The Crystal Structures of Methyl Bromide and Methyl Iodide

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(Received May 6, 1972)

The crystal structures of methyl bromide and methyl iodide have been determined by the X-ray diffraction method at about −120°C and about −80°C respectively. Both the crystals are isomorphous, with orthorhombic space group D_{2h}^{16}—*Pnma*. Unit cells containing four molecules have the dimensions: $a=4.47_4(1)$, $b=6.42_0(2)$, and $c=9.15_0(1)$ Å for methyl bromide, and: $a=4.59_7(2)$, $b=6.98_7(1)$, and $c=10.11_7(1)$ Å for methyl iodide. These structures are quite different from that of methyl chloride, which has a symmetry of C_{2v}^{12}—$Cmc2_1$. In the three crystals, all the molecules are found on the mirror planes; the difference lies in the mutual orientations of the molecules.

As part of a series of investigations of various halogenated methanes, the crystal structures of methyl bromide and methyl iodide have been determined by the X-ray diffraction method. Since Burbank reported the crystal structure of methyl chloride,[1] several spectroscopists have discussed whether or not the crystal structures of methyl bromide and methyl iodide are isomorphous with that of methyl chloride.[2] The present authors will here report the crystal structures of these two compounds.

Experimental

Methyl bromide and methyl iodide, both from commercial sources (Tokyo Kasei Industries, Ltd. and Wako Pure Chemical Industries, Ltd., respectively), were purified repeatedly by recrystallization by cooling and by vacuum distillation, followed by sealing in thin-wall glass capillaries in vacuum (0.3 mm in internal diameter and 0.01 mm in wall thickness). The specimen was placed on an X-ray goniometer head and was crystallized by letting flow thereby a cold gas stream from liquid nitrogen. By means of careful temperature control, it was possible to grow a seed of a crystal very near to the size of the capillary at temperatures directly below the melting point (−93.7°C for methyl bromide and −66.5°C for methyl iodide); the crystal was then cooled gradually. It was found later that a single crystal of methyl bromide was grown with the [110] axis, and that a single crystal of methyl iodide was grown with the [100] axis, of the respective orthorhombic lattices nearly along the capillaries.

The cell dimensions of the two crystals were determined from oscillation and Weissenberg photographs around the axes mentioned above. These measurements were made at about −120°C for methyl bromide and at about −80°C for methyl iodide. From systematic extinctions (0*kl* with $k+l$ odd and *hk*0 with *h* odd) and intensity distributions, both the crystals were found to belong to space group *Pnma* or $Pn2_1a$, with four molecules per cell. The crystal data for these two compounds are summarized in Table 1. The intensity data were collected by means of multiple-film oscillation photographs, using Ni-filtered Cu *Kα* radiation; 212 independent reflections around the [110] axis for methyl bromide, and 177 such reflections around the [100] axis for methyl iodide, were used for the following analyses. The intensities measured visually were corrected for Lorentz-polarization and absorption effects by the cylindrical approximation, after which they were brought into respective common scales by considering different time exposures.

Table 1. CRYSTAL DATA

Methyl bromide, CH_3Br		Methyl iodide, CH_3I	
MW	94.94	MW	141.94
Mp	−93.7°C	Mp	−66.5°C
Tr. p.	−99.4		
Exp. temp.	−120	Exp. temp.	−80
Orthorhombic		Orthorhombic	
a	=4.474±0.012 Å	a	= 4.597±0.016 Å
b	=6.420±0.019	b	= 6.987±0.012
c	=9.150±0.013	c	=10.117±0.011
V	= 262.8 Å^3	V	= 324.9 Å^3
D_X	=2.399 g/cm^3	D_X	=2.901 g/cm^3
D_m[3]	=2.346 (at −195°C)	D_m[3]	=2.840 (at −79°C)
Z	= 4	Z	= 4
μ	=188.64 cm^{-1} (Cu *Kα*)	μ	=815.77 cm^{-1} (Cu *Kα*)
D_{2h}^{16}—*Pnma*		D_{2h}^{16}—*Pnma*	

Structure Determination and Results

Approximate co-ordinates of the halogen (bromine or iodine) and carbon atoms, deduced from the three-dimensional Patterson diagrams, indicated that these atoms lie on the mirror planes given by the space group *Pnma*. Least-squares refinement, omitting the hydrogen atoms, was applied by using isotropic temperature factors. No positive evidence was found that the space group should not be *Pnma*. The discrepancy indices, $R=\sum||F_o|-|F_c||/\sum|F_o|$, dropped to 0.11 for methyl bromide and to 0.12 for methyl iodide.

The observed and calculated structure factors are listed in Table 2, while the final sets of the positional and thermal parameters of the halogen and carbon atoms are listed in Table 3. The two crystal structures are isomorphous, having the symmetry D_{2h}^{16}-*Pnma*. There are four molecules in each unit cell. The halogen and carbon atoms lie on the mirror planes. Figure 1 shows a schematic drawing of the molecular

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TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS

(a) Methyl bromide

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	55.91	50.85	1	1	5	57.16	61.39	1	5	5	34.02	28.54	2	3	7	9.86	8.76	3	1	6	17.59	-16.55	4	0	2	9.93	-10.17
0	0	4	71.34	-75.26	1	1	6	19.86	15.93	1	5	6	8.62	7.64	2	3	8	3.63	4.18	3	1	8	21.49	-23.68	4	0	3	23.85	24.90
0	0	6	60.80	-60.50	1	1	7	20.23	19.38	1	5	7	9.29	9.55	2	3	9	4.07	3.95	3	1	9	2.85	-2.81	4	0	4	19.30	18.01
0	0	8	6.93	4.99	1	1	8	23.65	21.93	2	0	0	46.02	-37.70	2	4	0	19.59	-20.67	3	2	1	33.61	37.71	4	0	6	14.95	15.83
0	1	1	79.60	-62.08	1	1	9	16.76	-16.69	2	0	1	67.33	-51.49	2	4	1	30.41	-28.72	3	2	2	9.54	10.80	4	1	0	21.71	22.14
0	1	3	71.34	-84.70	1	2	1	49.64	-39.46	2	0	2	12.07	-12.49	2	4	2	7.92	-7.02	3	2	3	11.88	-11.04	4	1	1	14.33	14.77
0	1	5	7.22	-3.93	1	2	2	70.06	61.29	2	0	3	66.95	-74.82	2	4	3	46.15	-43.39	3	2	4	4.39	6.27	4	1	2	7.73	6.85
0	1	7	41.94	40.83	1	2	3	12.25	11.34	2	0	4	21.97	20.09	2	4	4	12.07	11.91	3	2	5	28.05	-31.96	4	1	3	19.92	21.99
0	2	0	106.63	-124.91	1	2	4	35.83	32.79	2	0	5	6.85	-7.18	2	4	5	4.01	-4.32	3	2	6	2.86	-3.46	4	1	4	13.59	-13.72
0	2	2	42.37	-40.03	1	2	5	30.01	31.51	2	0	6	16.77	17.31	2	4	6	12.62	10.70	3	2	7	9.81	-8.89	4	1	5	1.61	1.37
0	2	4	60.02	63.58	1	2	6	20.65	-19.92	2	0	7	37.13	34.81	2	4	7	23.78	21.74	3	2	8	3.52	-4.68	4	1	6	10.41	-11.05
0	2	6	61.64	52.83	1	2	7	8.34	8.75	2	0	9	18.89	18.42	2	5	0	32.62	-32.63	3	2	9	8.45	10.54	4	1	7	7.70	-11.60
0	2	8	5.92	-4.39	1	2	8	22.80	-24.55	2	1	0	84.62	-71.38	2	5	1	8.52	6.84	3	3	2	36.03	-43.01	4	2	0	28.69	27.03
0	3	1	41.15	43.22	1	2	9	9.86	-9.87	2	1	1	19.74	14.69	2	5	2	12.19	-10.25	3	3	4	25.78	-25.46	4	2	1	17.80	-14.52
0	3	3	56.70	62.39	1	2	10	2.19	-1.90	2	1	2	20.32	-21.99	2	5	3	12.28	10.09	3	3	5	6.92	-7.17	4	2	2	8.05	9.02
0	3	5	3.47	3.22	1	3	1	71.63	59.60	2	1	3	23.70	21.21	2	5	4	25.38	20.00	3	3	6	11.95	13.09	4	2	3	19.72	-22.14
0	3	7	36.38	-31.96	1	3	2	49.20	42.82	2	1	4	37.08	41.90	2	5	6	17.25	16.43	3	3	7	1.51	-2.21	4	2	4	15.69	-16.02
0	3	9	16.79	-14.83	1	3	3	14.51	-14.50	2	1	6	30.72	33.81	2	5	7	6.72	-5.45	3	3	8	16.36	18.89	4	2	6	12.45	-14.11
0	4	0	53.61	73.31	1	3	4	27.91	24.51	2	1	7	11.67	-11.13	2	6	0	9.81	11.31	3	4	1	24.69	-25.97	4	3	0	16.23	-17.43
0	4	2	24.84	24.31	1	3	5	45.11	-46.54	2	1	8	4.60	-5.26	2	6	1	18.71	15.66	3	4	2	10.85	-7.49	4	3	1	10.18	-11.64
0	4	4	49.22	-41.64	1	3	6	14.72	-12.37	2	1	9	5.90	-4.99	2	6	2	3.40	3.84	3	4	3	6.66	7.68	4	3	2	4.73	-5.38
0	4	6	45.06	-36.36	1	3	7	17.00	-15.19	2	1	10	14.32	15.33	2	6	3	23.50	23.89	3	4	4	4.02	-4.36	4	3	3	15.63	-17.26
0	4	8	2.80	3.06	1	3	8	21.48	-17.32	2	2	0	35.39	31.72	2	6	4	6.25	-6.61	3	4	5	20.19	22.39	4	3	4	9.12	10.84
1	0	1	46.83	47.39	1	3	9	12.70	13.24	2	2	1	51.36	43.66	3	0	1	40.37	-42.81	3	4	6	2.36	2.44	4	4	0	16.08	-19.04
1	0	2	63.01	-72.56	1	4	1	27.37	25.74	2	2	2	9.79	10.60	3	0	2	12.63	-12.28	3	4	7	5.59	6.24	4	4	1	9.02	10.24
1	0	3	12.48	-13.38	1	4	2	42.03	-40.34	2	2	3	61.30	64.23	3	0	3	12.49	12.58	3	4	8	4.85	3.33	4	4	2	6.03	-6.34
1	0	4	38.72	-37.60	1	4	4	27.06	-22.41	2	2	6	14.20	-15.30	3	0	4	5.60	-7.09	3	5	1	6.15	-5.25	4	4	3	13.45	15.61
1	0	5	35.17	-35.98	1	4	5	25.43	-21.57	2	2	7	28.08	-30.87	3	0	5	34.49	36.25	3	5	2	24.35	26.61	4	4	4	9.18	11.35
1	0	6	22.80	22.64	1	4	6	18.26	13.80	2	2	9	15.31	-16.43	3	0	6	4.01	3.89	3	5	4	15.29	15.99	4	4	5	1.48	1.70
1	0	7	9.79	-9.89	1	4	7	7.49	-6.07	2	3	0	59.04	53.73	3	0	7	11.44	10.02	3	5	5	4.83	4.48	4	5	0	7.95	10.83
1	0	8	29.56	27.66	1	4	8	20.43	17.13	2	3	1	13.95	-11.22	3	0	8	4.69	5.26	3	5	6	7.21	-8.24	4	5	1	4.89	7.27
1	0	9	10.89	11.15	1	5	1	36.48	-34.14	2	3	2	18.28	16.87	3	1	1	11.31	-10.92	3	6	1	14.59	14.32	4	5	2	2.76	3.36
1	1	2	64.84	-61.12	1	5	2	29.63	-25.04	2	3	3	18.28	-16.43	3	1	2	52.90	55.38	3	6	2	3.36	4.16	4	5	3	7.19	10.87
1	1	3	25.46	19.95	1	5	3	8.74	8.66	2	3	4	31.21	-32.44	3	1	4	29.68	32.48	3	6	3	3.47	-4.27	4	5	4	4.20	-6.79
1	1	4	34.11	-33.02	1	5	4	19.74	-14.75	2	3	6	25.17	-26.38	3	1	5	10.79	9.11	4	0	0	30.86	-30.48	5	2	1	1.35	-1.32
																				4	0	1	16.93	16.37	5	2	2	10.57	-16.02

(b) Methyl iodide

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	4	111.01	-114.32	0	6	0	56.02	-57.59	1	1	9	30.29	-24.74	1	4	6	15.43	16.41	2	0	5	15.10	-12.91	2	3	10	18.39	17.90
0	0	6	90.68	-95.79	0	6	2	19.90	-19.89	1	1	10	6.67	5.93	1	4	7	10.81	-12.86	2	0	6	33.09	28.43	2	4	0	29.01	-33.49
0	0	10	37.98	37.86	0	6	4	27.55	33.35	1	1	11	27.18	-21.45	1	4	8	28.74	28.24	2	0	7	61.08	49.56	2	4	1	35.83	-40.68
0	0	12	12.47	13.36	0	6	6	24.41	-30.80	1	1	12	9.04	-8.21	1	4	9	9.57	8.64	2	0	9	35.71	28.21	2	4	2	13.34	-11.28
0	1	3	138.88	-141.92	0	7	1	18.03	18.53	1	2	1	62.01	-63.74	1	4	10	7.23	6.47	2	0	10	11.76	-11.92	2	4	3	63.15	-62.30
0	1	5	21.79	-20.80	0	7	3	22.02	29.18	1	2	2	90.74	98.38	1	5	1	51.17	-51.71	2	1	2	22.24	-39.36	2	4	4	20.49	19.27
0	1	7	49.27	60.95	0	7	5	2.86	4.57	1	2	3	15.89	13.20	1	5	2	36.01	-35.86	2	1	3	33.18	36.98	2	4	6	19.57	17.23
0	1	9	35.86	37.22	0	7	7	12.92	-14.36	1	2	4	67.79	60.97	1	5	3	10.37	12.32	2	1	4	57.78	60.27	2	4	7	36.20	30.46
0	1	11	6.13	-5.31	0	8	0	25.68	25.36	1	2	5	57.74	49.39	1	5	4	23.89	-21.98	2	1	6	57.92	56.47	2	4	9	16.57	17.71
0	2	0	212.32	-185.70	0	8	2	6.92	8.79	1	2	6	31.88	-24.12	1	5	6	9.16	10.23	2	1	7	23.04	-16.60	2	5	0	46.49	-49.49
0	2	2	66.61	-61.46	0	8	4	11.90	-14.97	1	2	7	18.35	18.67	1	5	7	13.13	15.37	2	1	9	13.80	-10.77	2	5	1	8.00	10.77
0	2	4	90.96	96.53	1	0	2	97.74	-115.47	1	2	8	48.49	-40.64	1	5	8	15.71	16.06	2	1	10	32.76	-22.65	2	5	2	23.82	-17.67
0	2	6	70.18	83.48	1	0	3	20.13	-15.38	1	2	9	15.39	-12.34	1	5	9	12.08	-12.38	2	2	1	49.77	62.01	2	5	3	21.87	16.95
0	2	10	32.89	-33.63	1	0	4	79.37	-70.36	1	2	10	8.63	-9.12	1	6	1	19.75	-21.49	2	2	2	14.91	17.13	2	5	4	37.28	27.86
0	2	12	12.52	-11.97	1	0	5	67.66	-56.92	1	2	11	16.49	-11.94	1	6	2	30.57	33.76	2	2	3	77.89	93.40	2	5	6	30.46	26.99
0	3	1	69.14	68.07	1	0	6	33.74	27.42	1	3	1	98.73	91.19	1	6	4	23.40	21.63	2	2	4	27.28	-28.62	2	5	7	11.75	-7.99
0	3	3	87.18	104.55	1	0	7	22.61	-21.19	1	3	2	69.78	62.22	1	6	5	18.75	18.01	2	2	5	14.73	11.28	2	6	0	14.04	18.01
0	3	5	14.35	15.60	1	0	8	55.87	46.14	1	3	3	20.85	-21.32	1	6	6	8.82	-8.95	2	2	6	31.77	-24.94	2	6	1	25.53	21.78
0	3	7	44.43	-47.17	1	0	9	11.20	13.96	1	3	4	40.57	37.05	1	6	7	6.14	7.10	2	2	7	52.87	-43.69	2	6	2	6.80	6.10
0	3	9	29.73	-29.14	1	0	10	11.52	10.27	1	3	5	72.67	-71.70	1	6	8	13.29	-15.76	2	2	9	26.89	-25.04	2	6	3	34.45	33.73
0	3	11	4.21	4.19	1	0	11	18.80	13.42	1	3	6	20.00	-16.71	1	7	1	20.60	24.86	2	2	10	12.44	10.67	2	6	4	11.73	-10.62
0	4	0	104.11	111.89	1	0	12	13.81	-10.55	1	3	7	26.73	-24.83	1	7	2	15.15	17.31	2	3	0	61.14	83.72	2	6	5	5.03	4.23
0	4	2	38.95	38.20	1	1	1	133.31	-130.38	1	3	8	27.75	-25.76	1	7	3	4.82	-6.01	2	3	1	14.38	-18.02	2	6	6	9.93	-9.65
0	4	4	56.97	-62.75	1	1	2	92.93	-87.41	1	3	9	21.63	19.57	1	7	4	8.86	10.76	2	3	2	37.49	29.74	2	6	7	15.92	-17.20
0	4	6	49.03	-56.37	1	1	3	33.89	29.58	1	3	11	19.26	17.13	1	7	5	17.35	-21.42	2	3	3	33.85	-28.15	2	7	1	8.35	-5.19
0	4	10	18.58	23.84	1	1	4	48.74	-49.94	1	4	1	41.43	40.96	1	7	6	4.49	-5.13	2	3	4	53.86	-46.19	2	7	2	9.18	8.62
0	5	1	41.88	-39.09	1	1	5	111.80	95.00	1	4	2	60.98	-64.32	1	7	7	5.18	-7.73	2	3	6	54.02	-43.87	2	7	3	8.51	-8.24
0	5	3	56.15	-60.86	1	1	6	24.20	21.92	1	4	3	6.38	-8.73	1	8	1	9.07	9.37	2	3	7	16.71	12.98	2	7	4	13.37	-13.71
0	5	5	7.73	-9.28	1	1	7	39.55	32.15	1	4	4	42.16	-40.53	1	8	2	11.56	-14.78	2	3	9	11.87	8.52					
0	5	7	25.81	28.98	1	1	8	39.79	32.87	1	4	5	32.98	-33.20	2	0	4	25.39	33.12										

Table 3. Positional and thermal parameters of the halogen and carbon atoms, with their e.s.d.'s in parentheses

compound	atom	X	Y	Z	B (Å^2)
CH_3Br	Br	0.1544(9)	1/4(—)	0.0968(4)	3.51(7)
	C	0.3330(88)	1/4(—)	−0.0871(42)	3.35(73)
CH_3I	I	0.1571(15)	1/4(—)	0.0946(4)	4.60(9)
	C	0.3144(214)	1/4(—)	−0.1039(61)	4.00(128)

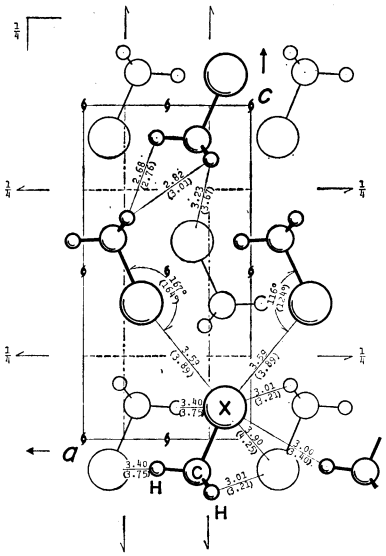

Fig. 1. Schematic drawing of the crystal structure of methyl bromide and methyl iodide, projected along the b axis. Interatomic distances and angles between neighboring molecules for methyl bromide and those for methyl iodide (in parentheses) are given.

arrangement of the two crystals, projected along the b axis. In this figure, an assumed orientation of the methyl group, as will be described later, is given, and the interatomic distances and angles between neighboring molecules for methyl bromide and those for methyl iodide (in parentheses) are given.

The bond distances between the halogen and carbon atoms are found to be $1.86_3\pm0.04$ for Br–C and $2.13_4\pm0.06$ Å for I–C. The corresponding values obtained by a microwave study[4] in the gaseous state are 1.9391 and 2.1392 Å. Because of the large e.s.d.'s of the carbon positions, it can not be said that these bond distances are different in their gaseous and crystalline states.

Each halogen atom is in contact with two halogen atoms of the neighboring molecules lying on the same mirror plane, with distances of 3.587 ± 0.008 for Br···Br and 3.895 ± 0.010 Å for I···I. These distances are much shorter than twice the conventional van der Waals radii, 3.90 for the bromine atom and 4.30 Å for the iodine atom. The juxtaposition of the molecules is such that:

	∠ C–X···X
Methyl bromide	116° and 167° ± 1°
Methyl iodide	124° and 164° ± 2°,

where X denotes the halogen atom. It should be noted that the smaller values, 116° and 124°, can be compared to the sp^3 tetrahedral angle, while the larger ones are not far from 180°.

Discussion

Egan and Kemp[5] have reported that there is a first-order phase transition in the crystal of methyl bromide, occurring at −99.4°C with a latent heat of 0.113 kcal/mol. Although the present structure determination was carried out for the crystal at about −120°C, much lower than the transition point, it might have been of a supercooled form of the high-temperature one (α). In order to clarify this question, the following experiment was carried out.

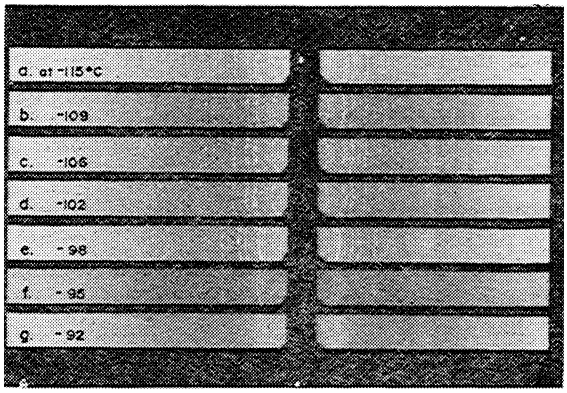

Fig. 2. Powder patterns for methyl bromide at various temperatures. a–d correspond to the low-temperature phase, e and f to the high-temperature phase, and g to the liquid phase.

A polycrystalline specimen of methyl bromide was heated to almost its melting point (−93.7°C), then cooled slowly, and subsequently repeatedly warmed-up and cooled-down. Powder patterns, given in Fig. 2, were taken at several temperatures, from −120° to −90°C. These patterns clearly show the existence of the phase transition between the temperatures of −102° and −98°C. The low-temperature phase (β) was identified as the crystal structure described in the previous section. The crystal structure of the high-temperature phase (α) must be of a form related to that of the low-temperature form, since the heat of transition is very small.

It is found that the crystal structure of methyl bromide (β) and methyl iodide are isomorphous and that they are quite different from that of methyl chloride. The crystal of methyl chloride is orthorhombic, with a tetramolecular cell with dimensions of a=6.495, b=5.139, and c=7.523 Å, and it belongs to space group C_{2v}^{12}—$Cmc2_1$.[1] However, if one replaces the methyl group by its counterpart halogen atom, the three

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5) C. J. Egan and J. D. Kemp, *J. Amer. Chem. Soc.*, **60**, 2097 (1938).

crystal structures will become almost the same as the structures of solid halogen crystals, Cl_2, Br_2, and I_2, which are known to be isomorphous.[6] The difference between the crystal structure of methyl chloride and those of methyl bromide and methyl iodide can be seen in the mutual orientation of the molecules. In the crystal of methyl chloride, the molecules lying on the mirror plane are aligned head to tail and are parallel with the molecules lying on the adjacent mirror planes. On the other hand, in the crystals of methyl bromide (β) and methyl iodide, the molecules lying on the mirror plane are aligned head to head and are antiparallel with the molecules lying on the adjacent mirror planes.

It was previously inferred by one of the present authors[7] that, in the crystals of Br_2 and, particularly, I_2, partial covelency, based upon the charge transfer from the $p\pi^*$- to the $p\sigma^*$-orbitals between the neighboring molecules lying on the mirror plane, plays a part in the intermolecular bonding. In the crystals of methyl bromide (β) and methyl iodide also, the mutual orientation of the molecules lying on the mirror planes seems to favor a covalent bonding between the halogen atoms of the neighboring molecules. It may be suggested that this intermolecular bonding is responsible for the exceedingly short distances for X···X; it can also explain why those crystal structures differ from that of methyl chloride.

As can be seen in Fig. 1, the methyl groups are loosely packed in the structures; this suggests that these groups are in a state of hindered rotation or reorientation. Indeed, an NMR study[8] of methyl iodide has shown that the observed second moment, ΔH_2^2, at -183°C is 8.4 gauss^2 and that the rotation sets in at about -150°C, where the line width, δH, decreases from 5 to 3 gauss. When an NMR study of powdered specimen of methyl bromide was carried out, it showed that an appreciable rotation of the methyl group occurred from its melting point down to the boiling point of liquid nitrogen. The line width, $\delta H \approx 4.7$ gauss, and the second moment, $\Delta H_2^2 \approx 7.5$ gauss^2, remain constant in this temperature range. Here, the theoretical values for the second moment are 27.6 and 5.0 gauss^2 for the stational and rotational states respectively. Figure 1 gives the most stable orientation of the methyl group, as suggested by the lattice-energy calculations.[9]

The actual alignment of molecules should correspond to the potential energy minimum. By keeping the unit-cell dimensions and the crystal symmetry, variations in the potential energies with the positional and orientational parameters of the respective molecules, which are X, Z, and θ for methyl bromide and methyl iodide and Y and θ for methyl chloride, were calculated by means of the lattice-energy calculations, as cited in the previous paper.[9] It was found that the potential minima based upon the rotational models of the methyl groups are in better agreement with the respcetive molecular arrangements than those based upon the stational models. Burbank assigned the crystal structure of methyl chloride the stational orientation of the methyl group by comparing the observed structure factors. However, it can be expected from the lattice-energy calculations that the rotation of the methyl group also occurs in the crystal of methyl chloride.

The authors wish to thank Professor Tokunosuké Watanabé for his helpful discussions during the preparation of this manuscript. They are also indebted to Dr. Akio Furusaki and Mr. Hiroyuki Utsumi for their assistance in these analyses, and to Dr. Asako Kawamori for her assistance in the NMR measurements.

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