Calcium ersetzt werden. Die Formel des Rhodonits ist also (Mn, Mg)$_{1-x}$Ca$_x$SiO$_3$($0 \leq x \leq 0{,}2$) zu schreiben.

Über die Polymorphie des MnSiO$_3$ wird an anderer Stelle berichtet (Liebau, Sprung & Thilo, 1958).

Herrn Prof. Thilo danken wir für die Anregung und sein ständiges Interesse bei der Durchführung dieser Arbeit, Frau Prof. Dornberger-Schiff für eine Reihe uns sehr wertvoller Diskussionen. Herr Dr Línek (Prag) hat uns in dankenswerter Weise bei der Durchführung eines Teils der Rechnungen unterstützt.

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# The Triiodide Ion in Tetraphenyl Arsonium Triiodide*

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Tetraphenyl arsonium triiodide crystallizes with the space-group symmetry $P2/n$. There are two formula weights of $(C_6H_5)_4AsI_3$ in the unit cell, for which $a = 15{\cdot}34 \pm 0{\cdot}01$, $b = 7{\cdot}63 \pm 0{\cdot}01$, $c = 10{\cdot}63 \pm 0{\cdot}01$ Å and $\beta = 93{\cdot}4^\circ$. A trial structure was deduced from two-dimensional Patterson and Fourier series, and refined by Fourier difference series.

The triiodide ion in this crystal is equibonded. The bond length is $2{\cdot}90 \pm 0{\cdot}02$ Å. Triiodide ions measured in crystals having cations which are small compared to $(C_6H_5)_4As^+$ have non-equivalent bond lengths. The small differences which have been reported in the configuration of the $I_3^-$ ion in different crystals are discussed with reference to the crystal environments. An explanation based on the general behavior of a simple linear triatomic system is suggested.

Two previous structural studies have been concerned with the size and configuration of the triiodide ion in crystals. The first, a crystal analysis of ammonium triiodide (Mooney, 1935), was based on qualitative intensities and the simple methods current at the time; the second, a structure determination of cesium triiodide (Tasman & Boswijk, 1955), was deduced from quantitative data by far more elegant methods. Nevertheless, the results are well in accord. In ammonium triiodide, the iodine distances in the $I_3^-$ ion are found to be 2·82 Å and 3·1 Å, with an angle of 177° between the bonds. In cesium triiodide, the comparable values are respectively, 2·83 Å, 3·03 Å and 176°. Therefore, it is established that, at least in crystals having small positive ions, the $I_3^-$ ion is asymmetric and non-linear; and that the interatomic distances are significantly larger than the iodine separation in the $I_2$ molecule, which is 2·70 Å (Harris, Mack & Blake, 1928).

Structure data has been reported for three polyiodides, namely, $(CH_3)_4NI_5$ (Hach & Rundle, 1951); $Cs_2I_8$ (Havinga, Boswijk & Wiebenga, 1954); and $(CH_3)_4NI_9$ (James, Hach, French & Rundle, 1955). All contain triiodide-like configurations as constituents of larger iodine complexes. In $(CH_3)_4NI_5$ five iodines are associated in a *V*-shaped group, with I–I distances of 3·14 Å and 2·93 Å. The larger distances are between the apex iodine and its two neighbors. A recent refinement of this structure (Broekema, Havinga & Wiebenga, 1957) modifies these distances to 3·17 Å and 2·81 Å. In $(CH_3)_4NI_9$, a configuration similar to the pentaiodide group is weakly associated with iodine molecules. In $Cs_2I_8$, the $I_8^{-2}$ complex consists of two triiodide groups loosely linked by a pair of iodines. The interatomic distances of the component triiodide groups are practically identical to those found in $CsI_3$.

The configuration of the triiodide ion differs from

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that of the $ICl_2^-$ ion, which is linear and symmetrical, with interatomic distances close to the sum of the covalent radii (Mooney, 1939); nor does the pentaiodide group remotely resemble the only other structurally known pentahalide ion, $ICl_4^-$, a square configuration of chlorine about iodine, with I–Cl distances comparable to the sum of the covalent radii (Mooney, 1938). The type of covalent binding postulated for the polyhalide ions (Pauling, 1940), while it seems applicable to the polychloriodide ions, cannot serve as an explanation of the polyiodide configurations.

As it happens, the triiodide ion has so far been studied only in crystals having comparatively small positive ions. It has long been known that the ionic radius of rubidium—or the comparable ammonium—is at the lower size limit required for the formation of solid, unsolvated triiodides at ordinary temperature and pressure (Grace, 1933), and that the stability of triiodide crystals increases with increasing cation size. This rise in structural stability must be due primarily to a more adequate cation–anion coordination as the positive and negative ions become more commensurate in size. However, in view of the high polarizability of iodine, effects on the configuration of the triiodide group may well be involved.

It would seem, therefore, that a structural study of the triiodide ion in a crystal having positive ions very different from the small, concentrated $Cs^+$ cation might well contribute to the understanding of the binding in complex iodine groups. For this reason, a crystal structure investigation of tetraphenyl arsonium triiodide was undertaken.

The halides of tetraphenyl arsonium were first prepared by Blicke *et al.* (1935), and further studied, with regard to their uses in quantitative analysis, by Willard & Smith (1939). The arsonium halides react instantly with halogens to form perhalides. The triiodide is characterized by extreme insolubility in water; it may be used for gravimetric titration of iodine in solution. The configuration of $[(C_6H_5)_4As]^+$ studied from the crystal structure of the iodide (Mooney, 1940), is a tetrahedral grouping of phenyl rings about arsenic, with As–C distances of 1·95 Å and average C–C distances of 1·39 Å. The tetrahedron edge measured between terminal carbons, is 7·76 Å long. For comparison, the tetrahedron edge of $[(CH_3)_4N]^+$ is about 2·5 Å. Therefore, tetraphenyl arsonium triiodide crystals may well serve as an example of a structure in which triiodide anions are combined with very large cations.

## Preparation of the crystals

The addition of tetraphenyl arsonium ion to a very dilute solution of iodine in water immediately results in the precipitation of the triiodide as a fine brown powder. In order to grow single crystals of the compound large enough for X-ray diffraction purposes, a very slow combination of the components is required. This was effected by diffusion in the following way. Solutions of iodine and of tetraphenyl arsonium iodide were submerged at opposite ends of a glass tank filled with a five percent alcohol in water solution. The tank was sealed against evaporation, and forgotten for some months. In due course, the bottom of the tank was found to be thinly strewn with a coarsely crystallized brown powder, from which small single crystals could be isolated.

The crystals are exceedingly thin flakes, rectangular or square in cross-section. They are generally somewhat less than a millimeter along the edges, and a few hundredths of a millimeter in thickness. The crystallographic axes, $b$ and $c$, lie in the directions of the plate edges. There is a good cleavage plane perpendicular to the $y$ direction, such that, under slight localized pressure, the fragile plates tend to split cleanly into lathes extended along $z$. The crystals are brown in reflected light, and golden yellow in transmitted light. This coloration is in decided contrast to the dark red-brown to wine-red of the triiodides of the alkali metal and alkyl-substituted ammonium ions.

## Diffraction data

Rotation and Weissenberg patterns were taken about the $b$ and $c$ crystal axes by means of nickel-filtered copper radiation. They were recorded by the multiple-film technique. The crystal used was an almost square plate, of dimensions 0·80 × 0·75 × 0·05 mm. Supplementary observations were made from a small tabular crystal, roughly 0·05 × 0·05 × 0·02 mm. in dimensions, and also from a thin lathe split off from a larger plate. The intensities were visually estimated by comparison with a multiple set of intensity scales prepared from a crystal reflection, and were graphically corrected for the polarization-Lorentz factor. Because of the crystal shape, the sharpness of the diffracted spots varied considerably. In order to collect a consistent set of estimated intensities, it was necessary to make careful intercomparisons of the same reflections on different parts of a film, or on films taken with crystals of different dimensions. Because of the rather high absorption coefficient of the crystal ($\mu$ = 339 cm.$^{-1}$) and because of its shape, the absorption effects were far from negligible. Individual absorption corrections were applied to the observed intensities by the method of Joel, Vera & Garaycochea (1955). The structural parameters were determined from the analysis of the $hk0$ and $h0l$ zones. Only the 165 independent reflections observed for these zones were fully corrected. Upper layer line intensities were used solely for qualitative comparisons, and are not included in this report.

For the calculation of the structure amplitudes, atomic scattering factors for arsenic and iodine were taken from the *International Tables*, and corrected for the dispersion of the $K$-electrons by means of Dauben & Templeton's (1955) tables. The carbon scattering factors given by McWeeny (1951) were used. The observed and calculated structure amplitudes were adjusted to the same scale by repeated comparisons at various stages of the investigation. The final value of $B$ in the expression

$$KF_o = F_c \exp\left(\frac{-B\sin^2\theta}{\lambda^2}\right)$$

was 1·28 and 1·58 for the $h0l$ and $hk0$ zones, respectively.

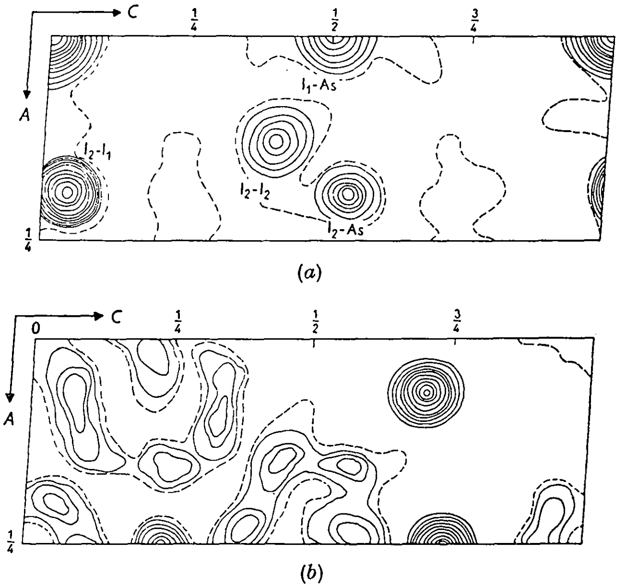
The Patterson and Fourier series were synthesized by means of Beevers and Lipson strips. Points were calculated at 3° intervals (0·128 Å) along $x$, and at 6° intervals (0·127, 0·177 Å) along $y$ and $z$.

## Cell dimensions and space group

Tetraphenyl arsonium triiodide is monoclinic, with cell dimensions:

$$a=15{\cdot}34\pm0{\cdot}01\ \text{Å},\ b=7{\cdot}63\pm0{\cdot}01\ \text{Å},\ c=10{\cdot}63\pm0{\cdot}01\ \text{Å};\ \beta = 93{\cdot}4^\circ .$$

The experimental density by a flotation method is 2 g.cm.$^{-3}$. The calculated density, for two formula weights per unit cell, is 2·04 g.cm.$^{-3}$. The diffraction data shows only one systematic absence; that is, $h0l$ is absent unless $h+l$ is even. This criterion does not distinguish between the space groups $C_s^2$–$Pn$ and $C_{2h}^2$–$P2/n$. If the crystal has the symmetry $Pn$, all of the atoms in the cell—that is to say, two arsenics, six iodines and forty-eight carbons—are distributed in twenty-eight sets of two-fold general positions, $x, y, z$; $x+\frac{1}{2}, y, z+\frac{1}{2}$. If, on the other hand, the symmetry is $P2/n$, the arsenic and two of the iodines must be in special positions, either symmetry centers or rotation axes; while the remaining iodines and carbons occupy the four-fold general positions of the space group. An attempt to resolve the space-group ambiguity was made by means of a simple test for pyroelectricity. The absence of any observed electrification in the crystal sample after its immersion in liquid air left the question still essentially unsettled. Since no decision concerning the space group was possible at this point, the $h0l$ and $hk0$ observations were synthesized into $F^2$ projections with the results shown in Fig. 1($a$) and Fig. 2.



($a$)

($b$)

Fig. 1. ($a$) Patterson projection on (010), showing principal interatomic vector peaks. ($b$) Electron-density projection on (010). Contour lines are drawn at equal, arbitrary intervals.

## Discussion of the $F^2$ projections

The $F^2$ synthesis of the $h0l$ data gives an exceedingly simple diagram. Only a few strong and well-resolved peaks appear clearly above background. Obviously, they must be attributed to heavy atom vectors. The position and relative height of the peak at $X = 0$, $Y = \frac{1}{2}$ on the diagram leads to the conclusion that the arsenic, and a two-fold set of iodines, $I_1$, are in the special positions (two-fold rotation axes) of $P2/n$, with $x$, $z$ parameters of $\frac{1}{4}, \frac{1}{4}$ and $\frac{1}{4}, \frac{3}{4}$ respectively. The remaining peaks can be entirely explained as representing vectors between $I_2$–$I_2$, $I_2$–As and $I_2$–$I_1$, where $I_2$ is a four-fold set of iodines. The peak positions give, as tentative values of the $I_2$ parameters, $x \cong 0{\cdot}06$, $z \cong 0{\cdot}70$.

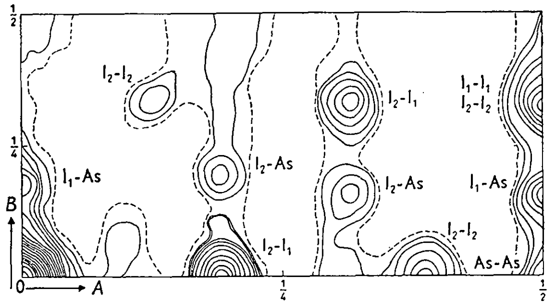


Fig. 2. Patterson projection on (001), showing principal interatomic vector peaks.

In the $F^2$ projection of the $hk0$ data (Fig. 2) the evidence again points to the distribution of the six iodines in a four-fold and a two-fold set, rather than in three two-fold sets. On the basis of the relative peak heights and the information obtained from the $F^2(h0l)$ projection, all of the heavy atom peaks can be identified. Their positions indicate that the arsenic $y$-parameter is not far from 0 (or 0·5) and that both the $I_1$ and $I_2$ $y$-parameters are near $\frac{1}{6}$ (or $\frac{1}{3}$) but may differ slightly from each other. It is easy to show, from the intensities, that 0 and $\frac{1}{6}$ or 0·5 and $\frac{1}{3}$ are the compatible pairs.

To summarize the results thus far, the two Patterson projections have yielded approximate parameters for the heavy atoms. These parameters, only five in number, correspond to the following distribution in the centrosymmetrical space group, $P2/n$.

| | | | |
|---|---|---|---|
| 2 As | *f* | 2 | $\pm(\frac{1}{4}, y, \frac{1}{4})$ |
| 2 $I_1$ | *e* | 2 | $\pm(\frac{1}{4}, y_1, \frac{3}{4})$ |
| 4 $I_2$ | *g* | 1 | $\pm(x_2, y_2, z_2;\ \frac{1}{2}-x_2, y_2, \frac{1}{2}-z_2)$ . |

If the space-group assignment is correct, it follows that the three iodines of the triiodide ion, while not necessarily collinear, must be equally spaced. The peak systems found on the two Patterson maps certainly lead to the higher space group. Nevertheless, it must be recognized that the peak systems attributed to four-fold iodine could be the superposition of a pair of two-fold sets with slightly differing parameters. The asymmetry found for the triiodide ion in other crystals is not very great, and if it exists in this crystal, might not be readily detected from the $F^2$ projections. Nevertheless, the evidence in favor of the higher symmetry seemed sufficient to justify the provisional adoption of $P2/n$ for the next stages of the investigation. This was done with the expectation that difficulties must surely arise if the crystal were pseudo-centrosymmetric after all. However, in the subsequent detailed examination of the data, no reason was found to doubt the correctness of the space-group assignment.

## Structure determination

The iodine and arsenic parameters obtained from the Patterson synthesis projected onto [010] were used to calculate the heavy atom contribution to the structure amplitudes of $h0l$. The results gave general qualitative agreement with observations, and permitted the calculation of a rough scale factor. It was quite apparent, however, that, if the interpretation of the Patterson diagram is correct, the carbon contributions to the structure amplitude must be far from negligible for many $h0l$ reflections, and crucially important for a few. For instance, the heavy atom contribution to plane 202 is roughly only a fourth of its observed $F$-value; while the heavy atom contribution to plane $30\bar{1}$ is more than twice as large as its observed $F$-value. It follows that some information concerning the phenyl group positions should be directly obtainable from the diffraction data despite the great disparity in the scattering power of the light and heavy constituents of the crystal. On the assumption that the signs of the structure amplitudes are the same as the signs of the heavy atom contribution alone, a Fourier projection, $\varrho(x, z)$, was calculated (Fig. 1(*b*)).

This projection, favorable because of the short $b$-axis, confirmed the structural arrangement deduced from the Patterson diagram, and gave more precise, but only slightly different values for the $I_2$ parameters. It also furnished some information concerning the carbon positions, in the form of a set of low density peaks surrounding the arsenic. Despite poorly defined contours, their spatial arrangement strongly suggests the projection on (010) of a tetraphenyl arsonium group of the size and shape found in the iodide, with its two-fold axis coincident with the crystal symmetry axis. Though a set of $x, y$ carbon parameters can be extracted from these peaks, the individual values are little more than estimates. In preference to imposing meaningless distortions on the phenyl groups by their use, a tetraphenyl arsonium group of regular geometry was postulated, and fitted into the orientation indicated by the Fourier map. This required no important departures from the density distribution indicated by the map.

Carbon parameters obtained in this manner, along with the readjusted $I_2$ parameters, were introduced into the structure amplitude calculations. It was found that the carbon contributions quite generally had signs and magnitudes which tended to improve the agreement between the observed and calculated structure amplitudes. In particular, the more striking discrepancies, two of which have been mentioned, were corrected by unusually large carbon contributions. Despite these far from negligible effects, it is interesting to note that, except for one weak and several unobserved reflections, the signs of the structure amplitudes are not altered by the carbon contributions.

The final refinement was carried out by means of successive $|F_o-F_c|$ syntheses. The $x$ parameter of $I_2$ changed very little throughout the process. The final value was 0·062. The $z$ parameter shifted from an original value of 0·707 to a final value of 0·703. Concerning the carbons, no evidence was found to warrant a change in the original assumption of a geometrically regular tetraphenyl arsonium group. However, the maps clearly indicated a small rotation of the tetraphenyl complex, as a unit, from its originally assigned orientation with respect to the crystal symmetry axis.

These changes, along with an improved scale factor, brought the residual factor, $R = \Sigma|F_o-F_c| \div \Sigma|F_o|$ to 0·08 for all observed planes, and to 0·09 when unobserved planes were included in the summations with half-values of the lowest observed $F_o$. The individual $F_o$ and $F_c$ values are compared in Table 1. The $R$-value for this zone is expectedly low, since the positions of $I_1$ and As are fixed by symmetry, and the 95 independent $h0l$ observations served to determine essentially three parameters; $x$ and $z$ for $I_2$, and the orientation angle of the tetraphenyl arsonium group about the symmetry axis. It is true that the carbon positions involve 24 parameters which have not been individually determined. However, the diffraction effect of the group as a whole is not sensitive to such departures from ideal geometry as undoubtedly exist among the various carbons.

The $hk0$ data was analyzed by a similar procedure. The approximate parameters, deduced from the $P(x, y)$ synthesis, were used to derive signs of $F_o$, by means of which the Fourier projection, $\varrho(x, y)$, was calculated. The improved parameters, measured from the Fourier map, were then refined by the use of repeated $F_o-F_c$ syntheses until the $R$-factor reached a minimum value. Eighty $hk0$ observations were avail-

Table 1. *Observed and calculated values of (h0l) structure amplitudes*

| *h0l* | $F_o$ | $F_c$ | *h0l* | $F_o$ | $F_c$ | *h0l* | $F_o$ | $F_c$ | *h0l* | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 200 | 21 | −22 | $60\bar{2}$ | 134 | 135 | $80\bar{4}$ | 15 | 20 | $40\bar{6}$ | 0 | 10 |
| 400 | 73 | 71 | $40\bar{2}$ | 25 | −27 | $60\bar{4}$ | 116 | −124 | $20\bar{6}$ | 127 | 131 |
| 600 | 110 | −113 | $20\bar{2}$ | 40 | 36 | $40\bar{4}$ | 0 | −5 | 006 | 60 | −54 |
| 800 | 0 | −3 | 002 | 138 | −140 | $20\bar{4}$ | 90 | −78 | 206 | 25 | 23 |
| 10,0,0 | 105 | −101 | 202 | 55 | −52 | 004 | 100 | 91 | 406 | 120 | −116 |
| 12,0,0 | 40 | 37 | 402 | 120 | −123 | 204 | 15 | 8 | 606 | 0 | −3 |
| 14,0,0 | 0 | 14 | 602 | 80 | 76 | 404 | 115 | 109 | 806 | 55 | 61 |
| | | | 802 | 0 | −10 | 604 | 25 | −31 | 10,0,6 | 95 | 89 |
| $13,0,\bar{1}$ | 35 | 39 | 10,0,2 | 128 | 120 | 804 | 30 | 30 | | | |
| $11,0,\bar{1}$ | 80 | 75 | 12,0,2 | 28 | −27 | 10,0,4 | 98 | −104 | $70\bar{7}$ | 60 | −70 |
| $90\bar{1}$ | 50 | 43 | | | | 12,0,4 | 19 | −24 | $50\bar{7}$ | 30 | −21 |
| $70\bar{1}$ | 0 | −4 | $11,0,\bar{3}$ | 85 | −79 | | | | $30\bar{7}$ | 0 | −13 |
| $50\bar{1}$ | 75 | −79 | $90\bar{3}$ | 42 | −42 | $90\bar{5}$ | 42 | 46 | $10\bar{7}$ | 65 | 63 |
| $30\bar{1}$ | 32 | −38 | $70\bar{3}$ | 75 | −83 | $70\bar{5}$ | 78 | 80 | 107 | 57 | 53 |
| $10\bar{1}$ | 70 | −58 | $50\bar{3}$ | 50 | 45 | $50\bar{5}$ | 20 | 20 | 307 | 65 | 78 |
| 101 | 10 | 13 | $30\bar{3}$ | 70 | 64 | $30\bar{5}$ | 20 | −25 | 507 | 0 | −4 |
| 301 | 45 | 41 | $10\bar{3}$ | 110 | 105 | $10\bar{5}$ | 110 | −97 | | | |
| 501 | 110 | 117 | 103 | 25 | 23 | 105 | 70 | 66 | $80\bar{8}$ | 75 | 84 |
| 701 | 22 | 27 | 303 | 0 | −12 | 305 | 55 | −60 | $60\bar{8}$ | 30 | −35 |
| 901 | 0 | −1 | 503 | 90 | −82 | 505 | 68 | 64 | $40\bar{8}$ | 15 | 10 |
| 11,0,1 | 67 | −61 | 703 | 68 | −75 | 705 | 34 | 37 | $20\bar{8}$ | 110 | −115 |
| 13,0,1 | 50 | −46 | 903 | 50 | −54 | 905 | 70 | 65 | 008 | 0 | −3 |
| | | | 11,0,3 | 50 | 45 | | | | 208 | 50 | −56 |
| $12,0,\bar{2}$ | 85 | −90 | | | | $10,0,\bar{6}$ | 0 | 8 | 408 | 92 | 95 |
| $10,0,\bar{2}$ | 60 | 52 | $12,0,\bar{4}$ | 95 | 107 | $80\bar{6}$ | 48 | −56 | 608 | 0 | 10 |
| $80\bar{2}$ | 0 | 8 | $10,0,\bar{4}$ | 28 | −32 | $60\bar{6}$ | 87 | 90 | | | |

Table 2. *Observed and calculated values of (hk0) structure amplitudes*

| *hk*0 | $F_o$ | $F_c$ | *hk*0 | $F_o$ | $F_c$ | *hk*0 | $F_o$ | $F_c$ | *hk*0 | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 010 | 75 | 107 | 260 | 10 | −5 | 560 | 0 | 3 | 930 | 0 | −10 |
| 020 | 80 | −108 | 270 | 30 | −24 | 600 | 114 | −113 | 940 | 0 | −4 |
| 030 | 90 | −94 | 310 | 85 | −82 | 610 | 72 | −78 | 10,0,0 | 110 | −101 |
| 040 | 50 | −45 | 320 | 30 | −34 | 620 | 15 | 21 | 10,1,0 | 75 | −69 |
| 050 | 70 | 69 | 330 | 10 | 18 | 630 | 66 | 71 | 10,2,0 | 15 | 21 |
| 060 | 115 | 130 | 340 | 34 | 37 | 640 | 23 | 19 | 10,3,0 | 70 | 68 |
| 070 | 55 | 57 | 350 | 15 | 26 | 650 | 55 | −48 | 10,4,0 | 15 | 20 |
| 110 | 49 | −48 | 360 | 21 | −17 | 660 | 75 | −81 | 11,1,0 | 90 | 86 |
| 120 | 75 | −81 | 400 | 79 | 71 | 710 | 0 | 2 | 11,2,0 | 85 | 74 |
| 130 | 10 | −7 | 410 | 38 | 36 | 720 | 10 | 13 | 11,3,0 | 0 | −1 |
| 140 | 53 | 59 | 420 | 20 | 14 | 730 | 0 | 8 | 11,4,0 | 60 | −66 |
| 150 | 49 | 48 | 430 | 0 | 2 | 740 | 0 | −8 | 12,0,0 | 45 | 37 |
| 160 | 0 | 7 | 440 | 12 | −14 | 750 | 13 | −8 | 12,1,0 | 35 | 33 |
| 170 | 20 | −34 | 450 | 24 | 16 | 800 | 0 | −3 | 12,2,0 | 0 | 13 |
| 200 | 21 | −22 | 460 | 43 | 47 | 810 | 15 | 9 | 12,3,0 | 0 | −13 |
| 210 | 35 | −40 | 510 | 98 | −107 | 820 | 38 | 38 | 13,1,0 | 16 | 13 |
| 220 | 45 | −38 | 520 | 83 | −77 | 830 | 44 | 48 | 13,2,0 | 25 | 23 |
| 230 | 27 | −22 | 530 | 0 | 8 | 840 | 25 | 20 | 14,0,0 | 0 | 14 |
| 240 | 12 | −14 | 540 | 75 | 73 | 910 | 15 | −13 | 14,1,0 | 19 | −12 |
| 250 | 0 | −4 | 550 | 67 | 74 | 920 | 0 | −8 | 14,2,0 | 32 | −35 |

able for the determination of five heavy atom parameters; $y$ for As, $y_{1'}$ for $I_{1'}$ and $x_2$ and $y_2$ for $I_2$. In the original Fourier calculation, the signs of the amplitudes were based on the assumption that $y$ was zero, and that $y_1 = y_2 = \frac{1}{6}$. In the resulting Fourier map, the arsenic peak was centered at $y = 0$, but the iodine peak positions showed $y_1$ to be slightly less, and $y_2$ slightly greater than $\frac{1}{6}$. The refining process brought $y_1$ to 0·158 and $y_2$ to 0·170; that is, the triiodide group, though symmetrical, is not quite linear. The $x_2$ parameter was in agreement with the value obtained from the *h0l* data.

Because of extensive overlapping, the *hk*0 projection gave little information concerning the carbon positions, which were represented by a confusion of low density contours. Therefore, the carbon $x$-parameters previously found from *h0l* data were adopted without change, and the associated $y$ parameters were calculated from the ideal configuration. There was no obvious contradiction between these assumed parameters and the Fourier density distribution, though the same statement might be made for somewhat different assumptions.

The observed and calculated structure amplitudes are shown in Table 2. Because the discrepancies in the first two reflections must be due to extinction, they have been omitted in the calculation of the residual factor. The $R$-factor for observed planes is 0·11. When unobserved planes, estimated at half the smallest $F_o$, are included in the summations, the $R$

value is 0·13. If the carbon contributions are omitted from the calculated structure amplitudes, no signs are changed, but the $R$-factor rises to nearly 0·19. The fact that the carbon contributions so substantially improve the agreement must mean that the assumptions which have been made concerning the cation group are not seriously in error. The final parameters, including those assumed for carbon, are listed in Table 3.

Table 3. *Atomic coordinates*

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| As | 0·250 | 0·0 | 0·750 |
| $I_1$ | 0·250 | 0·158 | 0·750 |
| $I_2$ | 0·062 | 0·170 | 0·703 |
| $C_1$ | 0·231 | 0·853 | 0·393 |
| $C_2$ | 0·146 | 0·800 | 0·421 |
| $C_3$ | 0·294 | 0·800 | 0·478 |
| $C_4$ | 0·131 | 0·695 | 0·518 |
| $C_5$ | 0·281 | 0·695 | 0·579 |
| $C_6$ | 0·197 | 0·642 | 0·600 |
| $C_7$ | 0·353 | 0·147 | 0·288 |
| $C_8$ | 0·367 | 0·200 | 0·410 |
| $C_9$ | 0·407 | 0·200 | 0·194 |
| $C_{10}$ | 0·439 | 0·305 | 0·438 |
| $C_{11}$ | 0·477 | 0·305 | 0·219 |
| $C_{12}$ | 0·500 | 0·358 | 0·346 |

## Structural details

In Fig. 3, the structure is illustrated by two projections, which together make clear the arrangement of nearest neighbors about the $I^{-3}$ ion. The projection on (010) best shows the relative positions of the large complex ions. The projection on (001) demonstrates the manner in which these groups are concentrated in layers perpendicular to the $y$ axis. These layers consist of two iodine-containing planes at $y = \pm\frac{1}{6}(1{\cdot}27$ Å), between which, at $y = 0$, the plane containing the centers of the cation groups is sandwiched. There are far fewer cation–anion contacts across the unpopulated space between the layers than there are within them, which explains the observed cleavage in the crystals.

The principal atomic distances in the structure are listed in Table 4. The triiodide ions are well separated from each other, and from arsenic as well, by distances greater than 5 Å. Thus, an $I_3^-$ ion in this crystal is isolated from the influence of any other iodines; and its interaction with the complex cation, in which the arsenic conventionally bears the positive charge, must be through the agency of dipoles induced on the CH groups. These induced charges must be individually small, since a large number of them surround the $I_3^-$ ion. Inasmuch as the carbon positions are approximate, only the average carbon–iodine distances have been tabulated. The individual $C–I_1$ distances are close to their average. The $C–I_2$ distances have a range of values, for which the average deviation from the mean is 0·25 Å. However, the average carbon–iodine distance, 4·1 Å, corresponds closely to the value found in the iodide of tetraphenyl arsonium, which is 4·12 Å.

Table 4. *Interatomic distances and bond angles*

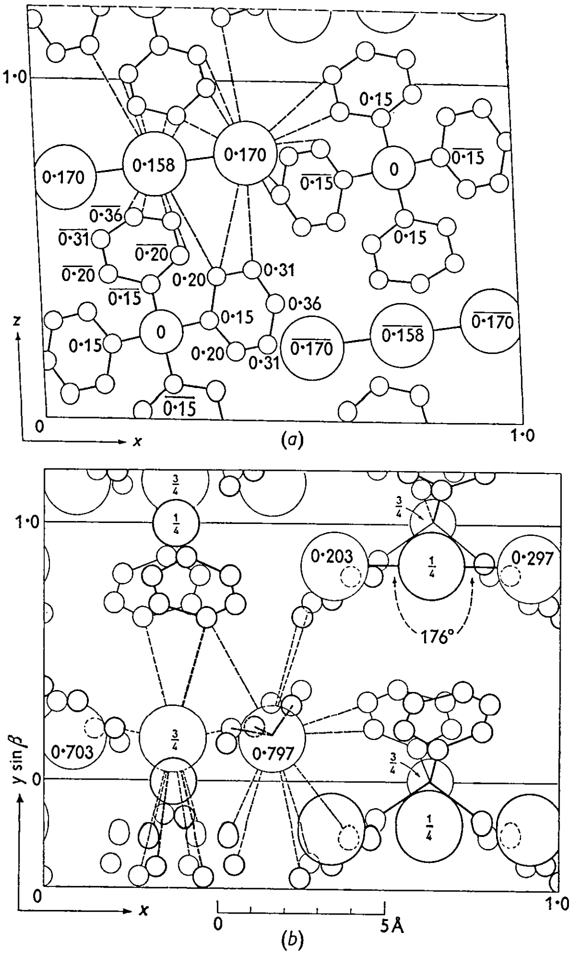
| (a) In $I_3^-$ ion | | (b) In $(C_6H_5)_4As^+$ ion* | |
|---|---|---|---|
| $I_1–2\ I_2$ | 2·90 Å | As–4 C | 1·95 Å |
| $I_2–I_2$ | 5·79 | C–C | 1·40 |
| $< I_1–I_2–I_1$ | 176.4° | < C–As–C | 109·4° |

(c) Between nearest neighbors

| | | | | |
|---|---|---|---|---|
| $I_1–10\ C$ | 4·11 Å | (average) | $I_1–2$ As | 5·45 Å |
| $I_2–13\ C$ | 4·07 | (average) | $I_2$–As | 5·03 |
| I–I | 5·29 | (min.) | $I_2$–As | 6·46 |
| C–C | 3·50 | (min.) | | |

* Values assumed.

The main purpose of this investigation was to learn whether the triiodide ion in $(C_6H_5)_4AsI_3$ retains unchanged the configuration which characterizes it in the crystals of $NH_4I_3$ and $CsI_3$. The results show that it does not. On the basis of the space-group assignment, the triiodide group in $(C_6H_5)_4AsI_3$ is centered in a twofold axis. Thus it is strictly symmetrical. The bond



(a)

(b)

Fig. 3. (a) Projection of the structure of $(C_6H_5)_4AsI_3$ on (010). (b) Projection of the structure on (001).

The unit cell is bounded by heavy lines. The circles, in descending order of size, represent I, As, and C. Fractional values of the displacements in the projection direction are given for some of the atoms; those omitted are obvious from symmetry. Intra-ion bonds are indicated by full lines, and iodine nearest neighbors by broken lines.

length is 2·90 Å, with an estimated standard deviation, calculated by the method of Cruickshank (1949), of 0·02 Å. In contrast, the triiodide group in $CsI_3$ and $NH_4I_3$ is unsymmetrical; the bond lengths are 2·83 Å and 3·04 Å in $CsI_3$, and are close to the same values in $NH_4I_3$. The distance between terminal iodines is 5·79 Å for the symmetrical group, and 5·86 Å for the unsymmetrical one. Thus, the triiodide ion configuration is measurably affected by crystal environment, though the bond angle remains close to 176° in both cases.

It is possible to compare the surroundings of the $I_3^-$ ion in $(C_6H_5)_4AsI_3$ and in $CsI_3$ in some detail. In the first case, approximate carbon positions must be used as stand-ins for the actual CH neighbors; in the second case, accurate $Cs^+$ positions are available. In $(C_6H_5)_4AsI_3$, (Fig. 3), the triiodide ion is surrounded by thirty-two CH groups, so shared that the terminal iodines each have thirteen neighbors, and the central iodine a rather unevenly grouped arrangement of ten neighbors. In $CsI_3$ as shown in Fig. 4, the triiodide ion is coordinated to eight $Cs^+$ ions, so shared that the terminal iodines each have a coordination of four, and the middle iodine a completely one-sided coordination of two. The unbalanced arrangement of nearest neighbors about the middle iodine, observed in both cases, may be related to the small departure from linearity in the ions. Now, the average Cs–I distance is 3·96 Å. Since the average C–I distance, 4·1 Å, is not very different, the envelopes of nearest neighbors surrounding each $I_3^-$ ion are comparable in area, but differ in population by a factor of four. The essential difference in the situations of the $I_3^-$ ions in these two crystals seems to be that, in $(C_6H_5)_4AsI_3$, the $I_3^-$ ion is held in equilibrium by a multiplicity of small charge densities which are dispersed over fairly large areas of the surrounding envelope, while, in $CsI_3$, it achieves electrical neutrality by the agency of comparatively concentrated positive charges, acting at a few widely separated points. To seek an explanation for the effect of these contrasting surroundings on the configuration of the $I_3^-$ ion, it is necessary to give some consideration to the nature of the group itself.

## Some views on the nature of the triiodide ion

Owing to the complexity of its electron configuration, the triiodide group has not been the subject of a detailed theoretical study. Attempts to explain its binding semiempirically or on the basis of simple theory has led to the assumption that the bonds should be equivalent, and the bond distances close to the covalent bond value of 2·70 Å (Pauling, 1940; Kimball, 1940; Pimentel, 1951). However, the group in $NH_4I_3$, in $CsI_3$, and as a component of higher complexes in $(CH_3)_4NI_5$, $(CH_3)_4NI_7$, and $Cs_2I_8$, has been shown to have bonds which are non-equivalent and longer than predicted.

To explain the long bonding distances, Hach & Rundle (1951) have interpreted the triiodide ion as a resonating system consisting of an $I^-$ ion and an $I_2$ molecule, in which equivalent bonds, of a length intermediate between the normal covalent and ionic distances, would ordinarily be expected. They attribute the observed dissymmetry of the group to crystal environment, in particular, to the influence of small positive ions, which, by unequal distribution about the terminal iodines, cause a difference in the state of polarization of the group ends. They concluded that the group might not have the same dimensions in different crystals, and that it might be found to be symmetrical in crystals with sufficiently large positive ions. These conclusions have been verified by the results of the present investigation. Further, the concept of the complex ion as an association between an iodine ion and an iodine molecule is in agreement with what is known of its formation and properties. However, in the light of additional experimental data, some question may be raised concerning the initial assumption that the bonds formed between the three iodines are normally equivalent, and that the non-equivalence of the bonds which characterize the group in several crystals is due primarily to local influences.

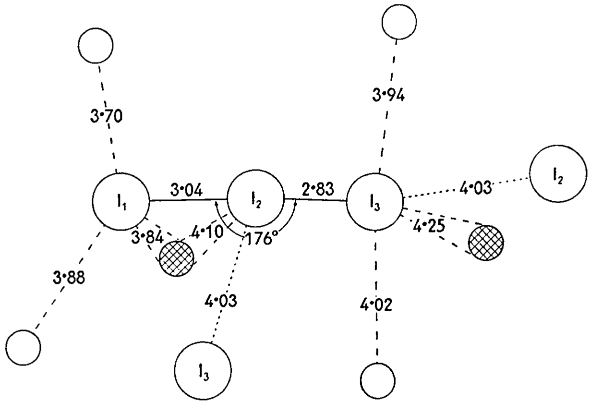


Fig. 4. The triiodide ion in $CsI_3$.

It is true that the triiodide group in $CsI_3$ (Fig. 4) does have a different arrangement of $Cs^+$ ions about each end. Further, the Cs–I distances fall neatly into two sets; the six surrounding the short-bonded pair of iodines have an average value of 4·11 Å, while the four around the longer bonded iodine have an average value of 3·86 Å. These structural details strongly suggest that the triiodide group in $CsI_3$ retains somewhat more of a negative ionic character at one end than at the other. Such a condition may be induced in the $I_3^-$ ion by the somewhat disparate distribution of the $Cs^+$ ions around the ends of the group, as Hach & Rundle (1951) suggest. On the other hand, a difference in the state of the two ends may be a property of the group to which the $Cs^+$ ions adjust themselves; that is, the molecule and the ion, though combined, may still preserve something of their original identities.

The surroundings of the unsymmetrical triiodide group can be described in two other crystals. In $NH_4I_3$, the coordination, though only approximately known, shows the same slight unbalance as in the isostructural $CsI_3$. In $Cs_2I_8$, the average distances of the four $Cs^+$ ions around each terminal iodine are about the same, but in this case, the long-bonded iodine is loosely connected to an iodine molecule.

In $(C_6H_5)_4AsI_3$, the triiodide group is in an environment of very large cations. Here, the bond distances are equivalent, in agreement with Hach & Rundle's (1951) expectations concerning the effect of large cations. The bond length is a little less than ordinarily predicted for an equibonded $I_2$–$I^-$ resonating system. However the group, shorter than in $CsI_3$, may be thought to be compressed longitudinally by the cage of CH groups in which it is enclosed. Two interpretations of the effect of the environment on the configuration are possible. Perhaps the ion is distorted in $CsI_3$, and attains its normal configuration in the more uniform environment of $(C_6H_5)_4AsI_3$. On the other hand, the unsymmetrical form of the triiodide group may be nearer to the configuration that would result from its bonding system if it were free of external influence, and then the symmetrical form must be due to constraints imposed by its environment. It would be interesting to know the configuration of the triiodide ion in solution, where its surroundings presumably would be statistically uniform.

It is apparent that, whatever the nature of the bonds formed in the triiodide group, its configuration is susceptible to the influence of its surroundings. However, it is not easy to decide from the available observations, whether the system forms fundamentally equivalent bonds, which become unequal only when affected by a special type of coordination; or whether it forms fundamentally non-equivalent bonds which, on occasion, may be constrained to equivalence by a suitable crystal environment.

## An explanation of the configurations of the $I_3^-$ ion

It is possible to account for the existence of the symmetrical and unsymmetrical forms of the triiodide group in a simple way, without assuming any specific type of bond formulation, but postulating a qualitative resemblance between the iodine molecule-ion system, $I_2$–$I^-$, and a much simpler linear triatomic system which is well understood. This approach has been suggested by Prof. J. C. Slater, to whom the author is indebted for interesting discussions. He has presented the complete argument in a note which accompanies this paper (J. C. Slater, 1959). Therefore, only a brief preliminary statement is included here, such as is necessary for the discussion of the experimental data which follows.

For the simple linear triatomic system, $H_2$–H, it has been shown that the equilibrium position of the middle hydrogen is a function of the total distance between the end ones (Hirschfelder, Diamond & Eyring, 1937). The relation may be described as follows. Consider the middle hydrogen to be moved along a line joining the outermost hydrogens. Then the energy of the $H_3$ molecule shows two minima when the distance, $D$, defined as the separation of the terminal hydrogens, is greater than a particular critical value, $D_c$; and only one minimum when $D$ is less than $D_c$. The minima are symmetrical about the center of the system. When $D$ is very large, they lie at essentially covalent bond lengths from the terminal hydrogens. As $D$ is decreased, they move toward each other until, at $D = D_c$, they fuse into a single, centrally located minimum. Thus, two general types of configuration are possible for the $H_3$ molecule. For any value of $D$ larger than $D_c$, the middle hydrogen occupies one or the other of the two available minima, so that the interatomic distances are non-equivalent. For any value of $D$ equal to or smaller than $D_c$, the middle hydrogen lies in the single, central minimum, and the interatomic distances are equivalent.

The behavior of the $H_2$–H system, that is, the dependence of the group configuration on the distance between its end members, immediately suggests an explanation for the decided difference in configuration of the triiodide group as it is found in $CsI_3$ and $(C_6H_5)_4AsI_3$. It is plausible to say that the triiodide group in $CsI_3$, since it is surrounded by only a few widely spaced cations in typical ionic coordination, has a value of $D$ larger than the critical value for the system, and consequently, the middle iodine must lie in one or the other of two minima slightly displaced from the center of the group. Further, the triiodide group in $(C_6H_5)_4AsI_3$, hedged in and slightly compressed by many closely spaced neighbors, has a value of $D$ equal to or less than $D_c$, so that the middle ion occupies the single, centrally located minimum.

The obviously different configurations in these two cases seem to fit very well into the theoretical behavior pattern of a linear triatomic system as exemplified by $H_2$–H. It becomes interesting to investigate the minor differences in configuration which occur in cases where the crystal environments are not very different from that of $CsI_3$, and to intercompare, for all known triiodide configurations, the values of $D$, the distance between the terminal iodines; $d_1$, the shorter bond length; $d_2$, the longer bond length; and $s$, the displacement of the middle iodine from the center of the group. These data have been collected in Table 5. The values given are of closely comparable accuracy, except in the case of $NH_4I_3$, the oldest of the measurements, where no estimate was made of the errors. In the other cases, the estimated standard deviation of the bond lengths is close to 0·02 Å. The small bond angle, about 176° in all cases, has been neglected, so that $D$ is given as the sum of $d_1$ and $d_2$.

The triiodide group, functioning as an independent anion, or as part of a higher iodine complex anion, has been measured only in the few crystals listed in Table 5, and one other, $(CH_3)_4NI_9$, which has been

Table 5. *Observed triiodide configurations*

| Crystal | $D$ | $d_1$ | $d_2$ | $s$ |
|---|---|---|---|---|
| $(C_6H_5)_4AsI_3$ | 5·80 Å | 2·90 Å | 2·90 Å | 0·00 Å |
| $Cs_2I_8$ | 5·84 | 2·84 | 3·00 | 0·08 |
| $CsI_3$ | 5·87 | 2·83 | 3·04 | $0{\cdot}10_5$ |
| $NH_4I_3$ | 5·92 | 2·82 | 3·10 | 0·14 |
| $(CH_3)_4NI_5$ | 5·98 | 2·81 | 3·17 | 0·18 |

omitted because its iodine groups, interconnected in sheets, are not comparable with a simple linear triatomic system. The crystal environments have already been described for four of the crystals. In the case of $(CH_3)_4NI_5$, the environment is not known, and the triiodide ion is not an independent entity, since the long bonded iodine is shared between two short bonded pairs to form the $V$-shaped $I_5^-$ ion. For this crystal, the bond lengths tabulated are those obtained from a refinement of the original structure determination. References to the papers on polyiodide structures have already been given in the introductory section of this report.

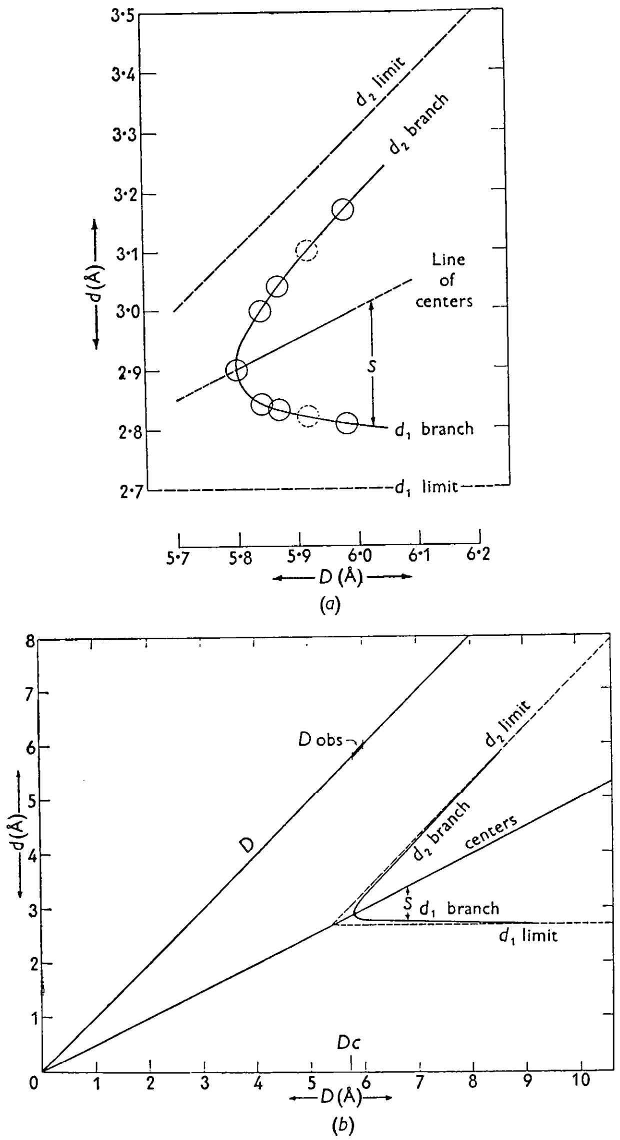


Fig. 5. The relation between $D$, the distance between terminal iodines in $I_3^-$ ions, and their bond lengths, $d_1$ and $d_2$. (*a*) Plot of experimental data, $D$ versus $d_1$ and $d_2$. (*b*) Extension of experimental curve to include a wide range of $D$ values.

It is seen from Table 5, that there are minor differences in the dimensions of the four unsymmetrical triiodide ions. Only a few of these differences might confidently be assumed to be significant. Nevertheless, it seems something more than a curious coincidence to find that the overall lengths of the groups are related to their bond lengths in exactly the way which would be predicted from the assumption of analogous behavior between the systems $I_2$–$I^-$ and $H_2$–H. This is illustrated in the large-scale diagram, Fig. 5(*a*), where the bond lengths, $d_1$ and $d_2$, are plotted as a function of $D$. All the points fall smoothly on a pair of curves which converge as $D$ becomes smaller. The curves meet at the point, $d_1 = d_2$, when $D$ attains the value of 5·80 Å, which may be taken as the critical value, $D_c$, of the $I_2$–$I^-$ system. These data seem sufficient evidence for assuming that, in the matter of its configurations, the $I_2$–$I^-$ system behaves in a manner comparable to $H_2$–H system.

## Discussion of the system, $I_2$–$I^-$

The experimental data supplies at least an approximate value for the critical distance in the $I_2$–$I^-$ system, and shows the dependence of $d_1$ and $d_2$ on $D$ for a very small range of $D$ values. In order to represent the whole range of possible $D$ values and their associated configurations, the diagram shown in Fig. 5(*b*) has been constructed. The experimental curves have been extended in both directions from the critical distance by simple analogy with the $H_2$–H system. In the direction of increasing $D$ values, the lower curve, representing the change in $d_1$, has been made to fall asymptotically toward a limiting value, 2·70 Å, the covalent bond length; while the upper curve, representing the change in $d_2$, has been made to rise in a corresponding fashion, so that at every point, $D$ remains equal to $d_1 + d_2$. In the direction of decreasing $D$ values, a straight line, directed toward the origin, shows the range where $d_1 = d_2 = D/2$.

Now all the possible changes in the configuration of the $I_3^-$ ion may be described. The initial state, assumed to consist of an iodine ion and an iodine molecule, is represented on the diagram at some very large value of $D$, where $d_1$ is indistinguishable from the covalent bond length. Now, as the distance $D$ is made to decrease, either by interactions within the group or by some outside agency, $d_1$ increases and $d_2$ decreases until the values become equivalent at $D_c$, and so remain as $D$ continues to diminish. Thus, in principle, there is a continuous range of possible triiodide configurations, limited at one end by values of $D$ too large for effective interaction of the components and on the other end by values of $D$ too small to permit any closer approach of the three atoms. Without knowledge of another function, that is, the manner in which the total energy of the $I_3^-$ ion varies with the relative positions of its components, there is no basis for predicting which of the $D$ values can be maintained by interactions within the group, that is, by stable bond formation, and which are wholly or partly dependent on external agencies. The diagram is useful only in predicting the configuration to be expected for any given $D$ value. For instance, it indicates that the bond lengths in any symmetrical triiodide group must be less than 2·92 Å, since a $D$ value of 5·84 Å corresponds to an unsymmetrical configuration; that no unsymmetrical group can exist with $d_1$ exactly equal to 2·70 Å, since any interaction between the components of the group must increase this distance, and if $d_1$ is only slightly larger than the covalent bond distance, $d_2$ must be considerably larger than 3·5 Å.

Though only surmises are possible, it is interesting to ask whether the symmetrical or the unsymmetrical configuration of the triiodide group is the 'normal' form; that is to say, the form due primarily to internal interactions rather than to external influences. Even though nothing is known concerning the relation between the energy of the $I_3^-$ group and its configuration, it may surely be assumed that the energy varies with $D$ in such a way as to fall to minimum values in the neighborhood of some specific value of $D$. If this is so, then there will be a configuration, or perhaps a very small range of configurations, with inherent stability. The degree of stability may be great or small, depending on the shape and depth of the energy minimum. There is no more reason to except this configuration to be equibonded than to expect it to be non-equivalently bound. However, the relatively stable configuration should be the one most commonly observed in crystals.

The observations of the triiodide group are few, and somewhat unsatisfactory as a basis for deducing a typical triiodide configuration, since with the exception of $CsI_3$, the crystals which have been structurally studied are all rather special cases. $NH_4I_3$ is on the borderline of stability; $(C_6H_5)_4AsI_3$, has an uncommonly large cation; the other two crystals contain the triiodide group as part of a higher complex. Crystals such as the triiodides of $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, which are quite stable, and have only moderately large cations, may well show less variation in the triiodide configuration than has been observed in the available series. These crystals have not been structurally studied, but some preliminary investigation by the author indicates the strong probability that the triiodide groups in these crystals are unsymmetrical. Whether or not this is so, the few triiodide groups which have been measured are preponderantly of the unsymmetrical type. Therefore, it is reasonable to assume that the configuration energy of the $I_2$–$I^-$ system has a minimum, probably not very pronounced, for a configuration corresponding to a value of $D$ slightly larger than $D_c$. Such a configuration would be characterized by two possible equilibrium positions for the middle iodine, off center by not much more than 0·1 Å. In this event, the unsymmetrical configuration, slightly modified by its particular environment, should be commonly found in crystals, while the symmetrical form could occur only when stabilized by an exceptional environment. This is essentially what has been observed so far; and it would not be surprising to find, eventually, that the groups in these five crystals cover very nearly the whole range of triiodide configurations which might be expected to exist in crystals.

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