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CRYSTAL AND MOLECULAR STRUCTURE OF In_2I_6[1]

J. D. Forrester, A. Zalkin and D. H. Templeton

July 1963

Crystal and Molecular Structure of In_2I_6[1]

BY J. D. FORRESTER, ALLAN ZALKIN, and DAVID H. TEMPLETON

Indium(III) iodide exists in the crystals as dimers, In_2I_6, according to a determination of the structure by single-crystal x-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, with a = 9.837 ± 0.004, b = 6.102 ± 0.004, c = 12.195 ± 0.009 Å, β = 107.69 ± 0.05°, 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° for I-In-I (bridge bonds) and 125.1° for I-In-I (terminal bonds).

Introduction

Most crystalline metallic trihalides exist as structures which are infinite complexes in one, two, or three dimensions.[2] Only a few (e. g., monomeric SbF_3[3] and $SbCl_3$[4] and dimeric Al_2Br_6[5] and Au_2Cl_6[6]) 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.[7] This fact is confirmed for the indium compound by the crystal-structure determination reported in the present paper. According to x-ray powder diagrams[8] it is likely that the aluminum and gallium iodides have the same crystal structure as In_2I_6.

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 $250°$ 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 dry box to silica glass capillary tubes (0.6 mm. diameter and 0.015 mm. wall thickness) and sealed off. The capillaries were heated to $250°$ 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 In_2I_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 X 0.11 X 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 MoKα radiation. Unit cell dimensions are based on $\lambda = 0.70926$ Å for Kα₁. The

intensities of 1236 independent reflections permitted by the space group with $\sin\theta/\lambda$ less than 0.596 ($2\theta < 50°$) were measured; of these, 230 were recorded as zero.

The linear absorption coefficient is estimated as 175.9 cm.$^{-1}$ which corresponds to μR = 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[9] with a dispersion correction[10] of -0.7 for In and -0.5 for I.

Results

Unit Cell and Space Group.—The crystals are monoclinic with unit cell dimensions:

$$\underline{a} = 9.837 \pm 0.004, \quad \underline{b} = 6.102 \pm 0.004, \quad \underline{c} = 12.195 \pm 0.009 \text{ Å},$$
$$\beta = 107.69 \pm 0.05°.$$

The systematic absences ($h0\ell$ absent if ℓ is odd, $0k0$ absent if k is odd) are characteristic of space group $\underline{P}2_1/\underline{c}$ ($\underline{C}_{2h}^5$), and this symmetry is confirmed by the ultimate agreement of observed and calculated structure factors. With two dimer molecules (In_2I_6) per unit cell the density is calculated as 4.72 g./cc. in agreement with the measured density[11] 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 Å, 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 $\underline{b}$ and $\underline{c}$ coinciding with cubic axial directions. The relation of $\underline{a}$ and $\underline{c}$ to the cubic lattice is shown in Fig. 1. If the fit were perfect the axial ratios and

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

The only way to arrange the iodine atoms in cubic closest packing in the sublattice that is consistent with the symmetry of $P2_1/c$ places them in general positions,

$$4(\underline{e}): \pm(\underline{x}, \underline{y}, \underline{z}; \underline{x}, 1/2 - \underline{y}, 1/2 + \underline{z}),$$

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 $\underline{x} = 1/2$ 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 $\underline{R} = \sum ||F_o| - |F_c|| / \sum |F_o|$ 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 $\underline{R}$ values because the two structures are equivalent as far as the $\underline{k}$-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, $\underline{R}$ was reduced to 0.136. Each atom was given an anisotropic temperature factor of the form $\exp(-\beta_{11}\underline{h}^2 - \beta_{22}\underline{k}^2 - \beta_{33}\underline{\ell}^2 - 2\beta_{12}\underline{hk}$

$-2\beta_{13}\underline{h\ell} -2\beta_{23}\underline{k\ell}$), making a total of 37 independent parameters. Several further cycles of refinement reduced R for the 1006 non-zero reflections to 0.105. The resulting atomic parameters are listed in Tables I and II.

TABLE I

ATOMIC COORDINATES AND STANDARD DEVIATIONS

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\sigma(\underline{x})$	$\sigma(\underline{y})$	$\sigma(\underline{z})$
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	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
			(each multiplied by 10^4)			
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

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

The observed and calculated structure factors are listed in Table III.

TABLE III

OBSERVED STRUCTURE FACTOR MAGNITUDES (FOB) AND CALCULATED

STRUCTURE FACTORS (FCA)

(Table submitted as photographic print)

```
 H,K= 0, 0
 L FCO FCA
  2 162 122
  4  45  37
  6 185-165
  8  69 -60
 10  99-102
 12 152-163

 H,K= 1, 0
 L FCB FCA
-14  10 -24
-12  66 -71
-10  98  93
 -8  59  50
 -6 173 148
 -4 353-331
 -2 159 120
  0  58  42
  2   0  -5*
  4 156-136
  6  98 -84
  8 195 177
 10  52 -50
 12  10  12

 H,K= 2, 0
 L FCB FCA
-14  80 -96
-12   0  -3*
-10  29  20
 -8 386 385
 -6 157 137
 -4  60  43
 -2   7  -0
  0 128-131
  2 187-169
  4 460-496
  6   0  16*
  8  46  41
 10 138 144
 12  14  20

 H,K= 3, 0
 L FOB FCA
-14  56  68
-12  73 -77
-10  33  27
 -8  39  29
 -6 201-177
 -4 183-152
 -2 195-176
  0 283 375
  2  43 -38
  4  65  61
  6   0   0*
  8 104 101
 10  21  20
 12  75 -79

 H,K= 4, 0
 L FOB FCA
-14  48  53
-12   0  -2*
-10  95  90
 -8  55 -48
 -6  86 -71
 -4 469-490
 -2  42 -38
  0  36  47
  2 147 144
  4  80  74
  6  80  73
  8 178 167
 10  45 -49

 H,K= 5, 0
 L FOB FCA
-14  83-103
-12  79 -85
-10 118-115
 -8 198 180
 -6  18  19
 -4  80  72
 -2 162 159
  0 143 145
  2  67  64
  4 251-240
  6  26 -18
  8  53 -55
 10   0  10*

 H,K= 6, 0
 L FOB FCA
-14   0 -11*
-12 143-156
-10  33 -34
 -8  39  39
 -6  16  -9
 -4  68  62
 -2  53  50
  0 274 290
  2  59 -59
  4  71 -64
  6 110-106
  8   0  -4*

 H,K= 7, 0
 L FOB FCA
-12  10  20
-10 148 153
 -8 116 112
 -6  91  82
 -4 246-242
 -2  60 -61
  0  97 -93
  2  58 -56
  4  66 -63
  6   9   9
  8 116 109

 H,K= 8, 0
 L FOB FCA
-12   0   9*
-10   0   3*
 -8 168 158
 -6  30 -24
 -4  64 -62
 -2  46 -43
  0  19 -10
  2  26   4
  4 100 -89
  6  53  53

 H,K= 9, 0
 L FOB FCA
-12  75 -80
-10  46 -46
 -8  55 -57
 -6 117-114
 -4  67 -66
 -2   9  -5
  0 194 178
  2  48  45
  4  47  43

 H,K=10, 0
 L FOB FCA
-10   0  10*
 -8   0   8*
 -6  21  22
 -4  98 -86
 -2  51  47
  0  36  38
  2  33  26

 H,K=11, 0
 L FOB FCA
 -8 108 109
 -6  50  50
 -4  43  42
 -2  36  32
  0  18  12

 H,K= 0, 1
 L FOB FCA
  1 186 151
  2   0  -4*
  3 100  79
  4  36  30
  5  34 -27
  6 364 349
  7  37 -33
  8  42 -40
  9  83 -77
 10   0 -12*
 11  52 -52
 12  79 -88
 13  25 -25

 H,K= 1, 1
 L FOB FCA
-14  15 -17
-13  42 -47
-12  32 -36
-11  59 -62
-10 193 187
 -9  19   9
 -8  36  35
 -7  82  72
 -6   9  -7
 -5 161 137
 -4 126 106
 -3 199 166
 -2  14  12
 -1 127 107
  0   0   2*
  1  34  29
  2 427-511
  3 153-136
  4  37  33
  5 141-126
  6   0   7*
  7 107-100
  8 115 109
  9  56 -40
 10  25 -26
 11   9   3
 12  17  18
 13  27  26

 H,K= 2, 1
 L FOB FCA
-14  73 -83
-13   0  -3*
-12  21 -24
-11  36  35
-10  29  19
 -9  89  81
 -8 136-127
 -7 101  90
 -6  29 -22
 -5  76  65
 -4  41 -35
 -3  63 -52
 -2 461 511
 -1  74 -69
  0   0   2*
  1 141-143
  2  11  10
  3 122-112
  4  84 -80
  5  55 -48
  6  22  24
  7  28  17
  8  37 -26
  9  58  58
 10 148-146
 11  30  35
 12  20  22

 H,K= 3, 1
 L FOB FCA
-14   0 -18*
-13  43  49
-12  96 106
-11  66  70
-10  39  32
 -9  52  49
 -8  53  47
 -7  26  23
 -6 367-347
 -5 127-107
 -4  53 -32
 -3 176-152
 -2  15 -16
 -1 142-147
  0   0  -7*
  1  80 -79
  2  25 -24
  3   0  13*
  4  15  17
  5  57  57
  6 267 253
  7 109 106
  8  28 -31
  9  54  56
 10   0  -4*
 11  17  23
 12  51 -59

 H,K= 4, 1
 L FCB FCA
-14  20 -24
-13  10  24
-12  33 -37
-11  26 -29
-10 190 186
 -9  52 -47
 -8  37  32
 -7 102 -90
 -6   0   3*
 -5 114 -98
 -4  99  90
 -3  49 -44
 -2  32  30
 -1  25  29
  0   0   5*
  1 111 115
  2 317-349
  3  80  79
  4  23  20
  5  79  75
  6  16  -4
  7  29  23
  8  69  69
  9   9 -14
 10  20 -25
 11  31 -34

 H,K= 5, 1
 L FCB FCA
-14  68 -82
-13  31 -37
-12  23 -25
-11  64 -69
-10   0   4*
 -9  77 -73
 -8 125-117
 -7  59 -53
 -6  45 -39
 -5  21  15
 -4  30 -28
 -3  60  58
 -2 318 349
 -1 132 141
  0   0   2*
  1  97 100
  2   0  13*
  3  46  42
  4  51 -47
  5  18 -16
  6  38  28
  7  45 -47
  8   9 -12
  9  41 -43
 10  86 -85

 H,K= 6, 1
 L FCB FCA
-13   0 -41*
-12  80  91
-11  20 -18
-10  39  38
 -9  26  20
 -8  41  39
 -7  96  89
 -6 267-249
 -5  85  79
 -4  16 -19
 -3  76  76
 -2  14 -14
 -1  28  28
  0   0  -7*
  1  34 -33
  2  32 -29
  3  62 -66
  4  18   8
  5  76 -77
  6 159 146
  7  25 -29
  8  17 -16
  9  14 -12

 H,K= 7, 1
 L FCB FCA
-13   0   7*
-12  31 -31
-11  21  25
-10 143 143
 -9  72  73
 -8  30  26
 -7  86  72
 -6  14  10
 -5  28  34
 -4  62  60
 -3  13 -16
 -2  37  34
 -1  81 -65
  0   0   5*
  1  67 -64
  2 196-190
  3  73 -71
  4   9  12
  5  10 -18
  6  10  -4
  7  22  14
  8  36  34

 H,K= 8, 1
 L FOB FCA
-12   0 -14*
-11  27  35
-10   0   2*
 -9  13  16
 -8  81 -78
 -7  24 -29
 -6  40 -39
 -5  63 -63
 -4  16 -20
 -3  92 -89
 -2 197 188
 -1  44 -41
  0   0  -1*
  1  12 -12
  2   9   7
  3  20  24
  4  21 -23
  5  38  42
  6  20  21

 H,K= 9, 1
 L FOB FCA
-12  56  65
-11   0  -9*
-10  28  34
 -9  36 -39
 -8  19  22
 -7  40 -43
 -6 152-144
 -5  57 -56
 -4   0 -11*
 -3  23 -21
 -2   9  -8
 -1  15  20
  0   0  -5*
  1  41  42
  2  30 -23
  3  46  45
  4   0   2*
  5  25  23

 H,K=10, 1
 L FOB FCA
-10  80  81
 -9  22 -29
 -8   0  11*
 -7   0  -5*
 -6   0   4*
 -5  19  23
 -4  33  32
 -3  46  49
 -2  28  26
 -1  50  49
  0  10   5
  1  43  37
  2 105 -85
  3  18  -2

 H,K=11, 1
 L FOB FCA
 -8  40 -40
 -7  18  31
 -6  29 -25
 -5  41  39
 -4   0  -9*
 -3  17  22
 -2 103  85
 -1   0  12*
  0   0  -1*

 H,K= 0, 2
 L FOB FCA
  0 369-327
  1  96 -74
  2 158 130
  3   0 -15*
  4  59  44
  5  27 -23
  6  75  69
  7  18  -5
  8  95 -91
  9  25  -7
 10  47 -41
 11   0  -8*
 12  62  67
 13  21  29

 H,K= 1, 2
 L FOB FCA
-13   0 -11*
-12  19 -21
-11   0  -3*
-10 122-127
 -9  20 -16
 -8  20   7
 -7   7  -6
 -6  23  52
 -5  80 -65
 -4 503 519
 -3  89  57
 -2 164 130
 -1  34  21
  0  37  42
  1  28  28
  2 110 -96
  3  23  22
  4 100 -86
  5   0  16*
  6 133-125
  7  33  29
  8 276-267
  9  46 -43
 10  18  16
 11   0  -1*
 12  17  29

 H,K= 2, 2
 L FOB FCA
-13   0   8*
-12  31  39
-11   6   6*
-10  95  94
 -9  59  55
 -8 167-151
 -7  16 -24
 -6  66  52
 -5   0 -16*
 -4  43  29
 -3  20 -20
 -2 126-105
 -1  27 -29
  0 125-138
  1   6 -14
  2 133-117
  3  47 -45
  4 261 248
  5  65  60
  6  49 -45
  7  17   4
  8  29  27
  9   9   8
 10  28 -28
 11   0  -4*
 12  95  66

 H,K= 3, 2
 L FOB FCA
-13  20 -28
-12 161 171
-11  13  16
-10  81  80
 -9  23  18
 -8  20  12
 -7   0  10*
 -6  76  68
 -5  26  24
 -4  94 -76
 -3   0  10*
 -2 130-111
 -1  95  59
  0 332-485
  1  61 -63
  2   9  -9
  3  13 -13
  4  44  41
  5  19 -18
  6 156 149
  7  18  -8
  8  41  38
  9   9  -8
 10  44  50
 11   0 -10*

 H,K= 4, 2
 L FOB FCA
-13   0  -7*
-12  23  26
-11   0  -2*
-10 134-136
 -9  25 -21
 -8 114-108
 -7  13 -14
 -6 152-134
 -5  67 -62
 -4 273 249
 -3  46  44
 -2   0  -3*
 -1  19  18
  0  62  68
  1  16  18
  2  72  67
  3   7  13
  4 124 116
  5  16   6
  6  38  34
  7  15  17
  8 140-133
  9  32 -30
 10  10  -6

 H,K= 5, 2
 L FOB FCA
-13   0   7*
-12  14 -14
-11   0   2*
-10  33 -29
 -9  41  40
 -8 277-260
 -7  27 -27
 -6  41 -38
 -5  31 -19
 -4  41  38
 -3   7 -13
 -2  58  54
 -1  20 -19
  0  68  67
  1   7  -7
  2  60  63
  3  28 -29
  4 223 214
  5  47  40
  6  53 -52
  7   9   4
  8  48 -46
  9  10   7
 10  73 -82

 H,K= 6, 2
 L FOB FCA
-13  29 -32
-12  65  68
-11   0   7*
-10  16  15
 -9   0  15*
 -8  39  38
 -7  18  11
 -6 171 161
 -5  25  24
 -4 131 124
 -3   7  12
 -2  72  71
 -1  40  38
  0 227-237
  1  38 -39
  2  43 -38
  3   8  -7
  4  71 -71
  5  10  -7
  6   9 -11
  7   0  -2*
  8  52 -49

 H,K= 7, 2
 L FOB FCA
-13   0  -9*
-12  22  31
-11   0   0*
-10  32 -33
 -9  18 -10
 -8  19  25
 -7   8  -5
 -6  42  19
 -5  14 -36
 -4 215 209
 -3  32  29
 -2  36 -37
 -1  16  12
  0  64 -60
  1  17   8
  2  79 -77
  3   9   8
  4   9  -7
  5   0   3*
  6   0  -4*
  7   0   9*

 H,K= 8, 2
 L FOB FCA
-12  65  73
-11   0  10*
-10  53  57
 -9  28  32
 -8 138-135
 -7  15 -17
 -6  50 -53
 -5  17 -16
 -4  72 -73
 -3   8 -11
 -2  88 -87
 -1   0 -13*
  0  67 -63
  1   0  -4*
  2   9   3
  3  16 -15
  4 141 137
  5  22  20
  6  25  29

 H,K= 9, 2
 L FOB FCA
-11   0   5*
-10   0 -14*
 -9   0   8*
 -8  39 -46
 -7   0   2*
 -6   0  -1*
 -5   0  10*
 -4   0   1*
 -3   0   4*
 -2  13  13
 -1  18  19
  0 100 -86
  1  25 -20
  2  53  49
  3  10  -4
  4  34  32

 H,K=10, 2
 L FOB FCA
 -9   0 -12*
 -8  48 -53
 -7   0  -7*
 -6  14 -11
 -5  14 -19
 -4 139 136
 -3  19  17
 -2  52  48
 -1  10   8
  0  46  43
  1   0   4*
  2  15  12

 H,K=11, 2
 L FOB FCA
 -6  27  31
 -5   0  -6*
 -4  26  31
 -3   0  -2*
 -2  10   4

 H,K= 0, 3
 L FOB FCA
  1 168 144
  2   0   8*
  3  95  85
  4  21 -20
  5  53  46
  6 263-242
  7 131-123
  8  40  31
  9  64 -67
 10  13  19
 11  49 -58
 12  64  73

 H,K= 1, 3
 L FOB FCA
-12  20  18
-11  16  19
-10 142-140
 -9  26 -25
 -8  28 -23
 -7  38  30
 -6  24  16
 -5  80  76
 -4  83 -70
 -3  85  70
 -2  12 -12
 -1  53  45
  0   0   2*
  1  84 -81
  2 342 338
  3  16  18
  4  10 -15
  5  84 -77
  6  13  -3
  7  56 -49
  8  80 -80
  9  25 -27
 10  16  24
 11   0  19*
 12  21 -16

 H,K= 2, 3
 L FOB FCA
-13   0   9*
-12  14  18
-11  44  46
-10   0 -12*
 -9  70  70
 -8 109 105
 -7 113 105
 -6  32  28
 -5  77  67
 -4  24  24
 -3  89  77
 -2 360-336
 -1 150-150
  0   0  -3*
  1 124-129
  2   0  -2*
  3 124-118
  4  63  60
  5  64 -56
  6  27 -24
  7  12  -2
  8  25  15
  9  16  19
 10 101 103
 11  72  81

 H,K= 3, 3
 L FOB FCA
-13  29  41
-12  67 -76
-11  35  33
-10  16 -22
 -9  30  26
 -8  32 -29
 -7  87 -80
 -6 265 242
 -5  19 -15
 -4  12  17
 -3  87 -76
 -2   0   4*
 -1  67 -70
  0   0   3*
  1  19 -21
  2  24  24
  3  30  28
  4  13 -15
  5  95  93
  6 193-187
  7   9   7
  8   9  15
  9  34  42
 10   0   2*

 H,K= 4, 3
 L FOB FCA
-13  10  26
-12  17  27
-11  44  45
-10 137-138
 -9  67 -67
 -8  31 -28
 -7 107 -99
 -6   0  -7*
 -5 104 -96
 -4  78 -72
 -3  80 -74
 -2  32 -31
 -1   7   2
  0   0  -3*
  1  10  12
  2 233 245
  3 143 146
  4  20 -13
  5  72  69
  6   0   1*
  7  34  34
  8  51 -54
  9  10  -9
 10  23  25

 H,K= 5, 3
 L FOB FCA
-12   0  10*
-11  42 -34
-10   0 -14*
 -9  48 -49
 -8  87  84
 -7  12  -6
 -6  38  34
 -5  29  29
 -4  24  22
 -3 128 126
 -2 231-242
 -1  29  30
  0   0  -1*
  1  49  53
  2  14  -9
  3   8  11
  4  38  36
  5  18 -24
  6  18 -24
  7  37 -45
  8  10  12
  9  49 -52

 H,K= 6, 3
 L FOB FCA
-12  66 -77
-11  28 -36
-10  30 -35
 -9   0   1*
 -8  15 -25
 -7   0  -5*
 -6 197 186
 -5 111 109
 -4  21  19
 -3  87  86
 -2  14  13
 -1  42  43
  0   0   7*
  1   0  -2*
  2  35  29
  3  41 -43
  4   0  -5*
  5  24 -31
  6 110-106
  7  72 -69
  8   0  10*

 H,K= 7, 3
 L FCB FCA
-12  21  25
-11  66  74
-10  97 -98
 -9  28  36
 -8   0 -10*
 -7  25  31
 -6   0  -2*
 -5   0  11*
 -4  43 -46
 -3  37 -41
 -2  33 -33
 -1  55 -61
  0   0  -5*
  1  92 -92
  2 147 139
  3   0  -4*
  4   0  -7*
  5   0  -8*
  6   0   3*

 H,K= 8, 3
 L FOB FCA
-11  41  47
-10   0   2*
 -9  17  21
 -8  57  62
 -7   0   2*
 -6  22  32
 -5  34 -37
 -4   0  11*
 -3  13 -22
 -2 146-141
 -1  76 -77
  0   0  -2*
  1  26 -24
  2   0  -7*
  3   0  10*
  4  10  17
  5  25  20

 H,K= 9, 3
 L FCB FCA
-10  29 -34
 -9  41 -43
 -8  10 -23
 -7  76 -79
 -6 104 101
 -5   0 -16*
 -4   0   5*
 -3  13   2
 -2   0   6*
 -1  24  26
  0   0   5*
  1  47  45
  2  27  22
  3  37  40

 H,K=10, 3
 L FOB FCA
 -8   0 -10*
 -7  18 -22
 -6   0  -4*
 -5   0  10*
 -4  17 -23
 -3  14  24
 -2  23 -21
 -1  34  34
  0   0  -2*

 H,K= 0, 4
 L FOB FCA
  0 406 359
  1  99  87
  2  85  66
  3  28  18
  4   0  13*
  5  36  30
  6  98 -93
  7  21  13
  8  37 -30
  9  19  21
 10  58 -60
 11  18  20

 H,K= 1, 4
 L FOB FCA
-11   0  -5*
-10  47  56
 -9  18  20
 -8  37  35
 -7  21  14
 -6  91  77
 -5 100  91
 -4 171-146
 -3  72 -62
 -2  77  60
 -1  37 -23
  0  27  28
  1  31 -31
  2   0  -3*
  3  18 -21
  4  92 -85
  5  20 -14
  6  56 -52
  7  37 -30
  8  94  89
  9  57  62
 10  20 -23
 11   0   0*

 H,K= 2, 4
 L FOB FCA
-12   0  -6*
-11  10  -2
-10  17  21
 -9  59 -62
 -8 217 208
 -7  51  43
 -6  86  74
 -5  34  28
 -4  15  16
 -3  24  25
 -2  13  -0
 -1  32  33
  0  50 -55
  1  18  20
  2  95 -89
  3  61  59
  4 258-253
  5  79 -75
  6   0   1*
  7   0  -8*
  8  26  28
  9  17 -17
 10  84  90

 H,K= 3, 4
 L FOD FCA
-12  29 -35
-11   0  -9*
-10  21  23
 -9   0 -16*
 -8  22  23
 -7  15 -11
 -6 113-101
 -5  39 -35
 -4 105 -94
 -3  19 -21
 -2  96 -91
 -1  69 -77
  0 151 170
  1  67  75
  2  18 -16
  3  14  15
  4  33  33
  5   9  17
  6   0   1*
  7   0   2*
  8  61  69
  9  17   6

 H,K= 4, 4
 L FOB FCA
-12   0  -5*
-11   0   1*
-10  50  54
 -9  13  19
 -8  30 -22
 -7   0   8*
 -6  52 -47
 -5  75  69
 -4 266-249
 -3  61 -60
 -2  21 -20
 -1  19 -24
  0  31  29
  1  20 -23
  2  81  81
  3  22 -18
  4  34  35
  5   0 -12*
  6  43  44
  7  25 -25
  8  93  92
  9  43  43

 H,K= 5, 4
 L FOB FCA
-11  10 -16
-10  53 -67
 -9  62 -66
 -8  94  89
 -7  20  28
 -6   0   6*
 -5  24  25
 -4  40  39
 -3  53  21
 -2  88  91
 -1  34  28
  0  89  94
  1  17  13
  2  39  38
  3  36  39
  4 130-128
  5  51 -51
  6  14 -18
  7   0  -1*
  8  33 -34

 H,K= 6, 4
 L FOB FCA
-11  18 -15
-10  10 -15
 -9  14 -19
 -8  21  27
 -7   0  -6*
 -6   0  -5*
 -5  25 -21
 -4  26  28
 -3   0  -9*
 -2  24  31
 -1  42 -47
  0 150 152
  1  54  52
  2  26 -32
  3   9  11
  4  34 -40
  5  10  12
  6  64 -66

 H,K= 7, 4
 L FOB FCA
-10  80  96
 -9  17  29
 -8  74  77
 -7   0  18*
 -6  45  48
 -5  49  52
 -4 129-128
 -3  38 -39
 -2  31 -37
 -1   9 -19
  0  54 -57
  1   0 -13*
  2  33 -35
  3   0 -10*
  4  45 -45
  5   0  -5*

 H,K= 8, 4
 L FOB FCA
 -9  34 -39
 -8  80  85
 -7  14  20
 -6   0 -19*
 -5   0  15*
 -4  34 -39
 -3   0   7*
 -2  19 -26
 -1  14  13
  0   0   1*
  1   0   5*
  2  10   2
  3  23  20

 H,K= 9, 4
 L FOB FCA
 -7   0 -11*
 -6  69 -72
 -5   0 -20*
 -4  46 -48
 -3   0  -9*
 -2   0  -3*
 -1  25 -26
  0 108 102
  1  33  28

 H,K= 0, 5
 L FOB FCA
  1  45  38
  2  26 -13
  3  25  15
  4  12  10
  5  47 -47
  6 133 132
  7  40  40
  8   0  -5*
  9  30 -33
 10  10  -6

 H,K= 1, 5
 L FOB FCA
-10  67  72
 -9  20  23
 -8  10  12
 -7  43  49
 -6   0  -9*
 -5  75  71
 -4  51  47
 -3 102  91
 -2  31  17
 -1  61  58
  0   0  -0*
  1  64  65
  2 180-170
  3 122-119
  4   9   9
  5  68 -67
  6   0  12*
  7  58 -63
  8  54  54
  9   0 -20*

 H,K= 2, 5
 L FOB FCA
-10  10  19
 -9  31  38
 -8  51 -54
 -7  21  23
 -6  13 -15
 -5  15  16
 -4   0  -7*
 -3  88 -82
 -2 188 171
 -1  22  26
  0   0   3*
  1  37 -42
  2   0  -1*
  3  24 -30
  4  34 -33
  5  18 -13
  6  16  20
  7  10  19
  8  14 -12

 H,K= 3, 5
 L FCB FCA
 10  14  26
 -9  24  33
 -8  14  16
 -7  64  66
 -6 136-130
 -5  87 -83
 -4   0 -13*
 -3  83 -84
 -2   0  -3*
 -1  72 -79
  0   0  -5*
  1  47 -51
  2  15 -23
  3   0  -6*
  4   0   5*
  5   0  -2*
  6  96  96
  7  89  95
  8   0  -9*

 H,K= 4, 5
 L FOB FCA
-10  63  71
 -9   0  -7*
 -8  10   4
 -7  21 -25
 -6   0  -9*
 -5  31 -34
 -4  38  36
 -3   0   2*
 -2  21  24
 -1  17  25
  0   0   1*
  1  77  92
  2 123-131
  3   0 -12*
  4   0   1*
  5  29  29
  6   0  -2*
  7   0   2*

 H,K= 5, 5
 L FCB FCA
 -9  29 -40
 -8  55 -60
 -7  40 -44
 -6  21 -29
 -5   0  -5*
 -4   0  -9*
 -3  13 -21
 -2 124 132
 -1  92 105
  0   0   5*
  1  50  59
  2   0   5*
  3  23  32
  4  14 -21
  5  10  -2
  6  10  23

 H,K= 6, 5
 L FCB FCA
 -9  18  20
 -8   0  17*
 -7  82  86
 -6  94 -92
 -5   0  12*
 -4   0  -2*
 -3  13  20
 -2   0  -3*
 -1   0   2*
  0   0  -3*
  1  24 -28
  2  20 -23
  3  35 -39
  4   0   4*

 H,K= 7, 5
 L FOB FCA
 -8   0  11*
 -7  45  51
 -6   0   6*
 -5  22  24
 -4  24  30
 -3   0   8*
 -2  20  25
 -1  17 -23
  0   0   1*
  1  14  -7
  2  73 -78
  3  62 -65

 H,K= 8, 5
 L FOB FCA
 -6  23 -29
 -5  34 -40
 -4   0 -12*
 -3  66 -73
 -2  71  73
 -1   0   4*
  0   0   0*

 H,K= 0, 6
 L FOB FCA
  0  76 -71
  1  67 -65
  2  38  39
  3  23 -16
  4  19  22
  5  17 -20
  6  10  24
  7  14  -2

 H,K= 1, 6
 L FOB FCA
 -8  10  -2
 -7   0  -8*
 -6  28  27
 -5  63 -62
 -4 161 149
 -3  64  52
 -2  44  43
 -1  13  21
  0   0   6*
  1  21  23
  2  34 -32
  3  21  18
  4  14 -21
  5  10  19
  6  36 -44
  7  29  30

 H,K= 2, 6
 L FOB FCA
 -8  29 -34
 -7  17 -23
 -6  26  25
 -5  14 -17
 -4  19  17
 -3   0 -16*
 -2  28 -35
 -1  19 -23
  0  43 -57
  1   0 -16*
  2  38 -41
  3  37 -42
  4  58  62
  5  54  59
  6   0  -8*

 H,K= 3, 6
 L FOB FCA
 -8   0  -1*
 -7   0   7*
 -6  10  24
 -5  17  21
 -4  10 -18
 -3   0  12*
 -2  42 -42
 -1  44  55
  0 110-137
  1  50 -58
  2   0  -8*
  3  10 -14
  4  20  18
  5  14 -17

 H,K= 4, 6
 L FOB FCA
 -7   0 -18*
 -6  43 -45
 -5  56 -63
 -4  54  61
 -3  37  41
 -2   0  -2*
 -1   0  18*
  0   0  21*
  1  10  16
  2  22  25
  3   0  11*
  4  49  53

 H,K= 5, 6
 L FOB FCA
 -6   0  -9*
 -5   0 -19*
 -4  10  17
 -3   0 -11*
 -2  17  20
 -1  10 -17
  0  10  15
  1   0 -10*
  2  14  24
  3  29 -30

 H,K= 6, 6
 L FOB FCA
 -5  21  24
 -4  51  57
 -3   0  15*
 -2  23  26
 -1  36  40
  0  60 -69

 H,K= 0, 7
 L FOB FCA
  1  51  47
  2  14   9
  3  27  33

 H,K= 1, 7
 L FOB FCA
 -3   0  13*
 -2   0 -10*
 -1   0   4*
  0   0   2*
  1  40 -45
  2  67  69
  3  21  30

 H,K= 2, 7
 L FOB FCA
 -3  46  48
 -2  63 -68
 -1  53 -64
  0   0  -3*
  1  33 -45
  2   0   4*

 H,K= 3, 7
 L FOB FCA
 -1   0 -15*
```

The largest discrepancies are for reflections 300, 112, and 320 which are observed too weak. These errors are larger than we expect for extinction or absorption, and we suggest that some other crystal in the capillary may have been in position to block part of the incident or diffracted x-ray beam. These three reflections cannot have much effect on the 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, Å
I(1)	2.838 ± .005
I(1)	2.839 ± .005
I(2)	2.641 ± .005
I(3)	2.643 ± .005
In	3.883 ± .007

TABLE V

IODINE-IODINE DISTANCES[a]

Neighbors of I(1)		Neighbors of I(2)		Neighbors of I(3)	
Atom	Distance, Å	Atom	Distance, Å	Atom	Distance, Å
I(1)	4.365	I(1)	4.361	I(1)	4.381
I(1)	4.365	I(1)	4.417[b]	I(1)	4.426[b]
I(1)	4.141[b]	I(1)	4.305	I(1)	4.330
I(1)	4.386	I(1)	4.470[b]	I(1)	4.471[b]

TABLE V (cont.)

I(2)	4.417[b]	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[b]	I(3)	4.110	I(2)	4.358
I(3)	4.426[b]	I(3)	4.122	I(2)	4.688[b]
I(3)	4.330	I(3)	4.358	I(2)	4.351
I(3)	4.381	I(3)	4.688[b]	I(3)	4.150
I(3)	4.471[b]	I(3)	4.351	I(3)	4.484
Ave.	4.368	Ave.	4.345	Ave.	4.346

[a] Standard deviations are 0.005 to 0.007 Å.

[b] Distance to neighbor in same dimer molecule.

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,[12] 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 deviation 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 Al_2Br_6, which has the
same molecular configuration, crystallizes in the same space group, but with

the bromine atoms in hexagonal closest packing.[5] 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.

Comparison with Structure in Liquid and Gas.—An electron-diffraction
study of the gas by Brode[13] showed dimer molecules with dimensions corresponding
to 2.67 Å for the In-I distance. Stevenson and Schomaker[14] 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[15] 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-I distances and that the
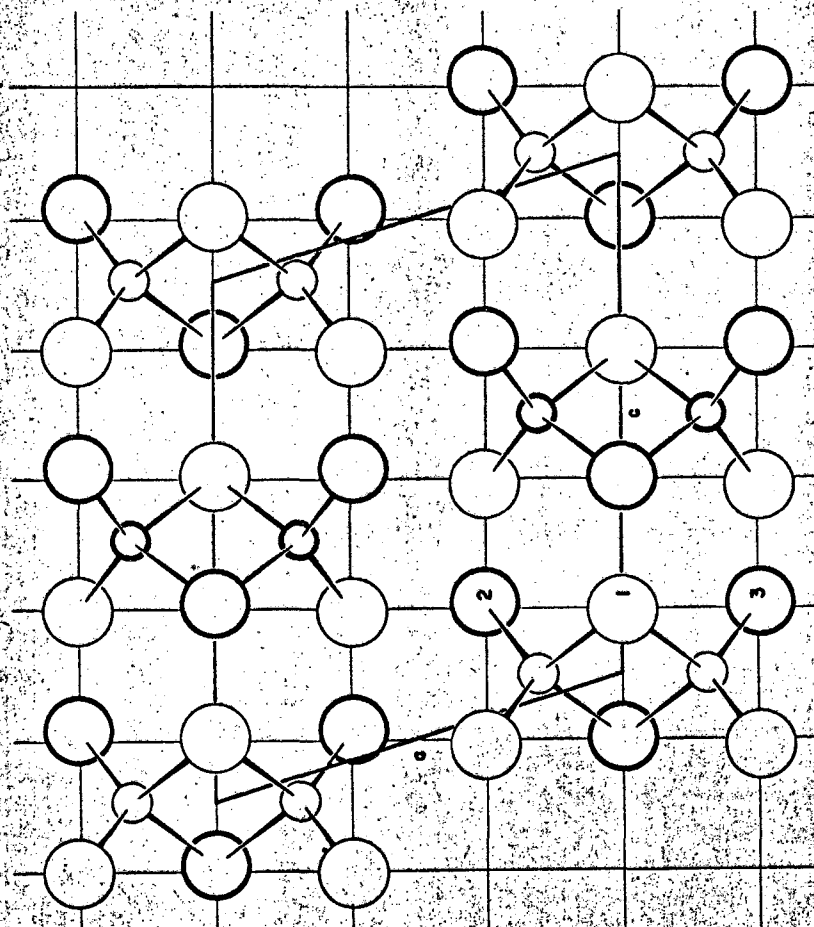details of the structure proposed by Wood and Ritter are incorrect.

(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. Nuclear Chem., 2, 345 (1956).

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

(6) E. S. Clark, D. H. Templeton, and C. H. MacGillavry, 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.

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

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

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

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

(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, *J. Am. Chem. Soc.*, 74, 1760 (1952).

(figure captions)

Fig. 1—Crystal structure of In_2I_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. MUB 1483

Fig. 2—Dimensions of the In_2I_6 molecule. Standard deviations are 0.005 to 0.007 for distances and about $0.3°$ for angles.

MUB 1484

I at y~0·25

I at y~0·75

In at y=0

In at y=0·5

Figure 1

MUB-1483

In_2I_6

Figure 2

MUB-1434