The Crystal Structures of Methylene Dibromide and Methylene Diiodide

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The crystal structures of methylene dibromide and methylene diiodide (Form II) have been determined by the X-ray diffraction method at about -90° C and about -20° C respectively. Both the crystals are isomorphous, with monoclinic space group $C_{ih}^{e}-C2/c$. Unit cells containing eight molecules have these dimensions: a=12.239 (12), b=4.459(15), c=15.212(16) Å, and $\beta=113.54(7)^{\circ}$ for methylene dibromide, and a=13.346(3), b=4.720(90), c=16.479(5) Å, and $\beta=114.48(8)^{\circ}$ for methylene diiodide. The orientations of the methylene groups have been obtained by lattice-energy calculations.

As part of a series of investigations of molecular interactions on various halogenated methanes, the crystal structures of bromoform, 1) iodoform, 2) methyl bromide and methyl iodide 3) have already been reported. It has been found that bromoform and iodoform are isomorphous, and that methyl bromide and methyl iodide are also isomorphous, but their chlorine congeners have quite different structures. In this and succeeding papers, the crystal structure sof methylene diodide, methylene dibromide, and methylene dichloride will be reported.

Marzocchi et al.⁴) ascertained, by their spectroscopic studies, that methylene diiodide exists in two solid phases; one is a metastable form, I, melting at 5.54° C, while the other is a stable form, II, melting at 6.01° C; Form I is easily and irreversibly transformed to Form II at temperatures above 0° C. They also reported that methylene dibromide and methylene diiodide (II) are isomorphous and have a structure based on $P2_1/c$, while methylene dichloride has a structure based on Pbcn.

Experimental

Methylene dibromide and methylene diiodide from Nakarai Chemicals, Ltd., were purified by vacuum distillation and were sealed in thin-wall glass capillaries (0.3 mm in internal diamter and 0.01 mm in wall thickness). A single crystal was carefully produced in a way which has previously been described. In all the experiments on these two crystals thus far carried out, it has been found that only one kind of zone axes grows nearly along the capillaries. This is the [010] axis of a monoclinic lattice. The single crystal obtained was gradually cooled to about -90° C for methylene dibromide and to about -20° C for methylene diiodide for the taking of oscillation and Weissenberg photographs.

The cell dimensions of both the crystals were determined

TABLE 1. CRYSTAL DATA

Methylene dibromide, CH ₂ Br ₂	Methylene diiodide, CH ₂ I ₂
MW 173.85	MW 267.84
Mp -52.8° C	Mp (II) 6.01°C
	(I) 5.54
Exp. temp. -90	Exp. temp. -20
Monoclinic; $C_{2h}^6 - C_2/c$	Monoclinic; $C_{2h}^6 - C_2/c$
Z=8	Z= 8
$a = 12.239 \pm 0.012 \text{Å}$	$a = 13.346 \pm 0.003 \text{Å}$
$b = 4.459 \pm 0.015$	$b = 4.72 \pm 0.09$
$c = 15.212 \pm 0.016$	$c = 16.479 \pm 0.005$
$\beta = 113.54 \pm 0.07^{\circ}$	$\beta = 114.48 \pm 0.07^{\circ}$
$V = 761.4 \text{Å}^3$	$V = 944.7 \text{Å}^3$
$D_{\rm x} = 2.994 {\rm \ g/cm^3}$	$D_{\rm x} = 3.765 \ {\rm g/cm^3}$
$D_{\rm m} = 2.4953 \; ({\rm at} \; 20^{\circ}{\rm C})$	$D_{\rm m} = 3.3326 \text{ (at } 15^{\circ}\text{C)}$
2.999 (at -79° C)	4.013 (at -195 °C)
$\mu = 274.0 \text{ cm}^{-1} \text{ (Cu } K\alpha)$	$\mu = 1121.2 \text{ cm}^{-1} \text{ (Cu } K\alpha \text{)}$
	139.2 (Mo $K\alpha$)

from oscillation and Weissenberg photographs taken around the [010] axis, using Cu $K\alpha$ radiation. Intensity distributions and systematic extinctions (h+k) odd for hkl and l odd for h0l) showed that the crystals belong to space group Cc or C2/c, with eight molecules per cell. The crystal data are summarized in Table 1. The densities calculated are much larger than that for liquid, much as in the cases of bromoform, methyl bromide, and methyl iodide. These intensity distributions and the cell dimensions strongly suggest that the two crystals are isomorphous.

Integrated intensities were collected by means of the multiple-film method and the equi-inclination Weissenberg technique, using Ni-filtered $\text{Cu}K\alpha$ radiation for methylene dibromide and Zr-filtered Mo $K\alpha$ radiation for methylene diiodide. Here, the intensity data for methylene diiodide were recorded jointly by means of different time exposures. Reflections were observed up to the third layers around the [010] axes, though for methylene dibromide, 205, and for methylene diiodide, 244 independent reflections from the zero-th and first layers were used in order to determine the respective structures. The intensities were measured visually and corrected for Lorentz–polarization and absorption effects with the cylindrical approximation; then the intensities were brought into respective common scales by considering them at different time exposures.

Structure Determination

Approximate co-ordinates of the iodine atoms of methylene diiodide were found from the Patterson diagrams. With isotropic temperature factors, these

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¹⁾ T. Kawaguchi, K. Takashina, T. Tanaka, and T. Watanabé, Acta Crystallogr., B28, 967 (1972).

²⁾ Y. Iwata, M. Oyama, T. Kawaguchi, and T. Watanabé, to be published.

³⁾ T. Kawaguchi, M. Hijikigawa, Y. Hayafuji, M. Ikeda, R. Fukushima, and Y. Tomiie, This Bulletin, 46, 53 (1973).
4) M. P. Marzocchi, V. Schettino, and S. Califano, J. Chem.

⁴⁾ M. P. Marzocchi, V. Schettino, and S. Califano, J. Chem. Phys., **45**, 1400 (1966); M. P. Marzocchi, P. Manzelli, V. Schettino, and S. Califano, *ibid.*, **49**, 5438 (1968); M. P. Marzocchi, and P. Maznelli, *ibid.*, **52**, 2630 (1970).

co-ordinates were refined by the least-squares method, based upon the centrosymmetric space group, C2/c. The reliability factor, $R=\sum ||F_o|-|F_c||/\sum |F_o|$, dropped from 0.25 to 0.16. The difference Fourier synthesis gave merely a hint of the position of the carbon atom. Further refinement was applied in order to determine the positions of the iodine atoms with anisotropic temperature factors, where the anomalous dispersion effect was considered. The R values were finally indicated to be 0.12.

Another refinement based upon the non-centrosymmetric space group, Cc, was made in parallel. However, this gave no significant improvement. It was, therefore, concluded that the crystal structure of methylene diiodide belongs to the space group $C_{2h}^6 - C_2/c$.

The crystal structure determination of methylene dibromide was started using the least-squares method by substituting the final co-ordinates of the iodine atoms of methylene diiodide for those of the bromine atoms. The R value was about 0.3 at the begining and decreased to 0.25 with isotropic temperature factors of bromine atoms, where the anomalous dispersion effect was also considered. The difference synthesis gave merely a diffuse indication of the position of the

carbon atom, much as for methylene diiodide. The least-squares refinement with anisotropic temperature factors for the bromine atoms reduced the R value to 0.21.

Results and Discussion

X-Ray Analysis. The observed and calculated structure factors are listed in Table 2, and the final sets of the positional and thermal parameters of the halogen atoms are summarized in Table 3. The two crystal structures are isomorphous, with the symmetry of C2/c. As has been mentioned in the previous section, Marzocchi et al. reported that the crystal of methylene diiodide has two forms, I and II, and that Form II is isomorphous with the crystal of methylene dibromide.⁴⁾ In view of our experimental procedure in obtaining the single crystal, the measurement for methylene diiodide must have been carried out on the stable form, II.

The interatomic distances for $X\cdots X$ in the molecules, where X denotes the halogen atom, are calculated to be 3.17 ± 0.02 Å for methylene dibromide and 3.56 ± 0.01 Å for methylene diiodide. These values are in excellent agreement with those given by electron dif-

Table 2. Observed and calculated structure factors

(a) Methylene dibromide

h 1	IF₀I	IF _C I	h I	$ F_{o} $	F _	h	ı	$ F_{O} $	F _C	h		P ₀ 1	$ F_C $
(k=0)	•	-	12 -8	92.93	103.26	3	2	131.98	118.75	1		1.96	28.13
0 6	104.02	54.83	14 -8	16.41	22.97	5	2	91.27	63.81	3		0.62	53.05
0 8	292.76	279.05	4 10	128.47	81.07	3	-2	147.06	125.42	7		1.69	43.63
0 10	86.21	52.23	8 10	40.19	54.43	5	-2	81.85	65.22	1		0.45	45.49
0 12	149.10	145.80	2 -10	12.00	13.87	11	-2	55.88	56.28			5.63	79.35
0 14	53.78	40.54	4 -10	138.24	162.66	1	3	157.78	123.90			3.66	62.54
0 16	53.45	60.70	6 -10	18.33	48.78	3	3	100.25	73.26	7		4.21	141.62
2 0	24.20	19.45	8 -10	211.12	211.74	7	3	50.73	49.28			5.79	72.96
4 0	248.16	275.51	10 -10	19.82	31.09	9	3	40.19	56.74			9.76	59.42
6 0	90.82	46.79	12 -10	104.76	75.26	11	3	72.53	66.40	1		4.15	94.35
8 0	55,01	50.02	14 -10	53.71	42.29	1	-3	192.13	218.52	3		2.95	90.50
10 0	44.86	22.00	2 12	21.47	1.76	3	-3	263.87	243.05	5 7		3.31	69.15 58.55
12 0	89.29	80.11	4 12	15.11	76.62	5	-3	190.73 143.75	172.56 171.05			3.82	45.96
14 0	8.82	7.31	6 12	13.20	9.34	7	-3 -3	49.16	51.00			6.79	32.35
2 2	14.40	12.80	4 -12	180.37	100.28	9	-3	47,25	46.58			3.72	48.69
6 2	34.45	32.33	6 -12 8 -12	50.37 49.88	21.35 14.90	11	-3 4	73.57	85.71			2.40	72.11
8 2 10 2	206.58	202.21 34.92	10 -12	49.43	2.21	5	4	45.59	62.33			9.15	81.62
10 2 12 2	29.26	84.21	12 -12	84.53	82.18	7	14	90.57	89.26		-9 12	8.14	103.12
2 -2	35.71	2.40	14 -12	12.55	25.26	9	4	48.64	39.06			8.74	84.20
10 -2	32.82	40.72	4 14	50.05	41.76	11	4	48.47	52.19		10 5	9.10	53.56
12 -2	63.60	101.77	2 -14	22.19	13.97	1	-4	35.22	41.29			3.36	29.76
14 -2	39.44	29.89	4 -14	53.00	89.10	3	-4	102.16	109.75	1 -		9.50	87.22
2 4	25.69	12.72	6 -14	13.72	35.05	5	-4	92.75	82.09			1.69	62.61
4 4	166.13	217,93	8 -14	124.97	135.52	7	-4	205.90	158.41			5.33	32.00
6 4	58.42	33,39	10 -14	15.24	18.71	9	-4	78.89	77.79	11 -		9.74	52.69
8 4	59.91	51.27	12 -14	90.17	43.20	11	-4	66.16	70.96			9.33	55.31
10 4	31.01	19.80	14 -14	29.26	36.15	1	5 5	159.09	160.63 157.74	3 1 -		1.49 7.63	32.65 90.54
12 4	49.43	52.41	4 -16	101.16	50.26	3 5	5 5	144.18 109.23	116.83	3 -		0.38	117.35
2 -4	25.95 302.52	8.23 256.37	8 -16 10 -16	44.08 33.38	21.72 5.70	7	5	109.49	103.90	5 -		2.09	86.16
4 –4 6 –4	98.02	49.25	12 -16	29.26	49.76	9	5	53.44	37.94	7 -		9.15	106.86
8 -4	16.90	30.70	4 -18	12.07	37.69	11	5	28.94	27.26	i		2.89	27.55
10 -4	58.80	18.66	8 -18	35.68	72.35	1	-5	75.40	86,86	1 -		3.70	37.72
12 -4	111.64	101.59				3	-5	42.80	58,35	3 -	12 6	3.48	45.62
14 -4	15.57	16.20	(k=1)			5	- 5	72.61	54.01	5 -		0.91	36.11
4 6	219.55	145.95	3 0	94.41	114.95	7	- 5	12.90	82.02	7 -		5.84	101.15
6 6	18.03	13.61	5 0	84.90	81.82	9	- 5	100.68	92.11	9 -		3.15	54.41
8 6	108.92	121.21	7 0	137.99	135.98	1	6	143.40	149.00	11 -		3.03	38.08
10 6	20.01	27.10	9 0	78.02	63.87	3	6	100.25	87.83			7.98	47.02
6 -6	22.77	57.72	11 0	79.94	67.03	5	6 -6	71.57 121.43	48.61 157.52	5 - 7 -		3.59 5.95	34.58 50.07
8 -6	258.73	267.55	3 1 5 1	209.39	227.79 161.00	1 3	-6	87.43	98.52	9 -		3.03	57.64
10 -6 12 -6	26.69 100.87	39.83 98.88	7 1	148.89 161.09	149.83	5	-6	43.15	51.26	11 -		3.39	76.62
12 -6 14 -6	54.04	40.09	9 1	63.98	49.88	11	-6	79.24	61.43	11 -		0.80	34.15
2 8	24.94	5.72	11 1	45.77	39.73	i	7	125.70	90.34	3 -		3.26	61.80
6 8	32.95	19.74	3 -1	74.97	78.61	3	7	80.98	53.78	5 -		.23	44.23
8 8	43.33	39.22	5 -1	53.44	43.61	ì	-7	144.79	152.95	7 -	15 43	3.50	60.81
10 8	11.45	14.81	7 -1	84.03	72.31	3	-7	179.22	187.13			.68	18.35
6 -8	76.03	36.92	9 -1	79.24	81.20	5	-7	125.18	137.43	5 -		.68	14.24
8 -8	29.84	3.57	11 -1	108.53	95.85	7	-7	141.30	152.33	7 -		1.12	60.63
10 -8	54.26	10.89	1 2	191.34	221.56	11	-7	66.60	43.18	7 -	17 43	3.50	28.52
			1			l				l			

(b) Methylene diiodide

C ≥ 0 4 2 316.36 302.45 5 6 4 22.78 217.76 1 5 6 14 9 24.78 317.76 1 5 6 14 9 217.83 117.76 1 5 6 14 14 14 15 14 4 822.69 94 14 12 17 37 14 18 14 14 14 14 14 14 12 13 13 16 10 13 13 16 14 14 12 13 14 12 13 14 14 12 13 14 14 12 13 14	h	z	$ F_0 $	[F _C]	h	ı	F ₀	Fc	h	ı	1F _O I	F _C	h	k	Fo	$ F_{\rm C} $	h	ı	IF₀ ^I	IF _C I
*** \$\frac{1}{2}\$ \$\frac{1}{3} \$\frac{1}{3} \$\frac{1}{2}\$ \$\frac{1}{3} \$\frac{1}{4}\$ \$\frac{1}{4}\$ \$\frac{1}{3} \$\frac{1}{2}\$ \$\frac{1}{4}\$ \$\	/ ½=0	1			_6	ы	146.97	124.40	(k=	1)			-5	6	134.81	96.58	-11	13	227.85	219.97
4 4 432,68 461,28 6 8 145,33 106,70 1 9 174,37 149,30 -5 8 112,68 82,38 -11 15 144,99 114,99 177,57 133,15 177,57 173,70 173,70 170,75 173,70 185,67 -5 10 70,73 173,70	4-0	ź	316.36	302.45							261.40	244.85	-5	7	243.68	205.24	-11	15		
4 6 204, 31 11, 64 6 10 171, 36 65, 99 1 170, 57 158, 71 -5 10 62, 98 62, 19 -11 177, 59 4 10 107, 43 91, 40 6 14 124, 12 132, 19 1 12 83, 86 58, 11 -5 11 81, 19 137, 59 4 16 110, 07 130, 40 -8 2 407, 97 429, 51 1 11 18, 28, 97 65, 15 -5 12 81, 85 56, 73 -1 81, 20 70, 70 70										9	174,37	149.30	-5	8	112.66	82.36	-11			
10	4	6	204.31	181.64	-6	10	171.36	163.46		10		158.71	-5	9	62.98					
12 213.87 218.07 218.07 26 18 71.18 39.74 1 13 88.29 76.51 -5 12 81.65 56.73 -15 2 71.20 71.83 16 110.07 130.44 -8 2 407.97 429.61 1 14 82.60 94.67 -7 0 220.69 218.38 -15 6 80.38 96.69 6 0 138.41 98.57 -8 4 179.93 153.27 1 15 104.43 107.61 -5 15 83.86 81.17 -15 5 151.27 184.58 6 2 158.51 118.28 -8 4 41.79.93 153.27 1 15 104.43 107.61 -5 15 83.86 81.17 -15 5 151.27 184.58 6 2 158.51 118.29 -8 4 41.79.93 153.27 1 15 104.43 107.61 -5 10 0.00 83.48 -15 6 86.71 94.21 6 6 117.65 89.74 -8 8 181.96 82.31 3 9 207.60 178.02 -7 2 121.84 124.60 -15 9 144.75 197.73 8 0 220.79 192.55 -8 14 289.34 287.98 3 11 104.12 83.22 -7 3 367.41 364.57 -15 10 121.21 108.110 8 2 352.94 331.41 -8 18 147.63 163.84 31 2 57.28 43.65 -7 4 260.45 259.78 -15 10 121.21 108.110 8 4 205.96 186.46 -10 2 193.77 179.15 3 13 101.59 166.33 -7 5 160.13 124.07 -15 13 136.65 106.68 8 8 110.95 153.65 -10 10 221.48 198.93 5 9 444.10 168.33 -7 5 160.13 124.07 -15 13 136.65 106.68 106.84 -7 10 10 10 10 10 10 10 1	4	8	369.74	332.05	-6	12	95,90	65.99	1	11	177.22	155.62	-5	10	74.69					
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1	4 :	12	213.87	218.07	-6	18	71.18	93.74	1	13			-5	12						
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Table 3. Positional and thermal parameters, with their e.s.d.'s in parentheses *The anisotropic thermal parameters for the halogen atoms are the form; $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{31}lh)].$

Parameter	Methylene	dibromide	Methylene diiodide					
rarameter	Br (1)	Br (2)	I(1)	I (2)				
X	0.0920 (7)	0.3499 (7)	0.0945 (4)	0.3591 (4)				
Y	0.6639 (53)	0.6330 (54)	0.6650(35)	0.6398 (32)				
\boldsymbol{Z}	0.1279 (7)	0.1270 (7)	0.1309 (4)	0.1276 (4)				
eta_{11}	0.0047 (6)	0.0050 (7)	0.0046~(3)	0.0022 (2)				
$oldsymbol{eta_{22}}$	-0.1232(377)	-0.1070(391)	0.0190(235)	0.0550 (221)				
$oldsymbol{eta_{33}}$	0.0050(5)	0.0055(6)	0.0040(3)	0.0025 (2)				
$oldsymbol{eta_{12}}$	-0.0009(68)	-0.0075(75)	-0.0018(42)	0.0020 (38)				
$oldsymbol{eta_{23}}$	-0.0044(60)	-0.0051 (64)	-0.0039(36)	0.0001 (34)				
eta_{31}	0.0053 (10)	0.0050 (10)	0.0066(5)	0.0015 (4)				

fraction studies for the gaseous state—3.16₄⁵⁾ and 3.57₀ Å⁶⁾ (see Table 4). It may, therefore, be permissible to assume a rigid molecule in these crystals. Schematic drawings of the crystal structures of methylene dibromide and methylene diiodide are given in Figs. 1 and 2. Figure 1 is the projection of the structure on the (010) plane, and Fig. 2, the bounded projection on the (001) plane of the molecules lying in $Z\approx\pm0.13$. In these figures, the orientations of the

methylene groups shown are those derived by the following lattice-energy calculations.

Lattice-energy Calculations. Though the carbon atoms of the two crystals were not located accurately on the basis of the X-ray intensity data, the most probable positions of these atoms could be derived by the following two methods. The first was to find the most plausible orientation of the methylene groups among their neighboring molecules. When the positions of the halogen atoms in the unit cell are accurately known, intermolecular atomic contacts can be obtained for various orientations by subjecting a rotation, θ , around the axis connecting the two halogen atoms,

⁵⁾ H. A. Levy and L. O. Brockway, J. Amer. Chem. Soc., 59, 1662 (1937).

⁶⁾ O. Bastiansen, Tidsskr. Kjemi Bergv., 6, 1 (1946).

Table 4. Positional parameters of the carbon and hydrogen atoms for the most probable orientation, $\theta = 190^{\circ}$.

The molecular structures used are also listed.

	Methyl	ene dibro	mide	Methylene diiodide					
	$\widehat{\mathbf{c}}$	H(1)	H(2)	$\hat{\mathbf{c}}$	H(1)	$\mathbf{H}(2)$			
X	0.2105	0.2347	0.1740	0.2164	0.2405	0.1810			
\boldsymbol{Y}	0.4129	0.2398	0.3143	0.4124	0.2490	0.3190			
\boldsymbol{z}	0.1120	0.1651	0.0420	0.1148	0.1642	0.0498			
	Br-C	1.9	91 Å ⁵⁾	I-C	2.12				
	H-C	1.0)7 Å ^{a)}	H-C	1.07	/ Å ^{a)}			
	∠BrCBr	112	2°5)	\angle ICI	114.	7°6)			
	\angle HCH	109	9.5°a)	\angle HCH	109.	5°a)			
	(BrBr	3.	16 ₄ Å) ^{b)}	(II)	3.57	′₀Å) ^{b)}			

- a) Assumed.
- b) Calculated by the present authors.

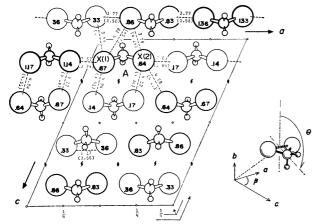


Fig. 1. Schematic drawing of the crystal structure of methylene dibromide and methylene diiodide, projected along the b axis. Numbers within circles indicate fractional co-ordinates, Y, of the iodine atoms. Interatomic distances for methylene bromide and those for methylene iodide (in parentheses) are also given.

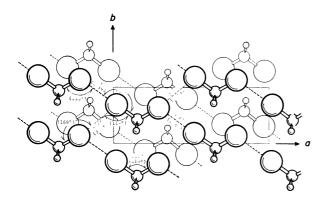
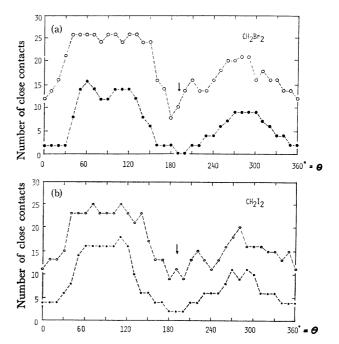


Fig. 2. Bounded projection of the crystal structure on the (001) plane. Molecules lying in $Z\simeq 0.13$ are drawn with thick lines and those lying in $Z\simeq -0.13$ with thin lines. Interatomic distances and angles for methylene dibromide and those for methylene diiodide (in parentheses) are also given.

 $X(1)\cdots X(2)$, of a reference molecule, **A** (see Fig. 1), accompanied by the rotations of other molecules around their similar axes in accordance with the symmetry of the space group C2/c. The starting point of θ is taken as the orientation where the X-C-X plane of the **A**



(a) for methylene dibromide and (b) for methylene diiodide.

molecule is parallel to the b axis. Figure 3 shows the variations with θ of a number of contacts. (a) indicates methylene dibromide, and (b), methylene diiodide. Both of them indicates that the most plausible orientation located in the vicinity of $\theta \approx 190^{\circ}$.

The most reasonable orientation of the methylene group can also be found quantitatively by obtaining the potential energy minimum of the crystal, which can be calculated from the molecular interactions. Here, it is assumed that the potential energy can be described by the dispersion, the exchange repulsive, the dipole-dipole coupling, and the induced dipole interactions. Calculations were carried out by using Eq. (2) and the constants of A_{ij} , B_{ij} , and C_{ij} , which have been given in a previous paper,¹⁾ together with the following constants:

Molecule	Dipole moment (debye)	Molecular polarizability (10 ⁻²⁴ cm³)
$\mathrm{CH_{2}Br_{2}}$	1.39	8.30
$\mathrm{CH_2I_2}$	1.10	11.84

The rotating scheme about the methylene group is the same as that described above.

In Fig. 4, (a) and (b) show the variations in the interaction energies for methylene dibromide and for methylene diiodide respectively. One can find results similar to those indicated in Fig. 3; the most probable orientation of the methylene group was found in the vicinity of $\theta \approx 190^\circ$ for both the crystals. In Table 4 the positional parameters of the carbon and hydrogen atoms corresponding to the $\theta = 190^\circ$ orientation are given. As has been mentioned ealier, the X-ray intensity data were not sufficient to be used in the refinement

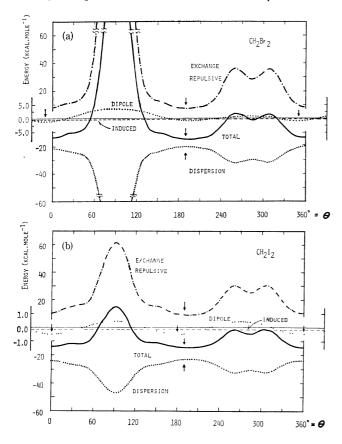


Fig. 4. Variations of the interaction energies with rotation θ . (a) for methylene dibromide, and (b) for methylene diiodide.

of the structures. In these orientations, the lattice energies arising from the four kinds of interaction amount to 14.4 for methylene dibromide and to 14.3 kcal/mol for methylene diiodide. The lattice energy of methylene diiodide can be compared with the sum of the experimental heats of vaporization, 10.2, and of fusion, 3.00 kcal/mol, for the stable form, II.7 Most of the energies calculated came from the dispersion and the exchange repulsive interactions (see

Table 5. Calculated lattice energies for the most probable orientation, θ =190°, of the methylene group (in kcal/mol)

Compound	Dispersion	Exchange repulsive	Dipole dipole	Induced dipole	Total
$\mathrm{CH_2Br_2}$	-20.57	7.24	-0.82	-0.26	-14.41
CH_2I_2	-23.06	9.35	-0.40	-0.15	-14.26

Table 5). As is shown in Fig. 4, the orientation of the methylene group is dominated by the repulsive term.

The crystal structure can be described as a sort of a layer structure parallel to the (001) plane. The X-C-X planes of all the molecules lie nearly on the layer planes. As can be seen in Fig. 1, the orientations of the molecular axes or the dipoles in the two immediate layers are almost parallel and almost antiparallel respectively.

Within the layer, the molecules are held together by noticeable short contacts. The interatomic distances between halogen atoms are 3.63 and 3.77 Å for Br...Br, and 3.84 and 3.98 Å for I...I; these are far less than twice the van der Waals radii, 3.90 for bromine and 4.30 Å for iodine. The two kinds of angles, C-X···X, between the neighboring molecules are not far from 90° (or the tetrahedral angle, 109.5°) and 180°. The quite close contacts and the characteristic geometries presented above with regard to the halogen atoms can be seen in other crystals, for example, solid bromine and iodine,8) methyl bromide and methyl iodide,3) and bromoform1) and iodoform.2) The partial intermolecular bonding effect between the bromine and, particularly, iodine atoms, which was suggested by Tomiie,9) may contribute appreciably to the molecular arrangements of simple molecules with bromine or iodine atoms.

The authors wish to express their thankfulness to Dr. Akio Furusaki and Dr. Akio Takenaka for their help in these analyses.

^{7) &}quot;Amercican Institute of Physics Handbook," McGraw-Hill Book Comp. Inc. (1957).

⁸⁾ L. W. G. Wyckoff, "Crystal Structures," Vol. 1, New York, London, Sydney: Wiley-Interscience (1964), p. 52.

⁹⁾ Y. Tomiie, Kwansei Gakuin Univ. Ann. Studies, 10, 208 (1961).