Acta Cryst. (1955). 8, 814

The Structure of Tetramethylammonium Enneaiodide*

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(*Received* 4 *April* 1955)

The structure of tetramethylammonium enneaiodide, $N(CH_3)_4I_9$, has been found by two-dimensional Fourier methods coupled with the use of inequalities, and has been refined by difference syntheses. The structure consists of planes of iodine atoms; within the plane there is some justification for singling out I_5^- ions, similar to, but less symmetrical than, the I_5^- ion in tetramethylammonium pentaiodide. Between these planes lie the $N(CH_3)_4^+$ ions, each cation surrounded by six I_2 molecules with their axes normal to the main planes of iodines, and weakly associated with them. Except for the I_2 molecules between planes all I–I distances are considerably longer than the distance in I_2, and comparable with those found in I_3^-, I_5^- and I_8^{2-}.

Introduction

A recent structural study (Hach & Rundle, 1951) suggests that the polyiodides are not closely related to other polyhalides. In tetramethylammonium pentaiodide V-shaped I_5^- ions were found with I–I distances of 2·93 and 3·14 Å, far greater than the I–I distance in I_2 (2·70 Å, Harris, Mack & Blake, 1928), but not unlike the distances reported by Mooney (1935) for the unsymmetrical I_3^- ion. The latter report had been given little weight in discussions of polyhalide ions (Pauling, 1940), since it was in contrast to reports of a symmetrical, linear ICl_2^- ion (Wyckoff, 1920; Mooney, 1939) and a symmetrical, square ICl_4^- ion (Mooney, 1938), both with I–Cl distances quite near the sum of the covalent radii. More recently long I–I distances, similar to those in I_3^- and I_5^- ions, have been reported for the complex I_8^{2-} ion (Havinga, Boswijk & Wiebenga, 1954).

Hach & Rundle have suggested that iodine forms strong bonds using 5*d* orbitals (outer *d* orbitals) only where forming bonds to the more electronegative halogens, and that the long bonds in polyiodide ions result from the interaction of a negative iodide ion with the highly polarizable iodine molecule. The interaction is strong enough, apparently, to lead to partial charge transfer through resonance of the covalent bond, and the final structure is further complicated by the influence of neighboring positive ions which, in the crystal, lead to non-equivalent bonds even in the case of I_3^-.

Though this picture of the nature of polyiodide ions appears relatively satisfactory, it permits no easy inference of the structure of the more complex polyiodide ions. It was to see if the more complex ions conform to some consistent structural pattern that the study of the I_9^- ion was undertaken.

Structure determination

Preparation of the compound

$N(CH_3)_4I_9$ was obtained in the form of lath-shaped crystals by adding a two- to threefold excess of iodine to tetramethylammonium iodide dissolved in boiling alcohol. Two separate phases formed, $N(CH_3)_4I_5$ and $N(CH_3)_4I_9$, the relative amounts depending upon the excess of iodine added.

Physical data

The monoclinic crystals of $N(CH_3)_4I_9$ possess a greenish-black metallic luster, and, on exposure to air, slowly lose iodine. The lattice constants were determined from zero-layer Weissenberg and precession photographs. The unit cell dimensions were found to be

$$a_0 = 11{\cdot}60,\quad b_0 = 15{\cdot}10,\quad c_0 = 13{\cdot}18\ \text{Å};\quad \beta = 95^\circ\,25'\,.$$

Samples were analyzed for tetramethylammonium iodide by volatilizing free iodine at about 200° C. The average of three determinations was 16·53%, as compared to the theoretical value of 16·53%. The observed density, obtained using a pycnometer with mineral oil, was 3·47 g.cm.$^{-3}$ as against a calculated density of 3·51 g.cm.$^{-3}$ obtained from X-ray data for 4 $N(CH_3)_4I_9$ per unit cell.

A primitive lattice was indicated by reflections from all types of planes, except that ($h0l$) reflections were observed for $h+l = 2n$ only, and ($0k0$) reflections were present only for $k = 2n$. The space group is, accordingly, $P2_1/n$, for this choice of axes.

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* Journal Paper No. J-2731 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 1116.

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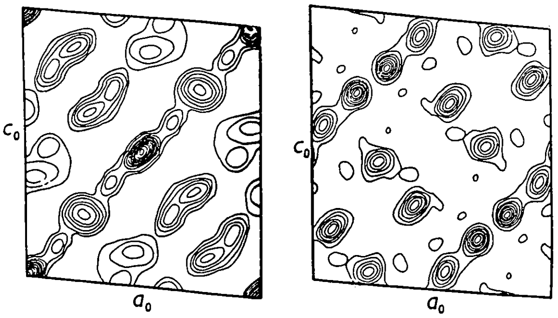
Parameter determination

About 350 independent reflections $(h0l)$, $(hk0)$, $(0kl)$, (hkh) and $(hk\bar{h})$ were obtained using a precession camera. Timed exposures were prepared on a G. E. XRD-3 diffraction unit employing regulated current and voltage. The intensities were judged by visual estimation methods and then placed on an absolute scale using the method of Wilson (1942).



(a) (b)

Fig. 1. (a) Patterson projection on to the (010) plane. (b) Fourier projection on to the (010) plane.

Patterson projections were synthesized on IBM, using punched cards. The high degree of coincidence in the projection precluded the possibility of obtaining more exact information for Fourier analysis, but the projection on to the (010) plane (Fig. 1(a)) did indicate that all the iodine atoms projected into lines in the direction of $(\mathbf{a}+\mathbf{c})$, approximately 3 Å apart.

Using trial-and-error procedures restricted by the possible interpretations of $P(x, z)$, the electron-density map shown in Fig. 1(b) was obtained. A study of this projection suggested that three iodine atoms coincided in projection at $x = 42/60$ and $z = 10/60$ of the respective axial lengths. It will be noted that the peaks are nicely defined and that the electron densities are those expected for three atoms in one peak and two in the remaining. In addition the peaks are elongated in the direction $(\mathbf{a}+\mathbf{c})$ suggesting that the iodine atoms do not project exactly upon one another.

The reliability factor, $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$, for this interpretation was 0·29.

Inequalities

Because of difficulties encountered in determining phases for further Fourier analysis, the method of inequalities was applied to the data in the form of Grison's (1951) relationships. Since the contribution to scattering was predominantly from iodine, the unitary structure factor reduced to $U(hkl) = F(hkl)/Nf(hkl)$.

To determine the feasibility of this approach the method was first applied to the $(h0l)$ data, since these data possessed the largest σ value. Signs of a total of 59 out of 79 observed reflections were obtained (Table 1). A Fourier projection (010) was synthesized on X-RAC. The results were almost identical with the first electron-density map obtained (Fig. 1(b)).

Having established the validity of the Fourier projection on to the (010) plane, inequalities were applied to other planes to obtain information concerning the y parameters. Owing to a smaller number of reflections of larger amplitudes for these other zones, it was necessary to apply the self-consistent technique based on the probable validity of the relation $S_{H+K} = S_H . S_K$, where S denotes the algebraic sign of three strong reflections (Zachariasen, 1952; Sayre, 1952; Cochran, 1952).

The signs of $27(0kl)$ reflections were obtained in this fashion, and a Fourier projection was prepared on X-RAC. The phases of weaker amplitudes were determined by the predominance of one sign among the vectors.

Table 1. *Unitary factors and signs*

Indices	$U(h0l)$
$(h00)$	
4	+0·10
8	−0·36
$(h01)$	
$\bar{7}$	−0·46
$\bar{5}$	+0·15
3	−0·21
5	−0·24
7	+0·25
9	+0·15
11	−0·40
$(h02)$	
$\overline{10}$	−0·41
$\bar{8}$	+0·24
$\bar{6}$	+0·25
$\bar{4}$	+0·37
$\bar{2}$	+0·33
2	−0·44
4	+0·19
6	−0·33
8	+0·12
$(h03)$	
$\bar{5}$	+0·15
$\bar{3}$	−0·71
1	−0·25
5	+0·46
7	+0·17
$(h04)$	
$\overline{10}$	+0·60
$\bar{6}$	+0·15
$\bar{4}$	+0·21
$\bar{2}$	−0·34
0	+0·09
2	+0·13
8	+0·31
$(h05)$	
$\bar{7}$	−0·52
$\bar{5}$	−0·55
1	+0·41
3	+0·47
5	−0·15
$(h06)$	
$\bar{8}$	−0·22
$\bar{6}$	+0·52
$\bar{4}$	−0·37
$\bar{2}$	+0·35
0	+0·13
2	−0·34
$(h07)$	
$\bar{9}$	−0·38
$\bar{7}$	−0·29
5	+0·65
$(h08)$	
$\bar{8}$	+0·39
$\bar{4}$	−0·24
0	−0·66
$(h09)$	
$\bar{7}$	+0·72
$\bar{5}$	−0·31
$\bar{3}$	−0·32
$(h,0,10)$	
$\bar{8}$	−0·75
$\bar{4}$	−0·36
2	+0·25
$(h,0,11)$	
$\bar{5}$	+0·40
$\bar{3}$	+0·39
$(h,0,12)$	
$\bar{6}$	+0·49
$\bar{2}$	+0·38

The application of inequalities by the above method to ($hk0$) data did not result in any useful information, despite the considerable degree of consistency obtained among signs of the structure factors.

These analytical methods, unfortunately, did not provide a structure with satisfactory holes for the large tetramethylammonium cation, but enough information was obtained from the projection on (100) to prepare scale models, whereby it was discovered that a simple shift in two y parameters led to satisfactory holes. This shift altered the signs of four major ($0kl$) reflections obtained from the inequalities, and permitted refinement, hitherto unattainable.

Refinement of the parameters

Successive difference syntheses for both ($0kl$) and ($hk0$) data were prepared until the change in the reliability factor, R, was negligible.

In addition, the parameters obtained from these two planes were used to calculate the R factors for ($h0l$) and (hkh) data. The R factors for observed ($h0l$), ($0kl$), ($hk0$) and (hkh) data, including missing reflections weighted as half of the lowest observed intensity, are respectively, 0·17, 0·18, 0·17 and 0·16. The final values of the parameters are given in Table 2.

Table 2. *Atomic coordinates*

Difference syntheses parameters

Atom	x	y	z
1	0·046	0·880	0·586
2	0·191	0·729	0·710
3	0·181	0·084	0·690
4	0·150	0·455	0·665
5	0·041	0·318	0·534
6	0·211	0·058	0·041
7	0·076	0·084	0·190
8	0·249	0·400	0·061
9	0·086	0·416	0·189

The agreement between calculated and observed structure factors is shown in Table 3. Important iodine distances are given in Table 4.

The refinement was hampered by the quality of the data and the fact that only 350 independent reflections were obtained for solving this 27-parameter problem. It was extremely difficult to obtain good single crystals of suitable size, and it proved to be extremely time consuming to obtain high-order reflections without the use of large crystals with a prohibitive degree of absorption. The crystals generally contained flaws, and were, as previously mentioned, unstable in air. This discouraged an attempt to make a complete three-dimensional study. Nonetheless, differences in I–I distances greater than 0·2 Å are certainly significant, and the general nature of the structure is clear from work of this accuracy.

Table 3. *Observed and calculated structure factors*

hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}
020	140	+146	660	35	+44	031	37	+23	094	0	+25
040	152	-151	670	40	-41	032	268	+227	095	26	+22
060	238	-235	680	0	-3	033	41	-50	096	61	-61
080	67	-76	690	40	+49	034	198	-181	097	0	+2
0,10,0	32	+30	6,10,0	27	-33	035	64	-50	098	14	+6
0,12,0	12	+16	6,11,0	17	+24	036	172	+161	099	28	+22
0,14,0	20	-14	710	73	-70	037	0	0	0,9,10	28	+6
130	0	+2	720	14	-14	038	14	17	0,10,0	27	+25
140	14	-7	730	20	-30	039	0	-16	0,10,1	0	+11
150	172	-158	740	74	-59	0,3,10	0	-18	0,10,2	0	-2
160	58	-69	750	33	+39	0,3,11	20	+15	0,10,3	42	+20
170	33	+35	760	14	-17	0,3,12	0	+12	0,10,4	14	+4
180	53	+44	770	0	-9	0,3,13	0	+11	0,10,5	14	-15
190	68	+75	780	41	+51	0,3,14	20	-22	0,10,6	28	-17
1,10,0	0	+8	790	10	-19	040	143	-141	0,10,7	0	-8
1,11,0	14	+6	800	99	-89	041	22	+21	0,10,8	20	-18
1,12,0	20	+35	810	0	+1	042	46	-61	0,10,9	0	-14
1,13,0	0	-1	820	0	+9	043	41	-20	0,11,1	20	-18
1,14,0	28	-18	830	49	+59	044	41	+25	0,11,2	20	-22
200	48	-58	840	0	+6	045	43	-35	0,11,3	33	+34
210	57	-79	850	0	+9	046	45	32	0,11,4	0	+2
220	56	-56	860	25	+35	047	22	-13	0,11,5	25	-21
230	309	-270	870	33	-24	048	58	+45	0,11,6	0	-8
240	74	-73	880	0	+13	049	0	+7	0,12,0	14	+18
250	135	-127	910	14	-3	0,4,10	0	-7	0,12,1	0	+9
260	109	+102	920	74	+72	0,4,11	0	-6	0,12,2	14	-21
270	72	-59	930	10	+12	0,4,12	14	-7	0,12,3	0	-16
280	0	-3	940	14	+19	051	167	+140	0,12,4	14	+12
290	68	+85	950	30	+36	052	127	+122	0,12,5	0	-3
2,10,0	0	+22	960	14	+10	053	0	-10	0,12,6	0	+12
2,11,0	28	+40	970	0	-5	054	14	-8	0,13,1	0	-1
2,12,0	14	+10	980	28	-21	055	0	+6	0,13,2	14	+16
310	33	-20	10,0,0	10	-13	056	0	+5	0,13,3	0	+6
320	114	+102	10,1,0	0	+7	057	72	-54	0,13,4	14	-6
330	0	+16	10,2,0	0	-4	058	30	+24	0,13,5	0	-11
340	22	+3	10,3,0	40	+38	059	0	-10	0,13,6	20	+5
350	10	+12	10,4,0	27	+24	0,5,10	14	-25	0,14,0	14	-10
360	60	+83	10,5,0	7	+9	060	209	-206	0,14,1	32	-24
370	0	+19	10,6,0	10	-17	061	0	+2	0,14,2	14	-13
380	39	+29	002	30	-38	062	109	+92	0,14,3	14	-10
390	32	+47	004	37	+41	063	45	+33	002	20	-25
3,10,0	36	-13	006	45	+57	064	0	-10	004	32	+34
3,11,0	67	-60	008	150	-140	065	0	-2	006	40	+51
400	49	+56	0,0,10	22	+13	066	14	-22	008	121	-113
410	70	-66	0,0,12	14	-14	067	74	+71	0,0,10	10	+12
420	68	-63	012	76	+87	068	77	+78	101	120	-116
430	123	+128	013	44	+31	069	50	+31	$\bar{1}$03	40	+37
440	62	-55	014	0	+9	0,6,10	28	-20	$\bar{1}$05	148	+121
450	14	+3	015	79	+57	071	31	-45	$\bar{1}$07	14	+14
460	14	+14	016	87	+76	072	39	+35	$\bar{1}$09	0	-17
470	14	+7	017	85	+64	073	0	-15	101	0	13
480	28	+31	018	94	+73	074	36	+35	103	120	-116
490	32	+39	019	0	-12	075	0	-5	105	20	-30
4,10,0	51	+33	0,1,10	0	-10	076	0	0	107	14	-14
4,11,0	14	+15	0,1,11	35	-22	077	14	+9	109	0	+16
510	98	+84	0,1,12	0	+11	078	14	+15	$\bar{2}$02	155	+170
520	127	+100	0,1,13	0	-3	079	20	-9	$\bar{2}$04	136	-128
530	69	+52	0,1,14	14	-7	0,7,10	25	+14	$\bar{2}$06	105	+111
540	39	-52	020	140	+146	080	48	-54	$\bar{2}$08	17	+29
550	82	-82	021	0	-5	081	72	+69	$\bar{2}$,0,10	0	-1
560	62	-73	022	0	-19	082	0	-9	$\bar{2}$,0,12	32	+37
570	0	-26	023	128	+108	083	0	-5	200	30	-36
580	47	-56	024	66	-60	084	17	-27	202	222	-168
590	20	-44	025	14	+24	085	14	+9	204	49	+73
5,10,0	6	-8	026	76	+52	086	73	-55	206	100	-100
5,11,0	0	+6	027	0	+2	087	0	+37	208	0	+13
600	41	-40	028	43	-46	088	0	+12	2,0,10	35	+43
610	0	+3	029	26	+30	089	0	-7	$\bar{3}$01	14	+15
620	51	-33	0,2,10	0	-8	0,8,10	14	+15	$\bar{3}$03	285	-293
630	23	-32	0,2,11	0	+1	091	76	-81	$\bar{3}$05	0	-19
640	69	+76	0,2,12	14	+10	092	69	-70	$\bar{3}$07	0	+10
650	0	0	0,2,13	14	+10	093	0	-25	$\bar{3}$09	50	-44
hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}	hkℓ	F_{obs}	F_{calc}
$\bar{3}$,0,11	39	+37	602	86	-81	$\overline{11}$,0,1	0	+2	373	22	-18
301	92	-87	604	10	-37	11,0,1	33	+22	383	41	+37
303	17	+18	606	30	-31	040	159	-151	393	68	-61
305	150	+166	608	14	+21	060	238	-235	3,10,3	33	+29
307	14	-16	$\bar{7}$01	101	-111	080	64	-76	404	30	-15
309	25	+40	$\bar{7}$03	0	+12	0,10,0	32	+30	414	137	-124
$\bar{4}$02	138	+125	$\bar{7}$05	89	-73	121	0	+10	424	64	+70
$\bar{4}$04	67	+70	$\bar{7}$07	37	-43	131	212	-172	434	58	-72
$\bar{4}$06	91	+79	$\bar{7}$09	67	+50	141	118	+118	444	36	+5
408	41	-15	701	57	+55	151	42	-52	454	26	-40
$\bar{4}$,0,10	43	-32	703	33	+46	161	71	-65	464	0	-20
$\bar{4}$,0,12	0	0	705	0	-9	171	115	+129	474	10	+4
400	33	+37	707	10	+25	181	0	+5	484	45	-47
402	72	+58	709	0	0	191	14	+40	494	33	+25
404	25	-12	$\bar{8}$02	40	+41	1,10,1	22	-29	4,10,4	22	-13
406	27	-44	$\bar{8}$04	14	-2	1,11,1	20	+11	505	45	-47
408	0	0	$\bar{8}$06	26	-35	202	234	-235	515	0	-9
4,0,10	0	-7	808	33	+32	212	28	+27	525	0	0
$\bar{5}$01	51	+60	800	65	-58	222	218	-206	535	41	-65
$\bar{5}$03	46	+65	802	20	+24	232	268	+274	545	0	+15
$\bar{5}$05	133	-116	804	46	-29	242	63	+77	555	64	-73
$\bar{5}$07	117	+94	806	0	+4	252	0	+29	565	64	+70
$\bar{5}$09	39	-32	808	0	+8	262	211	+261	575	0	+2
$\bar{5}$,0,11	33	-28	$\bar{9}$01	10	+22	272	93	-70	585	0	+10
501	78	-98	$\bar{9}$03	0	+7	282	39	+44	595	20	+22
503	137	+164	$\bar{9}$05	0	+16	292	28	-18	5,10,5	25	-22
505	36	-39	907	32	-30	2,10,2	14	-3	606	44	-49
507	0	-13	901	25	+51	2,11,2	10	+11	616	0	+8
509	0	-11	903	0	-8	303	33	+18	626	28	+41
$\bar{6}$02	64	+68	905	0	-2	313	52	+68	636	10	+10
$\bar{6}$04	36	+35	$\overline{10}$,0,2	39	-37	323	0	0	646	30	-9
$\bar{6}$06	102	+86	$\overline{10}$,0,4	50	+52	333	143	+168	656	30	+35
$\bar{6}$08	17	+16	$\overline{10}$,0,6	0	-1	343	89	-90	666	0	-3
$\bar{6}$,0,10	0	+13	10,0,0	10	-11	353	17	+27	676	0	0
600	28	-27	10,0,2	0	-9	363	10	-18	686	0	+1

Discussion

In tetramethylammonium enneaiodide five-ninths of the iodine atoms lie in densely packed layers separated by 9·1 Å. Between these widely separated layers are the tetramethylammonium ions, each ion surrounded by six I_2 molecules, also lying between the iodine

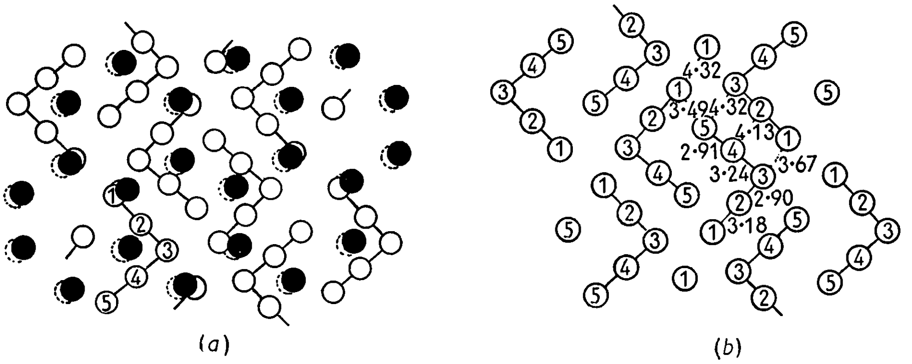


Fig. 2. (a) Projection, normal to a–c, of iodine molecules into one iodine net. Each solid circle represents an I_2 molecule with its axis normal to, and in front of, the net of iodines shown in (b), while each broken circle represents an I_2 molecule with its axis normal to, and behind, the same plane. Open circles with solid lines are iodines in the plane of the I_5^- ions. (b) Arrangement of iodine atoms in one net normal to a–c.

sheets, and with their molecular axes perpendicular to the main sheet of iodines. The overall nature of the complex can best be seen from Fig. 2(a), where the tetramethylammonium ions have not been shown; they reside in the large hexagonal holes between the solid circles in that figure. These hexagonal holes are some 10 Å across.

Table 4. *Interatomic distances in tetramethylammonium enneaiodide*

Atoms	Distance (Å)
1–2	3·18
1–7	3·43
1–8	3·24
1–5	3·49
2–3	2·90
3–4	3·24
4–5	2·91
6–7	2·66
8–9	2·67

Within each sheet (Fig. 2(b)) there is some justification for picking out I_5^- ions, within which I–I distances are 2·90, 2·91, 3·18 and 3·24 Å. (The difference between 3·24 Å and 3·18 Å within this ion is probably significant.) All other distances within the sheet are 3·49 Å or larger, and, since distances of about 3·5 Å occur between molecules in I_2, only weak interactions are implied for distances this great.

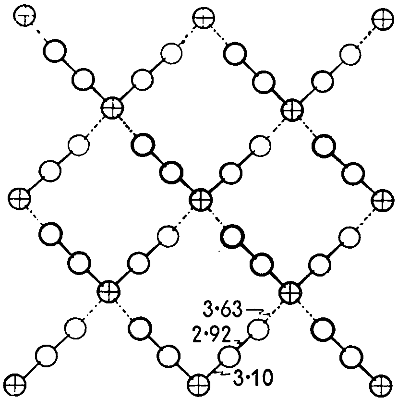


Fig. 3. I_5^- ion in tetramethylammonium pentaiodide.

The I_5^- ion in the enneaiodide sheet is again substantially V-shaped, as in the tetramethylammonium pentaiodide structure, with an apex angle of 86·5° and arms which are linear within about 7°. It does not, however, have the shape of the I_5^- ion in tetramethylammonium pentaiodide (Fig. 3), where the iodine at the apex appears to be most like an iodide ion. In the enneaiodide, Fig. 2(b), I(1), at one extreme, is most like an iodide, having only long distances (3·24 and 3·18 Å) to its nearest neighbors. That I(1) should be regarded as the iodide is also confirmed by the fact that it is the iodine in the sheet which interacts most strongly with I_2 molecules between the sheets (Fig. 4).

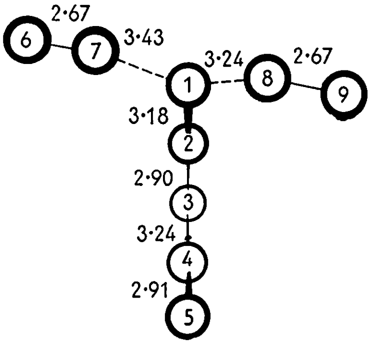


Fig. 4. Interaction of iodine molecules with I_5^- ion. Within-layer lighter shaded atoms are behind the plane of the paper.

Presumably the charge on the iodide is distributed by resonance of the type

$$I^-–I–I \rightleftharpoons I–I–I^- ,$$

and presumably the positions of the cations influence the extent of this type of resonance by favoring negative charges on iodines nearest the cations. Since, however, the cations have not been located directly, but only the holes into which they must fit, it is not possible to discuss this influence quantitatively.

The I_2 distances in the I_2 molecules between sheets are only about 2·67 Å, equal, within the experimental error, to the I–I distance reported for the I_2 crystal (2·70 Å). In view of this short distance it is surprising to find that the I_2 molecules are associated rather strongly with the sheets. As shown in Fig. 4, each I(1) of an I_5^- ion forms one link of 3·24 Å to an I_2 between sheets, and another, to a different I_2, of 3·43 Å. The shorter of these distances is as short as the longest distance in the I_5^- ion within the sheet, and gives some justification to picking out an I_7^- ion. If distances as long as 3·4 Å are considered to represent a significant amount of I–I bonding, then the enneaiodide is better thought of as continuous sheets, with I_2 branches sticking out on each side.

In all the polyiodides studied, more or less discrete ions can be picked out, with shorter distances of 2·8–2·9 Å alternating with distances of 3·1–3·25 Å in such a way as to suggest I_2 molecules interacting with iodide ions, and some resonance of the iodine–iodine bond with iodide–iodine bond. In all cases, also, where an iodide interacts with more than one I_2 molecule it forms iodide–iodine bonds at approximately right angles, tending to confirm a previous suggestion as to the nature of the bonding, i.e. that a *p*-orbital of the iodide is required for each bond and that 5*d*-orbitals are not important in polyiodide ions, though they must be used in mixed polyhalides. These right-angle bonds have now been observed in I_5^-, I_8^{2-} and I_9^-. In the two higher polyhalides, I_9^- and I_8^{2-}, there is a tendency toward a few more nearly discrete I_2 molecules interacting quite weakly with I_3^- or I_5^- ions, and there seems to be a significant increase in the iodide–iodine bond length in going from I_3^- or I_5^-, from 3·1 to 3·2 Å. Both effects would follow from partial delocalization on the iodide charges by resonance in interacting with I_2 molecules.

There is common to polyiodides and iodine a tendency to form dense planes within which prominent interionic or intermolecular distances are ~ 3·5 Å, while between planes van der Waals distances of 4·3 Å are found.

Thus, the polyiodides are structurally related, but also structurally complex. It seems likely that part of the structural complexity arises from the influence of cations in determining the distribution of charges, and, therefore, the bond character, in the polyhalide ions. The lack of similarity of polyiodides to other polyhalides, such as ICl_4^- and ICl_2^- is now well confirmed.

The authors are indebted to the Agricultural Experiment Station, Iowa State College, and to the Corn Industries Research Foundation for generous support, and to the Institute for Atomic Research of the College for use of X-ray facilities. In addition, we are greatly indebted to Prof. Ray Pepinsky of the Pennsylvania State University for the use of X-RAC, and for valuable discussions both with him and with the members of the X-ray group at Pennsylvania State University.

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