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The Crystal Structure of β-Iodine Monochloride

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β-ICl is monoclinic, $P2_1/c$, with $a = 8{\cdot}883$, $b = 8{\cdot}400$, $c = 7{\cdot}568$ Å, $\beta = 91{\cdot}35°$ and 8 molecules per cell. In β-ICl, as in α-ICl reported by Boswijk *et al.* (1956), the molecules are arranged in zig-zag chains; the bond lengths are I–Cl = 2·35 and 2·44 Å in the two independent molecules. Within chains the I · · · I distance is 3·06 and the I · · · Cl distance is 2·94 Å; between chains the distances are much longer. These short distances indicate interactions between molecules in one chain strong enough to be called weak bonds.

Introduction

In order to gain further understanding of the intermolecular forces which operate in halogen crystals, the structure of β-iodine monochloride has been determined for comparison with that of α-iodine monochloride (Boswijk, van der Heide, Vos & Wiebenga, 1956). The α forms melts at 27, the β form at 14 °C. It was hoped that a study of the two structures would help to reveal the factors most significant for determining the packing of the molecules in these crystals.

Experimental

The experimental part of this investigation is described more fully by Richards (1959).

Iodine monochloride, prepared by union of the elements at dry ice temperature and subsequent fractional crystallization, was sealed into Pyrex capillaries. Crystals were grown and preserved in these capillaries by cooling with a stream of cold nitrogen. Either the α or the β form could be grown by variation of the procedure. In both cases crystallization was initiated by touching the capillary lightly with a piece of dry ice. If the cooling gas was flowing while this was done, the α form resulted; if the cooling stream was started immediately after crystallization began, the β form was usually obtained. Subsequent partial melting and slow refreezing produced satisfactory crystals. (If a small portion re-froze, separated from the main body of material in the capillary, it usually produced a long needle of the α form; when this touched some of the β form, it was quickly converted to the more stable α form.) The two forms were readily distinguished under the microscope by slight differences in color and texture.

A series of multiple-film rotation and Weissenberg photographs was prepared about [001] and [011], the only orientations which were obtained along the capillary axis. The temperature was held at −15 to −20 °C. during these exposures. Zr-filtered Mo $K\alpha$ radiation was used. Intensities were estimated visually from multiple films by comparison with a set of standard intensities, and relative structure factor magnitudes were extracted in the usual way. A correction was made for differences in absorption among the three crystals used for intensities, based on cylindrical-sample absorption. Results from various photographs were then correlated by the method of Dickerson (1959). Eventually, when refinement of the structure was nearly complete, a rough correction for extinction and remaining absorption errors was applied to 25 intense reflections at small angles, by

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multiplication with exp $[cF_o^2]$; c was determined empirically from a plot of ln (F_c/F_o) against F_0^2. Because of the difficulties in preserving crystals and the considerable absorption, the range of F-values is not as large as desirable but a total of about 732 reflections were intense enough to measure.

Unit cell and space group

β-ICl is monoclinic (but pseudo-orthorhombic) with

$$a=8{\cdot}883,\ b=8{\cdot}400,\ c=7{\cdot}568\ \text{Å};\ \beta=91°21'.$$

The internal consistency of the film measurements justifies retaining the third decimal place but unknown systematic errors cause the total uncertainty in these values to amount to 0·3%.

For eight molecules in this unit cell, the calculated density is 3·82 g.cm.$^{-3}$. Birk (1928) reports 3·66 and the calculated value for α-ICl is 3·78. Although the agreement with the experimental value is only fair, it is clear that eight is the correct number.

The systematic absences and the Laue symmetry determine the space group to be the favorite $P2_1/c$. There are thus two independent molecules in the asymmetric unit. The space group and the number of molecules per cell happen to be the same for both crystal forms.

Structure determination

The iodine atoms were located readily by Patterson projections and Harker sections so that assumptions about the details of the structure were not required. The c-axis projection then refined readily and the chlorine atoms appeared spontaneously. The a-axis projection then refined slightly more slowly but still without forcing.

With the general structure then clear from zone data, the refinement was continued by least-squares. The course of the refinement is shown in Table 1 which includes atomic coordinates and discrepancy factors at three stages. The column headed 'Fourier' gives the results from the electron density projections referred to; the R-value is based on a rough over-all isotropic temperature factor for the zone data. Next the least squares program LSII of Senko & Templeton for the IBM 650 computer was used with the complete data to refine positions, the scale factor, and individual isotropic temperature factors by means of the diagonal approximation to the matrix of the normal equations. This refinement was carried to completion and the results are shown in the column 'Diagonal LS'.

Table 1. *Atomic coordinates and standard deviations*

Atom	Coord.	Fourier	Diagonal LS	Full LS	
I_a	x	0·500	0·5038	0·5028	(0·00025)
	y	0·118	0·1182	0·1182	(0·00024)
	z	0·261	0·2628	0·2629	(0·00027)
I_b	x	0·816	0·8140	0·8135	(0·00022)
	y	0·036	0·0332	0·0321	(0·00025)
	z	0·128	0·1255	0·1250	(0·00027)
Cl_a	x	0·245	0·2553	0·2547	(0·00093)
	y	0·174	0·1888	0·1898	(0·00108)
	z	0·378	0·3653	0·3695	(0·00121)
Cl_b	x	0·920	0·8912	0·8876	(0·00135)
	y	0·316	0·3037	0·3002	(0·00139)
	z	0·101	0·1050	0·1069	(0·00149)
R		0·267	0·119	0·078	

The preceding calculations were carried out on the IBM 650 computer in the Computing Laboratory of Brown University.

Finally the ORXLS program of Busing for the IBM 704 computer was used for three cycles of refinement of positions, the scale factor, and individual anisotropic temperature factors by use of the full matrix of the normal equations. In this calculation, observations were weighted $1/\sigma^2$ where σ is an estimated standard deviation. For convenience, σ was given an integer value $1, \ldots, 5$ approximating the value of the expression $\sigma=0{\cdot}75+0{\cdot}25|F|/n^{\frac{1}{2}}$, where n is the number of independent films used in obtaining the estimate $|F|$ of the relative structure factor magnitude. This proved eventually to be somewhat too large; as judged by the final agreement between calculated and observed values, the preceding expression should be multiplied by 0·30 to give the standard deviation on the correct scale.

This refinement was terminated after three cycles when most of the coordinate changes were much less than estimated standard deviations; only the changes in x and y coordinates of Cl_b were nearly as large as their standard deviations, but they were so small compared with the changes in the preceding cycle that further refinement seemed needless. The final coordinates are listed in Table 1 under the 'Full LS' heading; these are the best values. Numbers in parentheses are estimated standard deviations.

In all cases R represents the conventional discrepance factor based on observed reflections only. In the 'Full LS' case, the value refers to the penultimate parameters.

Final values of the temperature factor parameters are listed in Table 2. These are the quantities in the expression,

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{23}kl+2\beta_{31}lh)\right]$$

The standard deviations for the various parameters

Table 2. *Temperature factor parameters for* β-ICl

	I_a	I_b	Cl_a	Cl_b
B_{11}	0·0094	0·0074	0·0076	0·0157
β_{22}	0·0085	0·0092	0·0110	0·0115
β_{33}	0·0097	0·0123	0·0173	0·0186
β_{12}	0·0007	0·0002	0·0013	−0·0041
β_{23}	−0·0005	−0·0005	−0·0008	0·0008
β_{31}	0·0016	0·0023	0·0053	0·0001

Table 3. *Observed and calculated structure factors for* β-ICl

Each line gives in order the values of k, l, $|F|_o$, and F_c.

h = 0			
0	0	-	560
0	4	65	-58
0	6	81	-85
0	8	107	109
1	3	57	-60
1	4	42	-43
1	5	88	-89
1	6	41	40
1	7	68	66
2	0	96	102
2	1	196	-232
2	2	25	-19
2	3	98	103
2	4	59	-58
2	5	59	-57
2	7	75	71
2	8	38	36
2	9	43	-47
3	1	168	150
3	2	60	-58
3	3	120	-125
3	4	17	-19
3	5	58	-53
3	6	75	68
3	7	37	19
3	8	26	-29
3	9	42	43
4	0	28	-29
4	1	82	-87
4	2	117	124
4	3	47	-42
4	4	150	-165
4	5	32	16
4	6	69	57
4	7	46	38
5	2	108	-107
5	3	34	-28
5	6	42	34
6	0	31	31
6	1	36	31
6	2	20	24
6	3	114	-123
6	4	62	-57
6	5	99	102
7	1	25	22
7	2	69	-76
8	0	37	33
8	1	33	-26
8	2	59	-58
8	3	55	-62
8	4	53	66
9	2	42	-42
9	3	18	17
9	4	30	-3
10	1	55	-59
11	1	28	-16
h = 1			
0	4	159	-131
0	6	32	-28
0	10	46	54
1	2	61	-53
1	5	41	-44
1	7	40	-45
1	9	38	49
2	0	24	19
2	1	207	218
2	2	81	88
2	3	183	-181
2	4	40	-40
2	5	74	74
2	6	35	-32
2	7	29	-32
2	9	38	34
3	0	87	85
3	1	188	163
3	2	45	-39
3	3	79	82
3	4	25	-23
3	5	120	-115
4	0	173	177
4	1	41	35
4	2	41	-33
4	3	90	-95
4	4	64	65
4	6	110	-103
4	8	49	44
5	0	96	96
5	2	28	-23
5	3	29	20
5	4	82	-84
5	5	35	-33
5	6	38	37
5	7	37	22
6	0	45	43
6	1	47	-48
6	2	26	23
6	5	69	-75
6	6	38	-37
6	7	55	68
7	0	57	59
7	1	39	35
7	4	57	-64
7	6	41	34
8	0	71	-71
8	2	37	33
8	3	30	-35
8	4	39	-38
9	0	50	50
9	4	39	-27
10	1	46	46
10	3	63	-57
h = -1			
0	4	171	-196
0	6	157	172
0	8	31	-22
1	2	72	-73
1	3	130	-140
1	4	28	28
1	5	66	63
1	7	26	26
2	1	113	115
2	2	73	-74
2	3	89	-89
2	4	39	-35
2	5	118	127
2	6	63	59
2	7	80	-81
3	1	82	-74
3	2	29	-27
3	3	110	-117
3	4	84	90
3	6	26	-22
3	7	70	76
3	9	35	-29
4	1	81	-74
4	2	216	-207
4	3	29	-19
4	4	69	61
4	5	64	69
4	6	13	-21
4	8	50	52
5	1	13	-14
5	2	33	-24
5	4	57	55
5	6	19	33
5	7	27	36
6	1	148	-162
6	2	65	-66
6	3	121	124
7	2	24	-28
7	3	28	-33
7	6	53	41
8	1	81	-85
8	2	75	78
8	3	29	35
8	4	32	-41
9	4	41	47
h = 2			
0	4	213	223
0	6	111	-136
1	0	78	-72
1	3	150	141
1	4	69	-66
1	5	32	-32
1	6	19	23
1	7	26	-22
2	0	69	-64
2	1	90	-91
2	2	54	53
2	3	161	147
2	4	55	54
2	5	113	-116
2	6	37	-40
2	7	49	47
3	0	34	34
3	1	20	11
3	2	91	81
3	3	110	108
3	4	57	-55
3	5	29	27
3	7	69	-77
4	0	199	-191
4	1	67	66
4	2	205	175
4	4	39	-37
4	5	61	-66
4	6	28	25
4	8	49	-52
5	0	73	70
5	1	20	8
5	2	54	54
5	4	28	-29
5	5	28	21
5	6	48	-51
5	7	39	-30
6	0	63	-57
6	1	153	164
6	2	42	48
6	3	54	-55
6	7	43	-36
7	0	62	64
7	2	26	20
7	3	36	34
7	4	30	-27
8	0	76	71
8	1	80	84
8	2	61	-66
8	4	31	32
9	2	36	45
10	3	29	27
h = -2			
0	2	323	-315
0	4	188	220
0	6	20	-15
0	10	53	-45
1	1	156	-159
1	2	22	-19
1	3	23	19
1	5	63	65
1	6	41	41
1	7	31	28
1	8	29	-36
1	9	57	-58
2	1	109	-116
2	2	96	-88
2	3	212	193
2	4	78	73
2	5	111	-117
2	6	45	39
2	7	29	29
2	8	29	-25
2	9	31	-26
3	1	184	-152
3	2	86	89
3	4	11	5
3	5	103	102
3	7	20	-21
3	8	48	-38
4	1	80	-72
4	2	56	50
4	3	33	86
4	4	47	-48
4	6	86	97
4	7	22	-22
4	8	63	-56
5	1	29	-24
5	2	61	63
5	3	13	-16
5	4	61	60
5	5	55	49
5	6	40	-54
5	7	26	-19
6	1	112	116
6	5	37	38
6	7	63	-80
7	1	24	-25
7	2	33	21
7	4	60	63
8	2	47	-47
8	3	32	36
8	4	39	38
9	2	45	47
10	1	42	-41
10	3	58	60
h = 3			
0	0	320	-334
0	2	76	77
0	4	24	17
0	6	86	95
0	8	66	-81
1	0	73	69
1	1	119	-116
1	2	37	29
1	5	87	95
1	6	48	-49
1	7	41	-44
2	0	125	-128
2	1	135	125
2	2	28	-27
2	3	62	-57
2	4	62	58
2	5	81	78
2	6	23	21
2	7	68	-66
2	8	30	-29
3	0	63	-53
3	1	135	-126
3	2	33	31
3	3	61	59
3	4	62	56
3	5	48	46
3	6	51	-50
3	9	38	-41
4	0	37	34
4	1	95	98
4	2	116	-127
4	3	34	31
4	4	123	130
4	5	31	-29
4	6	44	-35
5	0	42	-45
5	1	45	-46
5	2	79	87
5	3	32	28
6	1	90	-77
6	2	42	-36
6	3	116	129
6	4	34	38
6	5	49	-52
7	2	73	73
8	0	49	-49
8	2	56	53
8	3	52	62
8	4	45	-47
9	0	34	-32
10	1	50	48
h = -3			
0	2	215	210
0	4	20	-9
0	6	45	42
0	8	85	-85
0	10	27	38
1	1	59	-60
1	2	39	34
1	3	93	98
1	4	63	60
1	5	68	66
1	6	42	-41
1	7	78	-80
2	1	223	225
2	2	60	56
2	3	137	-133
2	4	87	86
2	5	37	39
2	6	24	-17
2	7	58	-54
2	8	48	-49
2	9	49	51
3	1	47	-44
3	2	51	46
3	3	103	102
3	4	25	-22
3	6	65	-59
3	7	27	-22
3	8	49	39
4	1	74	69
4	2	92	-85
4	3	56	50
4	4	124	144
4	6	71	-72
4	7	43	-37
5	1	18	-22
5	2	78	81
5	3	60	55
5	4	39	-42
5	6	33	-29
6	3	74	75
6	4	43	35
6	5	107	-116
6	6	28	-21
7	2	71	71
8	1	29	31
8	2	37	48
8	3	40	44
8	4	48	-43
9	2	30	35
10	1	65	59
h = 4			
0	0	134	142
0	2	232	-241
0	4	87	89
1	0	33	-30
1	1	116	-115
1	2	80	75
1	3	51	-47
1	5	24	26
1	7	50	52
2	1	216	-186
2	2	121	-118
2	3	105	107
2	4	16	8
2	5	32	-35
2	6	41	42
2	7	34	35
3	0	83	-74
3	1	49	-47
3	3	75	-74
3	4	22	18
3	5	64	60
3	6	33	31
4	0	113	-110
4	1	35	-33
4	2	32	24
4	3	85	83
4	4	65	-63
4	6	70	79
4	8	33	-26
5	0	71	-75
5	1	34	-28
5	3	45	-46
5	4	68	72
5	5	39	37
6	0	18	-11
6	3	37	-34
6	5	78	79
6	6	35	24
7	0	64	-59
7	4	58	58
8	0	49	47
8	2	44	-45
8	4	37	34
9	0	54	-46
10	1	41	-46
10	3	59	44
h = -4			
0	2	26	-17
0	4	93	92
0	6	134	-128
0	8	45	51
1	1	65	94
1	2	72	64
1	3	105	109
1	4	32	-32
1	5	79	-81
1	7	28	-26
2	1	107	-113
2	2	116	120
2	3	57	54
2	4	20	17
2	5	96	-92
2	6	84	-82
2	7	85	76
3	1	69	64
3	3	37	33
3	4	78	-74
3	5	34	-26
3	7	40	-36
4	1	74	67
4	2	146	165
4	4	77	-73
4	5	58	-62
4	8	52	-38
5	1	44	41
5	3	31	34
5	4	46	-52
5	7	58	-47
6	1	105	108
6	2	48	38
6	3	116	-130
6	4	21	-22
6	5	24	23
7	4	40	-38
8	1	54	62
8	2	45	-43
8	3	48	-44
8	4	46	48
10	2	36	-32
h = 5			
0	0	42	-33
0	2	73	69
0	4	139	-134
0	6	65	68
1	0	46	-41
1	1	57	53
1	2	26	-22
1	3	110	-112
1	4	52	55
2	0	101	108
2	1	80	72
2	2	36	-35
2	3	120	-114
2	4	79	-77
2	5	72	74
3	2	73	-70
3	3	34	-30
3	4	28	25
3	5	38	-34
3	7	46	42
4	0	146	142
4	1	57	-57
4	2	97	-104
4	4	24	20
4	5	54	53
4	8	34	39
5	2	41	-46
5	3	36	-26
5	5	26	-31
5	6	43	45
6	0	28	34
6	1	111	-113
7	0	48	-39
7	2	31	-30
8	0	41	-37
8	1	53	-61
8	2	39	35
8	4	37	-34
9	2	42	-41
h = -5			
0	2	115	134
0	4	159	-153
0	6	52	55
1	1	115	125
1	3	49	-47
1	5	67	-66
1	9	56	53
2	1	67	70
2	2	74	68
2	3	127	-125
2	4	98	-99
2	5	92	93
2	6	30	-33
2	7	30	-34
2	8	45	39
3	1	54	53
3	2	75	-67
3	5	44	-45
3	7	39	32
3	8	32	24
4	2	69	-57
4	3	80	-78
4	4	33	28
4	6	63	-67
4	7	35	29
4	8	73	55
5	1	59	64
5	2	63	-59
5	4	36	-27
5	5	61	-65
6	1	108	-107
6	5	26	-21
6	7	48	62
7	2	35	-42
7	4	43	-39
8	1	29	-27
8	2	45	54
8	3	23	-27
8	4	49	-43
9	2	37	-37
10	3	52	-52
h = 6			
0	0	119	138
0	2	36	-42
0	4	27	26
0	6	59	-63
1	1	99	96
1	5	68	-79
2	0	97	97
2	1	78	-75
2	2	63	61
2	3	43	40
2	4	45	-46
2	5	58	-55
3	0	36	36
3	1	56	54
3	4	55	-47
4	0	36	-35
4	1	28	-32
4	2	93	93
4	3	39	-35
4	4	78	-77
5	0	48	45
5	1	66	69
5	2	43	-49
6	1	66	62
6	3	89	-89
6	5	29	25
7	0	39	35
7	2	49	-47
8	0	45	51
8	2	32	-28
8	3	43	-45
h = -6			
0	2	124	-143
0	4	46	48
0	6	23	-24
0	8	53	54
1	3	100	-95
1	5	27	-22
1	7	72	73
2	1	113	-126
2	2	85	-83
2	3	97	87
2	4	69	-71
2	5	48	-42
2	6	40	40
2	7	45	43
2	8	49	40
3	2	32	-27
3	3	47	-44
3	6	44	37
3	8	34	-30
4	1	78	-75
4	2	43	42
4	4	88	-94
4	6	67	67
5	2	39	-40
5	3	73	-69
5	4	43	38
6	3	49	-49
6	5	84	83
7	2	51	-47
7	4	47	40
8	2	49	-43
8	4	34	22
10	1	67	-53
h = 7			
0	0	103	-100
0	2	113	109
0	4	35	-38
1	0	37	30
1	1	51	51
1	3	52	49
2	0	41	-39
2	1	104	94
2	2	88	88
2	3	63	-63
2	4	25	19
3	0	53	40
3	3	37	41
4	0	47	50
4	1	50	57
4	3	33	-31
4	4	50	48
4	6	33	-46
5	0	45	39
5	2	28	23
5	3	47	52
5	4	41	-43
6	5	52	-53
7	0	50	43
7	4	42	-40
8	0	45	-35
8	2	40	39
h = -7			
0	2	36	33
0	4	48	-46
0	6	79	82
0	8	41	-43
1	1	86	-89
1	3	43	-47
1	5	75	77
1	6	25	-25
2	1	57	63
2	2	88	-90
2	3	51	-51
2	4	21	21
2	5	63	65
2	6	63	65
2	7	48	-47
3	1	32	-31
3	4	45	43
4	2	99	-102
4	3	42	43
4	4	68	65
4	7	41	-40
5	1	45	-51
5	3	26	-20
5	4	36	33
6	1	69	-69
6	3	82	83
7	4	38	35
8	2	29	21
8	3	54	41
8	4	29	-29
h = 8			
0	2	54	-53
0	4	65	71
1	1	61	-59
1	3	58	59
2	0	77	-78
2	1	39	38
2	3	54	54
2	4	55	57
2	5	41	-43
3	2	47	43
4	0	93	-87
4	1	27	21
4	2	44	47
6	1	66	69
h = -8			
0	2	62	-66
0	4	97	98
0	6	34	-38
1	1	50	-58
1	3	51	55
1	5	30	35
2	1	40	-55
2	3	77	75
2	4	71	75
2	5	45	-49
3	1	32	-27
3	2	34	36
4	2	50	49
4	3	40	38
4	5	47	-44
4	6	30	36
5	1	39	-36
5	2	47	39
5	6	36	-32
6	1	56	61
7	2	49	44
8	4	38	31
h = 9			
0	0	71	-73
1	1	46	-48
1	5	47	44
2	0	42	-30
2	1	46	45
2	2	43	-47
3	1	43	-36
4	2	59	-59
4	4	45	55
5	1	37	-36
6	1	37	-33
6	3	47	52
h = -9			
0	2	86	91
1	3	55	53
2	1	63	68
2	2	60	63
2	3	46	-40
3	3	32	34
4	3	27	-35
4	4	45	50
4	6	52	-51
6	3	30	30
6	5	54	-53
7	4	40	-39
h = 10			
0	0	60	64
0	2	54	-63
2	0	43	37
2	1	55	-48
2	3	39	36
3	3	47	-31
4	4	44	-32
h = -10			
0	6	61	-61
1	1	47	53
2	1	36	-26
2	2	39	28
2	5	45	-41
4	2	55	54
4	3	32	-29
4	4	47	-48
6	1	36	36
6	3	54	-52
h = 11			
0	4	47	-43
2	0	25	28
4	0	46	46
h = -11			
0	4	58	-71
2	3	38	-43
4	2	35	-35
h = 12			
0	0	36	32

range from 0·00021 to 0·00036 for iodine atoms, from 0·00093 to 0·00203 for chlorine atoms.

Observed and calculated structure factors are listed in Table 3. Entries are included for the 731 observed reflections only in order to save space, but upper limits were estimated for 684 unobserved reflections and structure factors were calculated for comparison; in a few cases only did the calculated magnitude exceed the observed, and then only by amounts within the range of error of the upper limits.

Results and discussion

Fig. 1 compares the structures of the two forms of crystalline iodine monochloride; the diagram for α-ICl is adopted from Boswijk *et al.* (1956), as is all other information for α-ICl mentioned in the following paragraphs.

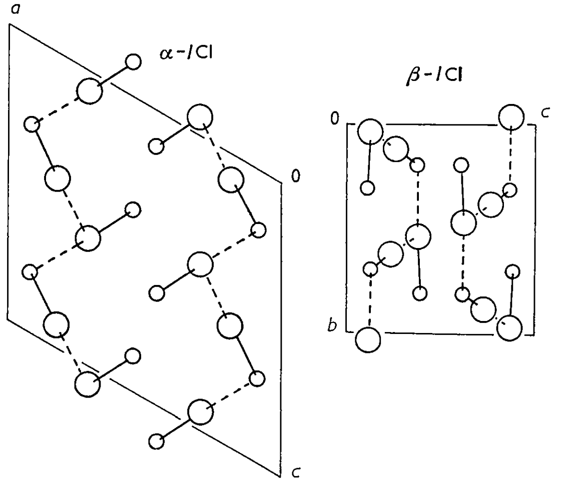

Fig. 1. Comparison of the structures of α- and β-ICl. The larger circles are iodine atoms, the smaller, chlorine.

The same general feature appears in both structures: chains of ICl molecules arranged in a zig-zag pattern. The two parts of the figure are oriented so that chains run vertically in both, but in β-ICl the chains are inclined 70·47° to the plane of the paper so that alternate links are foreshortened. The most conspicuous difference is that the chlorine atoms branching from the chain are *cis* in α-ICl, *trans* in β-ICl; i.e., in one the chain is periodically twisted through roughly 180° with respect to the chain in the other. A second difference is that in β-ICl the chains are nearly planar while in α-ICl they are distinctly puckered. In β-ICl the mean plane nearest to the cell origin has the equation $2{\cdot}9697x+7{\cdot}0711z=3{\cdot}2527$; its direction cosines on a and on a vector perpendicular to the ab plane are 0·33431 and 0·94246 respectively. The other chains are parallel to this one. The distances of the various atoms from this mean plane are I_a, 0·100; I_b, 0·047; Cl_a, 0·116; Cl_b, 0·139 Å; the atoms in the next pair of molecules are on the opposite side of this plane.

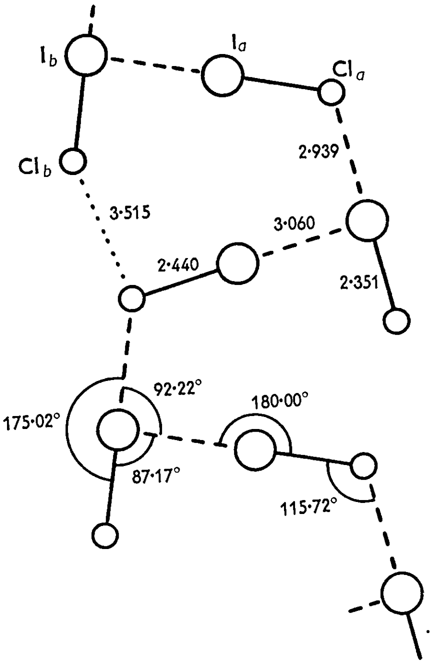

Fig. 2. Dimensions of the molecules and chains in β-ICl.

Certain significant angles and interatomic distances in β-ICl are shown in Fig. 2. These and others are recorded in Table 4, together with the corresponding distances in α-ICl.

Inasmuch as the errors are nearly isotropic, and almost the same for the two different kinds of iodine atoms, the standard deviations in the different kinds of interatomic distances can be summarized as follows: $I \cdots I$, 0·009; $I \cdots Cl_a$, 0·012; $I \cdots Cl_b$, 0·014; $Cl_a \cdots Cl_a$, 0·015; $Cl_a \cdots Cl_b$, 0·017; and $Cl_b \cdots Cl_b$, 0·018 Å. These include a contribution for the estimated errors in axial lengths; this is the major contribution to the $I \cdots I$ variance.

It is obvious that the bond lengths in the two different structures agree very well for each kind of molecule and that the difference between the I–Cl bond lengths in the two different molecules is (in both crystals) highly significant. Other corresponding distances along the chains of molecules are not significantly different in the two crystals, in view of the standard deviation of 0·04 Å in $I \cdots Cl$ distances in α-ICl. The angles are similar but show, of course, larger differences.

Table 4. *Interatomic distances and inter-bond angles in α-ICl and in β-ICl*

Distance or angle	β-ICl	α-ICl
Bond lengths		
I_a–Cl_a	2·440 Å	2·44 Å
I_b–Cl_b	2·351	2·37
Distances within chains		
$I_b \cdots Cl_a$	2·939 Å	3·00 Å
$I_a \cdots I_b$	3·060	3·08
$Cl_a \cdots Cl_b$	3·515	—
Distances between chains		
$I \cdots I$	3·892, 4·103, 4·209, ... Å	4·10, ... Å
$I \cdots Cl$	3·835, 3·950, 4·002, ...	4·03, ...
$Cl \cdots Cl$	3·514, ...	3·52, 3·54, ...
Angles within chains		
$Cl_a \cdots I_b$–Cl_b	175·02°	178·6°
Cl_b–$I_b \cdots I_a$	87·17	94·2
$I_b \cdots I_a$–Cl_a	180·00	179·3
I_a–$Cl_a \cdots I_b$	115·72	102·3

The shortest distances between atoms in adjacent β-ICl chains, listed in Table 4, are somewhat shorter than those in α-ICl, but there is no ground to consider that they represent anything but normal van der Waals contacts. The most notable of these is the $I_b \cdots I_b$ distance of 3·892 Å across a center of symmetry but this is still much longer than iodine contacts within a chain, 3·060 Å.

The dimensions of the chains in both β- and α-ICl can be interpreted in terms of a pattern of secondary bonding which links the diatomic molecules together. A kind of special strong interaction between molecules was recognized in α-ICl (Boswijk *et al.*, 1956); the observation of the same pattern in β-ICl emphasized its significance. According to the interpretation now suggested, those interatomic distances in Fig. 2 shown by dashed lines, while weaker than ordinary bonds, are strong enough and specific enough to be usefully called bonds. They are, firstly, 1 Å or more shorter than van der Waals distances. Secondly, the angles they form with other bonds are quite specific and reasonable for bonding interactions. These angles are approximately 90° and 180° at an iodine atom and 116° at a chlorine atom.

Furthermore the I_a–Cl_a molecule which is included in the chain is significantly longer (2·44 Å) than the one I_b–Cl_b hanging from the chain (2·35 Å). We may use Pauling's (1960) relation

$$D(n) = D(1) - 0{\cdot}60 \log n$$

to estimate bond numbers. If the normal covalent radii are used to compute $D(1)$, then the $I_a \cdots I_b$ bond number is 0·21, the $I_b \cdots Cl_a$ bond number is 0·09. In the same way the nominally single bonds have numbers 0·89 for I_a–Cl_a, 0·63 for I_b–Cl_b.

The secondary bonds may be interpreted in the following way as coordinate bonds. A previously-unshared electron pair on Cl_a or I_b forms a coordinate bond to I_b or I_a, respectively. Both I_a and I_b must therefore expand their valence shell to accommodate five electron pairs. Presumably a $5d$ orbital is called into play, and this appears to hybridize with the normally occupied $5s$ and $5p$ orbitals to give sp^3d hybrid orbitals directed toward the vertices of a trigonal bipyramid. (This pattern was mentioned by Burbank & Bensey (1953) to account for the molecular structured of ClF_3.) If the three remaining unshared pairs on such an iodine atom occupy the equatorial positions of the bipyramid, in order to remain as far apart as possible, then the coordinate bond to I_a or I_b must be about 180° away from the original normal single bond, as observed. Further, the coordinate bond formed by I_b should be at about 90° to the original single bond, as observed. Since the coordinate bond formed by Cl_a is 116° from the Cl_a–I_a bond, the chlorine atom must utilize orbitals intermediate between unhybridized ones and sp^3 hybrids. This angle is larger than the corresponding one in α-ICl, perhaps to relieve the strain produced by the close approach of Cl_a and Cl_b in one chain.

A more extensive application of this intermolecular bond interpretation to related crystal structures is intended for publication elsewhere.

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Note added in proof.— Dr R. E. Rundle (Iowa State) has pointed out to us that the intermolecular bonds found here can be explained also by the formation of nearly linear three-center bonds, without use of $5d$ orbitals.

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