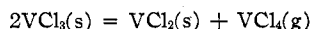


TABLE V  
 VAPORIZATION CHARACTERISTICS OF  $\text{VCl}_3$  AND  $\text{VBr}_3$ 

| Compd.         | Process                | $\log P_{\text{mm}}$ | $\Delta H^\circ$ , kcal. | $\Delta S^\circ$ , e.u. | $T$ , °K. |
|----------------|------------------------|----------------------|--------------------------|-------------------------|-----------|
| $\text{VCl}_3$ | Subl.                  | $-9777/T + 11.20$    | $44.7 \pm 1.4$           | $38.0 \pm 0.8$          | 625-740   |
|                | Dispropn. <sup>a</sup> | $-7801/T + 9.84$     | $36 \pm 1$               | $32 \pm 1$              | 625-740   |
|                | Dispropn. <sup>b</sup> | $-8350/T + 11.58$    | $38 \pm 1$               | $39.6 \pm 1$            | 700-900   |
| $\text{VBr}_3$ | Subl.                  | $-9470/T + 11.12$    | $43.3 \pm 1.2$           | $37.7 \pm 1$            | 590-700   |

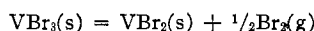
<sup>a</sup> This work. <sup>b</sup> Data derived from ref. 21.

Disproportionation pressures for the reaction



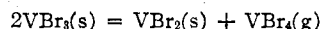
are also given in Table IV and were derived from measurements with both cell 1 and cell 2. A comparison of the results derived from this work and those of Oranskaya, *et al.*,<sup>21</sup> is given in Table V; the latter authors utilized the transpiration technique to measure the disproportionation pressure. As indicated the agreement of these results is poor.

Although the results from the cells of different orifice areas were in good agreement for disproportionation of  $\text{VCl}_4$ , the results of measurements to determine the equilibrium pressures from the reactions



(21) M. A. Oranskaya, Yu. S. Lebedev, and I. L. Perfilova, *Zh. Neorgan. Khim.*, **6**, 259 (1961).

and



showed a definite dependence on the orifice area. This was taken to indicate that in reactions of this type the condensation coefficients may be much less than unity, and thus equilibrium pressures were not obtained. Therefore, in spite of the agreement between the data from the two cells, it is probable that nonequilibrium pressures were obtained for the disproportionation of  $\text{VCl}_3$ . Consequently it is likely that the previous workers' results on the disproportionation of  $\text{VCl}_3$  are the more reliable. Equilibrium pressures for the reactions of  $\text{VBr}_3$  given above have been determined by the transpiration technique and are the subject of another paper.<sup>22</sup>

(22) R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 54 (1964).

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## Crystal and Molecular Structure of Indium(III) Iodide ( $\text{In}_2\text{I}_6$ )<sup>1</sup>

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Indium(III) iodide exists in the crystals as dimers,  $\text{In}_2\text{I}_6$ , according to a determination of the structure by single-crystal X-ray diffraction. The crystals are monoclinic, space group  $\text{P2}_1/\text{c}$ , with  $a = 9.837 \pm 0.004$ ,  $b = 6.102 \pm 0.004$ ,  $c = 12.195 \pm 0.009$  Å.,  $\beta = 107.69 \pm 0.05^\circ$ ,  $Z = 2$ ,  $d_x = 4.72$  g./cc. Twinning is common. Iodine atoms are approximately in cubic closest packing. Indium atoms are in adjacent tetrahedral holes so that the structure consists of pairs of tetrahedra sharing edges. The In-I bond distances are 2.84 Å. for the bridge bonds and 2.64 Å. for the terminal bonds. The In-In distance in the molecule is 3.88 Å. Bond angles are  $93.7^\circ$  for I-In-I (bridge bonds) and  $125.1^\circ$  for I-In-I (terminal bonds).

### Introduction

Most crystalline metallic trihalides exist as structures which are infinite complexes in one, two, or three dimensions.<sup>2</sup> Only a few (*e.g.*, monomeric  $\text{SbF}_3$ <sup>3</sup> and  $\text{SbCl}_3$ <sup>4</sup> and dimeric  $\text{Al}_2\text{Br}_6$ <sup>5</sup> and  $\text{Au}_2\text{Cl}_6$ <sup>6</sup>) are known to have structures consisting of discrete molecules, although dimeric molecular structures are very common for trihalides in the liquid and gaseous states. Dimers

exist also in the solid triiodides of aluminum, gallium, and indium according to iodine nuclear quadrupole spectra reported by Segel and Barnes.<sup>7</sup> This fact is confirmed for the indium compound by the crystal structure determination reported in the present paper. According to X-ray powder diagrams<sup>8</sup> it is likely that the aluminum and gallium iodides have the same crystal structure as  $\text{In}_2\text{I}_6$ .

This substance was originally investigated in this laboratory as part of a search for trihalides with structures like rare earth halides. Because of unrecognized twinning in the first samples, we thought at one time that the structure was triclinic with a unit cell containing 64 atoms in the primitive unit. In trying to

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, England, 1962, p. 353.

(3) A. Byström and A. Westgren, *Arkiv Kemi Mineral. Geol.*, **17B**, No. 2, 1 (1943).

(4) I. Lindqvist and A. Niggli, *J. Inorg. Nucl. Chem.*, **2**, 345 (1956).

(5) P. A. Renes and C. H. MacGillivray, *Rec. trav. chim.*, **64**, 275 (1945).

(6) E. S. Clark, D. H. Templeton, and C. H. MacGillivray, *Acta Cryst.*, **11**, 284 (1958).

(7) S. L. Segel and R. G. Barnes, *J. Chem. Phys.*, **25**, 578 (1956).

(8) E. L. Amma, private communication, 1963.

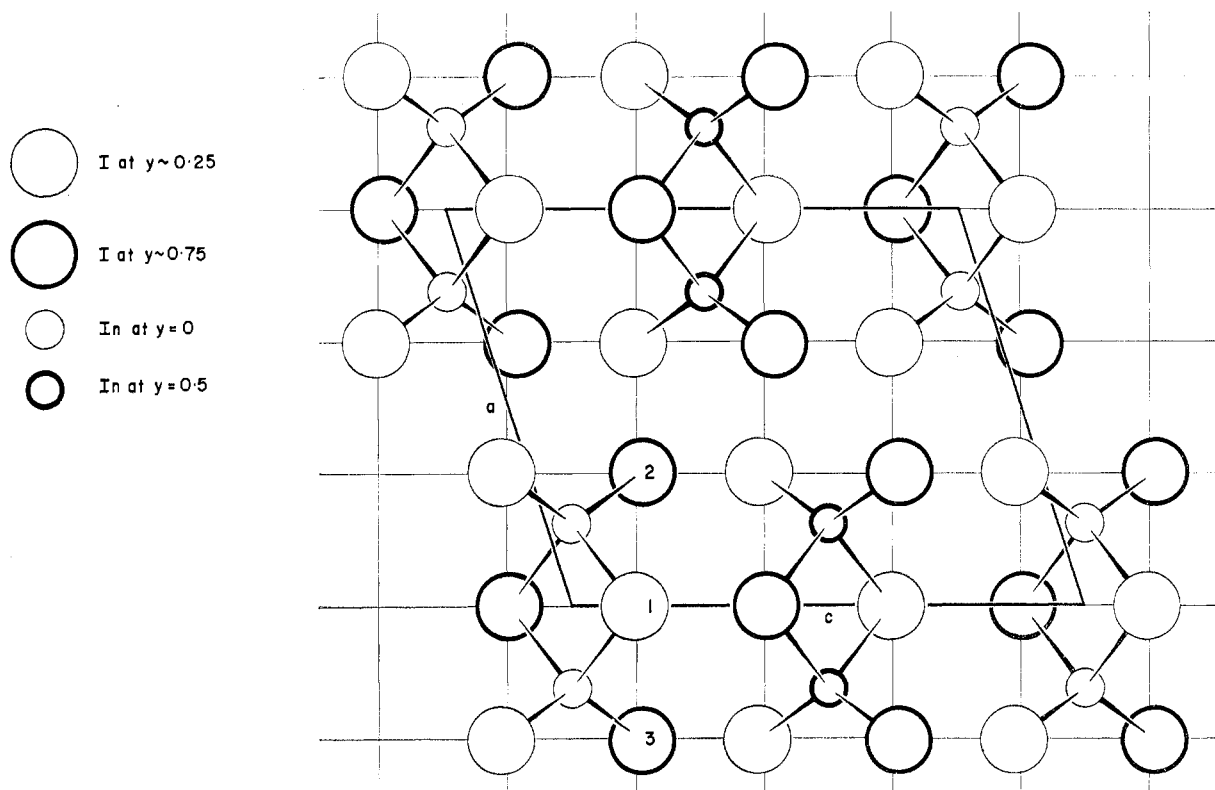


Fig. 1.—Crystal structure of  $\text{In}_2\text{I}_6$ , projected down the  $b$  axis. The square grid has half the spacing of the cubic sublattice to show that the iodine atoms are nearly in cubic closest packing.

explain the existence of such a complicated structure we found the rather simple result described in this paper.

### Experimental

Indium(III) iodide was synthesized from the elements in an evacuated bent Pyrex tube containing iodine in one end and indium metal in the other. The indium was heated to  $250^\circ$  while the iodine remained at room temperature. As the indium reacted with iodine vapor the product condensed in a ring in the cooler zone of the tube. Small quantities of crystals were transferred in a drybox to silica glass capillary tubes (0.6 mm. in diameter and 0.015 mm. wall thickness) and sealed off. The capillaries were heated to  $250^\circ$  in an oven and then cooled slowly. This treatment produced small crystals attached at various places to the walls of the capillaries.

Twinning of the crystals is common and causes the diffraction patterns to seem to correspond to a unit cell much larger than the true one. Diffraction photographs of twinned crystals of  $\text{In}_2\text{I}_6$  were taken by R. E. Jones in this laboratory in 1954, but the correct interpretation of them as multiple patterns was made only after untwinned crystals were found in the present investigation. Photographs by the Weissenberg and precession techniques established the correct unit cell.

The final structure reported here is based on data from a crystal in the form of an approximately hexagonal plate of dimensions  $0.13 \times 0.11 \times 0.06$  mm. The data were measured using a General Electric XRD-5 X-ray goniostat equipped with a scintillation counter and a pulse-height discriminator and using  $\text{Mo K}\alpha$  radiation. Unit cell dimensions are based on  $\lambda = 0.70926 \text{ \AA}$ . for  $\text{K}\alpha_1$ . The intensities of 1236 independent reflections permitted by the space group with  $\sin \theta/\lambda$  less than 0.596 ( $2\theta < 50^\circ$ ) were measured; of these, 230 were recorded as zero.

The linear absorption coefficient is estimated at  $175.9 \text{ cm.}^{-1}$ , which corresponds to  $\mu R = 1.1$  for the largest diameter of the crystal. No corrections were made for either absorption or extinction.

Calculations were made with the IBM-7090 computer using the Zalkin data processing program and our version of the Gantzel-Sparks-Trueblood least-squares program (both unpublished). The function minimized in least squares was  $\sum (|F_o| - |F_c|)^2 / \sum F_o^2$ . We used atomic scattering factors for neutral In and I from Ibers<sup>9</sup> with a dispersion correction<sup>10</sup> of  $-0.7$  for In and  $-0.5$  for I.

### Results

**Unit Cell and Space Group.**—The crystals are monoclinic with unit cell dimensions  $a = 9.837 \pm 0.004$ ,  $b = 6.102 \pm 0.004$ ,  $c = 12.195 \pm 0.009 \text{ \AA}$ .,  $\beta = 107.69 \pm 0.05^\circ$ . The systematic absences ( $h0l$  absent if  $l$  is odd,  $0k0$  absent if  $k$  is odd) are characteristic of space group  $P2_1/c$  ( $C_{2h}^5$ ), and this symmetry is confirmed by the ultimate agreement of observed and calculated structure factors. With two dimer molecules ( $\text{In}_2\text{I}_6$ ) per unit cell the density is calculated as 4.72 g./cc. in agreement with the measured density<sup>11</sup> 4.69 g./cc.

**Determination of the Structure.**—The strong lines of the powder pattern correspond to a face-centered cubic lattice with cell dimension about 6.1  $\text{\AA}$ ., which is large enough to hold four I atoms. We expected from the beginning of our study that I atoms are approximately in cubic closest packing. The monoclinic unit cell is easy to fit to such a cubic sublattice with  $b$  and  $c$  coinciding with cubic axial directions. The relation of  $a$  and  $c$  to the cubic lattice is shown in Fig. 1. If the fit were perfect the axial ratios and angle would be  $a/b$

(9) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p. 211.

(10) D. H. Templeton, "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p. 216.

(11) W. Klemm and F. Dierks, *Z. anorg. allgem. Chem.*, **219**, 42 (1934).

$= 0.5\sqrt{10} = 1.581$ ,  $c/b = 2$ ,  $\beta = 108.4^\circ$ , compared with the observed  $a/b = 1.612$ ,  $c/b = 1.999$ ,  $\beta = 107.7^\circ$ .

The only way to arrange the iodine atoms in cubic closest packing in the sublattice that is consistent with the symmetry of  $\text{P}2_1/\text{c}$  places them in general positions 4(e):  $\pm(x, y, z; x, 1/2 - y, 1/2 + z)$ , with the coordinates (or other equivalent choices), I(1):  $0, 1/4, 1/8$ , I(2):  $1/3, 3/4, 5/24$ , I(3):  $2/3, 3/4, 1/24$ . There are then three distinct structures which result if In atoms are placed in tetrahedral holes. The holes at  $x = 1/2$  give a layer structure in which I(1) atoms have no In neighbors and which therefore is not acceptable. Placing In at  $1/6, 0, 7/24$  gives a chain structure of tetrahedra sharing corners. The coordinates  $1/6, 0, 1/24$  give a structure of dimers of tetrahedra sharing an edge. These structures were deduced from the unit-cell data before the intensities were measured.

Both the chain structure and the dimer structure were tested by least squares using isotropic temperature factors and all the intensity data including zero reflections and several which were in error by card punching. The conventional unreliability factor  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  was reduced to 0.28 for the dimer structure and 0.42 for the chain structure by 4 cycles in each case. The results favored the dimer structure more than indicated by the  $R$  values because the two structures are equivalent as far as the  $k$ -even data are concerned.

After correction of the card-punching errors refinement of the dimer structure was continued. With isotropic temperature factors and omitting the zero

intensities,  $R$  was reduced to 0.136. Each atom was given an anisotropic temperature factor of the form  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ , making a total of 37 independent parameters. Several further cycles of refinement reduced  $R$  for the 1006 nonzero reflections to 0.105. In the final cycle no parameter changed as much as 0.002 times the corresponding standard deviation. The program used the full matrix. The resulting atomic parameters are listed in Tables I and II. The coordinates from the isotropic refinement are within two standard deviations of those listed in Table I.

The refinement moved the In atom about  $0.4 \text{ \AA}$ . in the direction away from the center of the dimer. No iodine atom moved as much as  $0.2 \text{ \AA}$ . from the "ideal" positions where they were started.

TABLE I

ATOMIC COORDINATES AND STANDARD DEVIATIONS

| Atom | $x$    | $y$     | $z$    | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|------|--------|---------|--------|-------------|-------------|-------------|
| In   | 0.2072 | -0.0005 | 0.0510 | 0.0003      | 0.0006      | 0.0003      |
| I(1) | .0001  | .2360   | .1220  | .0004       | .0006       | .0003       |
| I(2) | .3361  | .7293   | .2198  | .0004       | .0006       | .0003       |
| I(3) | .6617  | .7306   | .0531  | .0004       | .0006       | .0003       |

TABLE II

ANISOTROPIC THERMAL PARAMETERS

| Atom | $\beta_{11}^a$ | $\beta_{22}^a$ | $\beta_{33}^a$ | $2\beta_{12}^a$ | $2\beta_{13}^a$ | $2\beta_{23}^a$ |
|------|----------------|----------------|----------------|-----------------|-----------------|-----------------|
| In   | 71             | 204            | 41             | -12             | 35              | 30              |
| I(1) | 96             | 205            | 48             | -5              | 51              | -62             |
| I(2) | 114            | 230            | 46             | 47              | 39              | 41              |
| I(3) | 120            | 224            | 57             | -71             | 84              | 14              |

<sup>a</sup> Multiplied by  $10^4$ .

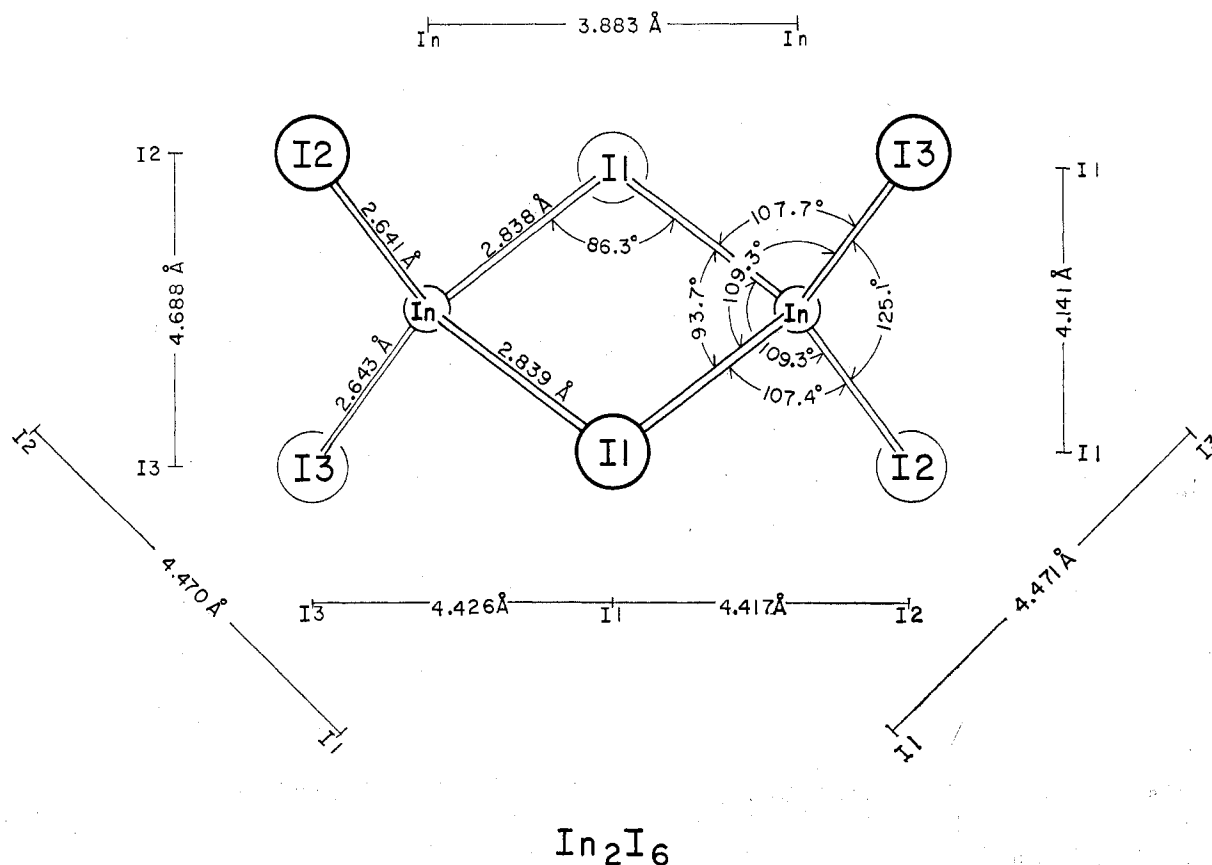


Fig. 2.—Dimensions of the  $\text{In}_2\text{I}_6$  molecule. Standard deviations are 0.005 to 0.007 for distances and about  $0.3^\circ$  for angles.

TABLE III  
 OBSERVED STRUCTURE FACTOR MAGNITUDES (FOB) AND CALCULATED STRUCTURE FACTORS (FCA)

|            |             |             |            |             |            |             |            |            |            |            |            |
|------------|-------------|-------------|------------|-------------|------------|-------------|------------|------------|------------|------------|------------|
| H,K=0,0    | -12 0 3*    | -11 66 70   | 0 0 5*     | 9 46 -43    | -8 39 38   | -12 20 18   | 1 49 53    | -10 47 56  | L FOB FCA  | 8 14 -12   | -4 161 149 |
| L FOB FCA  | -10 0 3*    | -10 39 32   | 1 67 -64   | 10 15 16    | -7 18 11   | -11 16 19   | 2 14 -9    | -9 18 20   | -11 18 -15 | -3 64 52   | -3 64 52   |
| 2 162 122  | -8 168 158  | -9 52 49    | 2 196-190  | 11 0 -1*    | -6 171 161 | -10 142-140 | 3 8 11     | -8 37 35   | -10 10 -15 | H,K=3,5    | -2 44 43   |
| 4 45 37    | -6 30 -24   | -8 53 47    | 3 73 -71   | 12 17 29    | -5 25 24   | -9 26 -25   | 4 38 36    | -7 21 14   | -9 14 -19  | L FOB FCA  | -1 13 21   |
| 6 185-165  | -4 64 -62   | -7 26 23    | 4 9 12     |             | -4 131 124 | -8 28 -23   | 5 18 -24   | -6 91 77   | -8 21 27   | 10 14 26   | 0 0 6*     |
| 8 89 -60   | -2 46 -43   | -6 367-347  | 5 18 -18   | H,K=2,2     | -3 7 12    | -7 38 30    | 6 18 -24   | -5 100 91  | -7 0 -6*   | -9 24 33   | 1 21 23    |
| 10 99-102  | -1 19 -10   | 5 127-177   | 6 10 -4    | L FOB FCA   | -2 72 71   | -6 28 16    | 7 37 -45   | -6 171-146 | -6 0 -5*   | -8 14 16   | 2 34 -32   |
| 12 152-163 | 2 26 4      | -3 33 -32   | 7 22 14    | -13 0 8*    | -1 40 38   | 9 88 76     | 8 10 12    | -3 72 -62  | -5 25 -21  | -7 64 66   | 3 21 18    |
|            | 4 100 -89   | -3 176-152  | 8 36 34    | -12 31 39   | 0 227-237  | -4 83 -70   | 9 49 -52   | -2 177-160 | -4 26 28   | -6 136-130 | 4 14 -21   |
|            | 6 53 53     | -2 15 -16   |            | -11 0 6*    | 1 38 -39   | -3 85 70    |            | -1 37 23   | -3 0 -9*   | -5 87 -83  | 5 10 19    |
| H,K=1,0    | -1 142-147  | H,K=6,1     | -10 95 94  | 2 43 -38    | -2 12 -12  | H,K=6,3     | 0 27 28    | -2 24 31   | -4 0 -13*  | -6 36 -44  | 7 29 30    |
| L FOB FCA  | 0 0 -7*     | L FOB FCA   | -9 59 55   | 3 8 -7      | -1 53 45   | L FOB FCA   | 1 31 -31   | -1 42 -47  | -3 83 -84  | 7 29 30    |            |
| -14 10 -24 | H,K=9,0     | 0 0 -7*     | 1 80 -79   | -12 0 -14*  | -8 167-151 | 4 71 -71    | 0 0 2*     | -12 66 -77 | 2 0 -3*    | 0 150 152  | -2 0 -3*   |
| -12 66 -71 | L FOB FCA   | 1 80 -79    | 2 25 -22   | -11 27 35   | 7 17 4     | 5 18 -7     | L FOB FCA  | -11 28 -36 | 3 18 -21   | 1 54 52    | -1 72 -79  |
| -10 98 93  | -12 75 -80  | -2 25 -22   | -11 27 35  | 7 17 4      | -6 42 19   | 1 17 8      | L FOB FCA  | -10 30 -35 | 4 92 -85   | 2 26 -32   | 0 0 7*     |
| -8 54 50   | -10 64 -66  | 3 0 3*      | -10 0 2*   | -6 46 42    | 6 4 11     | 1 34 338    | -10 90 -9  | 5 20 -14   | 3 9 11     | 1 47 -51   | -8 29 -34  |
| -6 173 148 | -8 55 -57   | 4 15 17     | -9 13 16   | -5 0 -16*   | 7 0 -2*    | 1 86 18     | -9 0 1*    | 5 20 -14   | 3 9 11     | 1 47 -51   | -8 29 -34  |
| -4 353-331 | -6 117-114  | 5 57 57     | -8 81 -78  | -4 43 29    | 8 52 -49   | 4 10 -15    | -8 15 -25  | 6 56 -52   | 4 34 -40   | 2 15 -23   | -7 17 -23  |
| -2 159 120 | -4 67 -66   | 6 267 253   | -7 24 -24  | -3 20 -20   |            | 5 84 -77    | -7 0 -5*   | 7 37 -30   | 5 10 12    | 3 0 -6*    | -6 26 25   |
| 0 58 42    | -2 9 -5     | 7 109 106   | -6 40 -39  | -2 126-105  | H,K=7,2    | 6 13 -3     | -6 197 186 | 8 94 89    | 6 64 -66   | 4 0 5      | -5 14 -17  |
| 2 0 -5*    | 0 194 178   | 8 28 -31    | -5 83 -63  | -1 27 -29   | H,K=7,2    | 6 56 -49    | -5 111 109 | 9 57 62    | 5 0 -2*    | -4 19 17   |            |
| 4 156-136  | 2 48 43     | 9 54 54     | -4 16 -20  | 0 125-138   | -13 0 8*   | 8 88 -80    | -4 21 19   | 10 20 23   | H,K=7,4    | 6 96 96    | -3 0 -13*  |
| 6 98 -84   | 2 47 43     | 10 0 4*     | -3 92 -81  | 1 4 -4*     | -1 22 31   | 9 55 27     | -2 14 13   | 11 0 6*    | L FOB FCA  | 7 64 96    | -2 28 -35  |
| 8 195 177  | 4 100 -89   | -3 176-152  | 8 36 34    | -12 31 39   | 0 227-237  | -4 83 -70   | 9 49 -52   | -2 177-160 | -4 26 28   | -6 136-130 | 4 14 -21   |
| 10 52 -50  | H,K=10,0    | 12 51 -59   | -1 44 -41  | 3 47 -45    | -10 32 -33 | 11 0 15*    | -1 42 43   | H,K=2,4    | -9 17 25   | 0 43 -57   | 0 43 -57   |
| 12 10 12   | L FOB FCA   | 0 0 -1*     | 4 261 248  | -9 18 -10   | 12 21 -16  | 0 0 7*      | H,K=0,7*   | L FOB FCA  | -8 74 77   | H,K=4,5    | 1 0 -16*   |
|            | -10 0 18*   | H,K=4,1     | 1 12 -12   | 5 65 60     | -8 19 25   |             | 1 0 -2*    | -12 0 -6*  | -7 0 18*   | L FOB FCA  | 2 38 -41   |
| H,K=2,0    | -8 0 8*     | L FOB FCA   | 2 9 7      | 6 49 -49    | -7 8 -5    | H,K=2,3     | 2 35 29    | -11 10 -2  | -6 45 48   | -10 63 71  | 3 37 -42   |
| L FOB FCA  | -12 23 -22  | -12 23 -22  | 4 7 17     | 4 5 18      | 1 17 8     | L FOB FCA   | 3 41 -44   | -10 17 21  | -5 42 -52  | -2 21 24   | -7 0 7*    |
| -14 80 -96 | -4 98 -86   | -13 10 10   | 4 21 -23   | 8 29 27     | 5 14 -36   | -13 0 9*    | 4 0 -5*    | -9 59 -62  | -4 124-128 | -8 10 15   | 5 54 59    |
| -12 0 -3*  | -2 51 47    | -12 33 -37  | 5 38 42    | 9 9 8       | -4 215 209 | -12 14 18   | 5 24 -31   | -8 217 208 | -3 38 -39  | -7 21 -25  | 6 0 9*     |
| -10 29 20  | 0 36 38     | -11 26 -29  | 6 20 21    | 10 28 -28   | -3 32 29   | -11 44 46   | 6 110-106  | -7 51 43   | -2 31 -37  | -6 0 -9*   |            |
| -8 386 385 | 2 33 26     | -10 190 186 | 6 20 21    | 11 0 -4*    | -2 36 37   | -10 0 -12*  | 7 72 -69   | -6 86 74   | -1 9 -19   | -5 31 -34  | H,K=3,6    |
| -6 157 137 | -9 52 -47   | H,K=9,1     | 12 55 66   | 0 64 -60    | -8 109 105 | -9 70 70    | 8 0 10*    | -5 34 28   | 0 54 -57   | -4 38 36   | L FOB FCA  |
| -4 60 43   | H,K=11,0    | 9 37 32     | L FOB FCA  | 0 64 -60    | -8 109 105 | H,K=7,3     | 3 17 8     | -4 15 16   | 1 0 -13*   | -3 0 2*    | -8 0 -1*   |
| -2 12 -0   | L FOB FCA   | -9 102 -90  | H,K=3,2    | 2 79 -77    | -6 32 28   | L FOB FCA   | -2 13 -0   | 3 0 -10*   | -1 17 25   | -6 10 24   | -7 0 7*    |
| 0 128-131  | -8 108 109  | -6 0 3*     | -11 0 -9*  | L FOB FCA   | 2 79 -77   | -6 32 28    | L FOB FCA  | -2 13 -0   | 3 0 -10*   | -1 17 25   | -6 10 24   |
| 2 187-169  | -6 50 50    | -5 114 -98  | -10 28 34  | -13 20 -28  | 3 9 8      | -5 77 67    | -12 21 25  | -1 32 33   | 4 45 -45   | 0 0 1*     | -5 17 21   |
| 4 460-460  | -4 43 42    | -4 99 90    | -9 36 -39  | -12 161 171 | 4 9 -7     | -4 24 24    | -11 66 74  | 0 50 -55   | 5 0 -3*    | 1 77 92    | -4 10 -18  |
| 6 0 16*    | -2 36 32    | -3 49 -44   | -8 19 22   | -11 13 16   | 5 0 3*     | -3 89 77    | -10 97 -98 | 1 18 20    | 2 123-131  | -3 0 12*   |            |
| 8 46 41    | 0 18 12     | -2 32 30    | -7 40 -43  | -10 81 80   | 6 0 -4*    | -2 360-336  | -9 28 36   | 2 95 -89   | H,K=8,4    | 3 0 12*    | -2 42 -62  |
| 10 138 144 | H,K=0,1     | 0 5*        | -6 152-144 | -9 23 18    | 7 0 9*     | -1 150-150  | -8 0 -10*  | 3 63 39    | L FOB FCA  | 5 24 39    | -1 44 55   |
| 12 14 20   | L FOB FCA   | 1 111 115   | -4 0 -11*  | -7 0 10*    | H,K=8,2    | 1 124-129   | -6 0 -2*   | 5 79 -75   | -8 80 85   | 6 0 -2*    | 1 50 -58   |
|            | H,K=3,0     | 1 186 151   | 2 317-349  | -3 23 -21   | -6 76 68   | L FOB FCA   | 2 0 -2*    | -5 0 11*   | 6 0 1*     | -7 14 20   | 7 0 2*     |
| L FOB FCA  | 2 0 -4*     | 3 80 79     | -2 9 -8    | -5 24 24    | -12 65 73  | 3 124-118   | -4 43 -46  | 7 0 -8*    | -6 0 -19*  | 3 10 -14   |            |
| -14 56 68  | 3 100 79    | 4 23 20     | -1 15 20   | -4 94 -76   | -11 0 10*  | 4 63 60     | -3 37 -41  | 8 26 28    | -5 0 15*   | H,K=5,5    | 4 20 18    |
| -12 73 -77 | 4 36 30     | 5 79 75     | 0 0 -5*    | -3 0 10*    | -10 53 57  | 5 64 -56    | -2 33 33   | 9 17 -17   | -4 34 -33  | L FOB FCA  | 5 14 -17   |
| -10 33 27  | -12 34 -27  | -6 16 -4    | 1 41 42    | -2 130-111  | -9 28 32   | 6 27 -24    | -1 55 -61  | 10 84 90   | -2 19 -26  | -8 55 -60  | H,K=4,6    |
| -8 39 29   | 6 364 349   | 7 22 23     | -2 30 -23  | -1 55 59    | -8 138-135 | 7 12 -2     | 0 0 -5*    |            | -2 19 -26  | -8 55 -60  | H,K=4,6    |
| -6 201-177 | 7 37 -33    | 8 69 69     | 3 46 45    | 0 332-485   | -7 15 -17  | 8 25 15     | 1 92 -92   | H,K=3,4    | -1 14 13   | L FOB FCA  | 7 40 -94   |
| -4 183-152 | 8 42 -40    | 9 9 -14     | 4 0 2*     | 1 61 -63    | -6 50 -53  | 9 16 19     | 2 147 139  | L FOB FCA  | 0 0 1*     | -6 21 -49  | -7 0 -18*  |
| -2 195-176 | 9 83 -77    | 10 20 -25   | 5 25 23    | 2 9 -9      | -4 72 -73  | 10 101 103  | 3 0 -4*    | -12 29 -35 | 1 0 5*     | -5 0 -5*   | -6 43 -45  |
| 0 283 375  | 10 0 -12*   | 11 31 -34   | 3 13 -13   | -4 7 13     | -3 8 -11   | 11 72 81    | 4 0 -7*    | -11 0 -9*  | 2 10 2     | -4 0 -9*   | -5 56 -63  |
| 2 43 38    | 11 52 -52   | H,K=5,1     | 4 44 41    | 1 4 4       | -3 8 -11   | H,K=3,3     | 5 0 -8*    | -10 21 23  | 3 23 20    | -3 13 -21  | -4 54 61   |
| 4 65 61    | 12 79 -68   | L FOB FCA   | 5 19 18    | -2 88 67    | H,K=3,3    | 6 193-187   | 6 0 3*     | -9 0 -16*  | H,K=9,4    | -1 92 105  | -2 0 2*    |
| 6 0 0*     | 13 25 -25   | L FOB FCA   | 6 156 149  | -1 0 -13*   | L FOB FCA  | 1 29 41     | H,K=8,3    | -7 15 -11  | L FOB FCA  | 0 0 5*     | -1 0 18*   |
| 8 104 101  | H,K=1,1     | -13 31 -37  | -8 0 11*   | 8 41 38     | 1 0 -4*    | -12 67 -76  | L FOB FCA  | -6 113-101 | -7 0 -11*  | 1 50 59    | 0 0 2*     |
| 10 21 20   | L FOB FCA   | -12 23 -25  | -7 0 -5*   | 9 9 -8      | 2 9 3      | -11 35 33   | -11 41 47  | -5 39 -35  | -6 69 -72  | 2 0 5*     | 1 10 16    |
| 12 75 -74  | -14 15 -17  | -11 64 -69  | -6 0 4*    | 10 44 50    | 3 16 -15   | -10 16 -22  | -10 0 2*   | -4 105 -94 | -5 0 -20*  | 3 23 32    | 2 22 25    |
| H,K=4,0    | -13 42 -47  | -10 0 4*    | -5 19 23   | 11 0 -10*   | 4 141 137  | -9 30 26    | -9 17 21   | -3 19 -21  | -4 46 -48  | 4 14 -21   | 3 0 11*    |
| L FOB FCA  | -12 34 -27  | -12 34 -27  | 4 33 32    | 7 7 -7      | 5 22 20    | 6 25 29     | -7 87 -80  | -7 0 2*    | -1 69 -77  | -2 0 -3*   | 6 10 23    |
| -14 48 53  | -11 59 -62  | -8 125-117  | -3 46 49   | H,K=4,2     | -13 0 -7*  | -6 265 242  | -6 22 32   | 0 151 170  | -1 25 -26  | H,K=5,6    | 1 50 59    |
| -12 0 -2*  | -10 193 187 | -7 59 -53   | -2 28 26   | L FOB FCA   | -13 0 -7*  | -5 19 15    | -5 34 -37  | 1 67 75    | 0 108 102  | H,K=6,5    | L FOB FCA  |
| -10 95 90  | -9 19 9     | -6 45 -39   | -1 50 49   | -1 0 5*     | -11 0 5*   | -4 12 17    | -4 0 11*   | 2 18 -16   | 1 33 28    | L FOB FCA  | -6 0 -9*   |
| -8 55 -48  | -8 36 35    | -5 21 15    | 0 10 5     | -12 23 26   | -11 0 5*   | -3 87 -76   | -3 13 -22  | 3 14 15    | L FOB FCA  | -8 18 20   | -5 0 -19*  |
| -6 86 -71  | -7 82 72    | -4 30 -28   | 1 43 37    | -11 0 -2*   | -10 0 -14* | -2 0 4*     | -2 146-141 | 4 33 33    | H,K=0,5    | -8 0 17*   | 0 10 17    |
| -4 469-490 | -6 9 -7     | -3 60 58    | 2 105 -85  | -10 134-136 | -10 0 -14* | -2 0 4*     | -1 76 -79  | 5 17 21    | L FOB FCA  | -7 82 86   | -3 0 11*   |
| -2 163 -18 | -5 16 137   | -2 18 -16   | -4 41 32   | -2 0 2*     | 5 22 20    | 6 25 29     | -8 67 -79  | 6 0 1*     | 1 45 38    | -6 94 -92  | -2 17 20   |
| 0 36 47    | -4 126 106  | -1 132 141  | -1 132 141 | -8 114-108  | -8 39 -46  | 0 0 3*      | 0 0 -2*    | 6 0 1*     | 1 45 38    | -6 94 -92  | -2 17 20   |
| 2 147 144  | -3 199 166  | 0 0 2*      | H,K=11,1   | -7 13 -14   | -7 0 -2*   | 1 19 -21    | 1 26 -24   | 7 0 2*     | 2 26 -13   | -5 0 12*   | -1 10 -17  |
| 4 80 74    | -2 14 12    | 1 97 100    | -6 152-134 | -6 0 1*     | 2 24 24    | 2 0 -7*     | 8 61 69    | 3 25 15    | -4 0 -2*   | 0 10 15    |            |
| 6 80 73    | -1 127 107  | 2 0 13*     | -8 40 -40  | -5 67 -62   | -5 0 10*   | 3 30 28     | 3 0 10*    | 4 12 10    | -3 13 20   | 1 0 -10*   |            |
| 8 178 167  | 0 0 2*      | 3 46 42     | -7 18 31   | -4 273 249  | -4 0 1*    | 4 13 -15    | 4 10 17    | 5 47 -47   | -2 0 -3*   | 2 14 24    |            |
| 10 45 -49  | 1 34 29     | 4 51 -47    | -6 29 -25  | -3 46 44    | -3 0 6*    | 5 95 93     | 5 25 28    | H,K=4,4    | 6 133 132  | -1 0 2*    | 3 29 -30   |
|            | 2 427-511   | 6 41 39     | -4 0 2*    | -2 13 13    | 6 193-187  | H,K=9,3     | 3 12 -0    | -5 0 -5*   | L FOB FCA  | 0 0 -3*    |            |
| H,K=5,0    | 3 153-136   | 6 38 28     | -4 0 -9*   | -1 19 18    | 0 100 -86  | 8 9 15      | L FOB FCA  | -11 0 1*   | 9 30 33    | 2 20 -23   | H,K=6,6    |
| L FOB FCA  | 4 37 33     | 7 45 -47    | -3 17 22   | 0 62 68     | 1 25 -20   | 9 34 42     | -10 29 -34 | -10 50 54  | 10 10 -6   | 3 35 -39   | -5 21 24   |
| -14 83-103 | 5 141-126   | 8 9 -12     | -2 103 85  | 1 16 18</   |            |             |            |            |            |            |            |

results. The zero reflections, which were given no weight in the final refinement, are calculated to be very weak in almost every case and therefore serve as a good check of the correctness of the structure.

**Interatomic Distances.**—The shortest interatomic distances are listed in Tables IV and V, and the dimensions of the dimer molecule are shown in Fig. 2.

TABLE IV  
NEIGHBOR DISTANCES OF INDIUM

| Neighbor | Distance,<br>Å. |
|----------|-----------------|
| I(1)     | 2.838 ± 0.005   |
| I(1)     | 2.839 ± 0.005   |
| I(2)     | 2.641 ± 0.005   |
| I(3)     | 2.643 ± 0.005   |
| In       | 3.883 ± 0.007   |

TABLE V  
IODINE-IODINE DISTANCES<sup>a</sup>

| Neighbors of I(1) |                    | Neighbors of I(2) |                    | Neighbors of I(3) |                    |
|-------------------|--------------------|-------------------|--------------------|-------------------|--------------------|
| Atom              | Distance,<br>Å.    | Atom              | Distance,<br>Å.    | Atom              | Distance,<br>Å.    |
| I(1)              | 4.365              | I(1)              | 4.361              | I(1)              | 4.381              |
| I(1)              | 4.365              | I(1)              | 4.417 <sup>b</sup> | I(1)              | 4.426 <sup>b</sup> |
| I(1)              | 4.141 <sup>b</sup> | I(1)              | 4.305              | I(1)              | 4.330              |
| I(1)              | 4.386              | I(1)              | 4.470 <sup>b</sup> | I(1)              | 4.471 <sup>b</sup> |
| I(2)              | 4.417 <sup>b</sup> | I(2)              | 4.336              | I(2)              | 4.283              |
| I(2)              | 4.361              | I(2)              | 4.336              | I(2)              | 4.122              |
| I(2)              | 4.305              | I(3)              | 4.283              | I(2)              | 4.110              |
| I(2)              | 4.470 <sup>b</sup> | I(3)              | 4.110              | I(2)              | 4.358              |
| I(3)              | 4.426 <sup>b</sup> | I(3)              | 4.122              | I(2)              | 4.688 <sup>b</sup> |
| I(3)              | 4.330              | I(3)              | 4.358              | I(2)              | 4.351              |
| I(3)              | 4.381              | I(3)              | 4.688 <sup>b</sup> | I(3)              | 4.150              |
| I(3)              | 4.471 <sup>b</sup> | I(3)              | 4.351              | I(3)              | 4.484              |
| Av.               | 4.368 <sup>c</sup> | Av.               | 4.345 <sup>c</sup> | Av.               | 4.346 <sup>c</sup> |

<sup>a</sup> Standard deviations are 0.005 to 0.007 Å. <sup>b</sup> Distance to neighbor in same dimer molecule. <sup>c</sup> Standard deviations are 0.004 Å. Individual distances deviate by as much as 0.34 Å. from the averages because of chemical bonding.

## Discussion

**Molecular Structure.**—The molecule has the same configuration as the tetrahedral dimers found in the gas for many group III halides. The bridge bonds are longer than the terminal ones as is expected. The bond angles are reasonably consistent with covalent bonding involving s-p hybrids on the indium atom. If the terminal and bridge bonds are assigned respectively 38.5 and 11.5% s-character,<sup>12</sup> they point in directions (corresponding to bond angles 128.9 and 97.5°) which are within 2° of the bond directions.

The crystal symmetry requires the dimer molecule to be centric, but requires no further symmetry. Within the experimental accuracy, however, there is no devia-

tion of the molecular shape from the symmetry  $2/m$  ( $C_{2h}$ ) and hardly any from  $mmm$  ( $D_{2h}$ ), the symmetry expected for the gaseous molecule.

**Molecular Packing.**—The iodine atoms deviate rather little from ideal cubic closest packing (Fig. 1), and each has 12 neighbors at approximately the same distance (Table V). It is interesting that  $\text{Al}_2\text{Br}_6$ , which has the same molecular configuration, crystallizes in the same space group, but with the bromine atoms in hexagonal closest packing.<sup>5</sup> Thus the two structures are very closely related but quite different in detail. There are many other simple ways that such molecules can be packed with the halogen atoms in closest packing, and perhaps other examples will be found in the future.

**Twinning.**—The structure consists of molecules in layers perpendicular to the reciprocal  $a$  axis, which is a 4-fold axis of the cubic sublattice. If the stacking sequence of these layers contains an error corresponding to rotation about this axis by 90°, no neighbors closer than 6 Å. are appreciably affected. Rotation by 180° affects no neighbors closer than 15 Å. We have no direct proof of the nature of the twinning, but twinning by such stacking defects is consistent with our observations.

**Comparison with Structure in Liquid and Gas.**—An electron-diffraction study of the gas by Brode<sup>13</sup> showed dimer molecules with dimensions corresponding to 2.67 Å. for the In-I distance. Stevenson and Schomaker<sup>14</sup> questioned the treatment of the data and suggested that they correspond rather to 2.76 Å. for this distance. The average distance in our structure is 2.74 Å., in excellent agreement with the value of Stevenson and Schomaker.

In an X-ray study of the liquid state, Wood and Ritter<sup>15</sup> found a peak in the radial distribution function at 2.70 Å. for the In-I distances, also in good agreement with our result. For the shortest I-I distances they found a peak at 4.52 Å. It is reasonable that this value should be larger than the average in the crystal, because poorer packing of the molecules in the liquid would increase the intermolecular I-I distances. A small shoulder at 3.15 Å. in the radial distribution function was interpreted as the In-In distance, which is 3.88 Å. in the crystal. This discrepancy is unreasonable. We conclude that the shoulder does not represent In-In distances and that the details of the structure proposed by Wood and Ritter are incorrect.

(13) H. Brode, *Ann. Physik*, **37**, 344 (1940).

(14) D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.*, **64**, 2514 (1942).

(15) R. E. Wood and H. L. Ritter, *ibid.*, **74**, 1760 (1952).

(12) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).