coulombic integrals are probably not equal. It does, however, indicate that resonance of this type is reasonable.

These ideas of resonance may be extended to the pentaiodide anion. Three contributing structures can be drawn



The iodine-iodine bonds on the ends of the arms of the V contain two-thirds covalent character while the other bonds contain only one-third. This should lead to unequal length bonds, as are observed, assuming equal contribution of each form. In the case of the triiodide anion, equal contribution from both contributing forms should lead to a linear, symmetrical anion. If, however, the electrostatic field is different at opposite ends of the linear ion, one would expect unequal contributions from the two forms thus leading to a linear but asymmetrical ion. This is believed to be the case in ammonium triiodide. An unequal field about the apex and ends of the arms of the pentaiodide anion could also change the contribution of the various forms thus affecting the bond lengths.

As the cation in a polyiodide is made smaller, thus concentrating the positive charge, the resonating form with the negative charge closest to the positive charge will be dominant. The iodide-iodine bond length will then get progressively larger and eventually a sufficiently small cation will be reached so that there is insufficient resonance stabilization to make the structure stable. This is offered as an explanation for the fact that small cations do not form polyiodides.

The structure of iodine is a layer structure similar in some respects to the pentaiodide structure. Each iodine atom has a nearest neighbor at 2.67 Å and two second nearest neighbors at 3.54 Å. The separation of the pentaiodide anions is 3.55 Å. The layer separation in both structures is about 4.3 Å. The expected van der Waals iodine-iodine distance (1, p.189) is 4.3 Å.

In both structures the 3.55 Å distances are within the plane of the iodine bonding. Apparently these short van der Waals distances are due to the strong interaction of iodines in a plane because of the high polarizability in the direction of the bonds.

Though no direct evidence has ever been obtained concerning the position of the tetramethylammonium cation, its position is greatly restricted by the symmetry of the space group and the positions of the iodine atoms. When the nitrogen is placed upon the 2-fold axis the methyl groups may be positioned in such a manner as to take advantage of the nonplanarity of the iodine nets in order to obtain maximum room. Indeed, the nonplanarity is thought to be due to the movement of the arms of the V-shaped pentaiodide anion into the space between methyl groups. Though the iodine-carbon distances are 4.2 Å or larger, free rotation of the methyl group about the 2-fold axis is unlikely since there would then be no immediately obvious reason for this particular type of nonplanarity observed.

It would be interesting to see what the structure of the pentaiodide anion is with other cations present. With a cation slightly smaller than the tetramethylammonium cation the nets of iodine atoms may become coplanar. With an appreciably smaller cation the pentaiodide does not form. Probably no new structures would be found as one decreases the size of the cation from the size of tetramethylammonium cation. However, if the cations were made progressively larger, eventually a point would be reached at which the holes in the present anion packing were too small to contain the cation and then certainly a new packing would be found. Probably the pentaiodide anion would remain V-shaped since resonating negative charges can remain close to a positive charge inside the V. There seems to be no apparent reason why a linear anion could not form since a molecular orbital treatment indicates resonance stabilization would be present. The central atom would make use of only one p-orbital in a linear configuration, unlike the apex iodine in the V-shaped configuration which uses two different p-orbitals. These two cases are certainly different, however they both seem possible. It is, however, not possible to have a resonance of the type described above with a V-shaped triiodide anion or with a W-shaped pentaiodide anion.

From the work so far completed upon the enneaiodide structure, little can be said with certainty concerning the structure. There is no information obtained so far, however, which makes a resonating structure impossible. In fact the present electron density projection seems to support the idea of iodine molecules interacting with iodide ions. However, there are some indications that the interaction may be weaker. The interpretation of the sheet of iodine molecules packed parallel to each other with their axis in the a_o-c_o direction leads one to suggest that the enneaiodide structure may be a solid solution type structure in which iodine molecules have packed with the cation and possibly some type pentaiodide anion. The peak separations, however, are not sufficient to rule out a distance of as low as 3.1 Å from these iodine molecules to an iodide ion.

There are several configurations which the enneaiodide anion could conceivably have. Since the pentaiodide anion uses two different p-orbitals in its resonance one might expect the heptaiodide anion to have the configuration of an iodide at the origin of a set of Cartesian coordinates with three iodine molecules on the positive axes with their axes aligned with the Cartesian coordinates. If the use of separate p-orbitals were required the heptaiodide would be the largest polyiodide to form. Since the enneaiodide forms, some other bonding explanation is necessary. It is difficult to understand why the I_{11}^- and I_{13}^- ions do not form if the same p-orbitals may be used on opposite sides of the iodide ion. Packing considerations may be sufficient to prevent formation of the solid, however, these higher ions are not found in solution. One could hybridize sp^3 bonds for the iodide ion and thus make I_9 the upper limit of the polyiodides. If this is postulated it is difficult to explain why the pentaiodide has a 90° angle, and also the indications are a tetrahedral enneaiodide is impossible from the work so far completed in the enneaiodide structure determination.

Though little can be said with certainty only a few possible structures for enneaiodide seem reasonable. A structure with iodine molecules packed with the cation and a triiodide or pentaiodide anion seems quite possible from the present status of the structure determination. Another possible arrangement is that of an X-shaped ion with one arm removed and made normal to the paper. This would use all the p-orbitals at least once and one of them twice.

The heptaiodide does not crystallize with the tetramethylammonium cation; however, it does form with the trimethylphenylammonium cation. This is difficult to understand since the stability is a function of symmetry of the cation. One possible explanation may be that coincidently the packing is such that no tetramethylammonium heptaiodide forms while the tetramethylammonium enneaiodide and the trimethylphenylammonium heptaiodide may be isomorphic with the phenyl group occupying one of the positions occupied by I_2 in the enneaiodide structure.

VI. SUMMARY

The bonding in polyiodides is quite different from the bonding in polyhalogen compounds which contain two or more different halogens. The bonding in the polyiodides is interpreted without the use of d-orbitals above the valence shell. The bonding may be thought of as an interaction of iodine molecules with an iodide ion. Resonance of the various forms of the ions leads to stabilization. The size of the cation and the packing in the crystal affect the contribution of the various resonating forms and thus the length of the bonds. The decrease of the resonance stabilization when the cation is small is offered as an explanation for why the stability of polyiodides is a function of the size of the cation present and why higher polyiodides form only with large cations.

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