62 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 62—66 (1973) [Vol. 46, No. 1

The Crystal Structure of Methylene Dichloride, CH_2Cl_2

Takemi Kawaguchi,[*] Kazuo Tanaka, Toru Takeuchi, and Tokunosuké Watanabé
Faculty of Science, Kwansei Gakuin University, Nishinomiya

(Received May 6, 1972)

The crystal structure of methylene dichloride has been determined by the X-ray diffraction method at about −120°C. The structure has a symmetry $D_{2h}^{14}-Pbcn$, and its orthorhombic tetramolecular cell has these dimensions: $a=4.249\pm0.001$, $b=8.138\pm0.020$, and $c=9.492\pm0.002$ Å. The positional parameters of the chlorine and carbon atoms are obtained by a three-dimensional Patterson function, followed by a least-squares refinement including the hydrogen atom. The structure thus obtained is in excellent agreement with the results of lattice-energy calculations. The crystal structure is quite different from that of methylene dibromide (and of methylene diiodide).

The crystal structures of various halogenated methanes have been reported on in previous papers in order to elucidate the molecular interactions in these molecular crystals. It has been shown that, in the crystals of mono- and tri-halogenated methanes, CH_3X and CHX_3, those of bromine- and iodine-substituted methanes are isomorphous, while those of chlorine-substituted methanes are quite different.[1–3]

Marzocchi *et al.* reported, based upon their spectroscopic measurements, that the crystals of methylene dibromide and the stable form of methylene diiodide, Form II, are isomorphous, but not with that of methylene dichloride.[4,5] In the preceding paper, it has been shown that the crystals of methylene dibromide and methylene diiodide (II) are isomorphous, with a symmetry $C_{2h}^{6}-C2/c$.[6]

In this paper the crystal structure of methylene dichloride, as determined by the X-ray diffraction method, will be reported. It will also be shown that the structure is in good agreement with that derived by means of lattice-energy calculations.

Experimental

Methylene dichloride from Wako Pure Chemical Industries, Ltd., was sealed in thin-wall glass capillaries (0.3 mm in internal diameter and 0.01 mm in wall thickness). A single crystal was carefully produced in the way described in previous papers.[1,3] The crystal used grew with the [010] zone axis of an orthorhombic lattice nearly along the capillary, and was then gradually cooled to about −120°C.

The unit-cell dimensions were determined from oscillation and Weissenberg photographs around the [010] axis taken by using Cu*Kα* radiation. The intensity distributions and systematic extinctions (none for *hkl*, *0kl* with *k* odd, *hk0* with $h+k$ odd and *h0l* with *l* odd) indicated that the crystal belongs to the orthorhombic system, with a symmetry of space group $D_{2h}^{14}-Pbcn$. There are four molecules per cell and the X-ray density amounts to 1.718 g/cm³, where the observed densities, 1.327 at 20° and 1.761 g/cm³ at −194°C,[7] are referred to. The crystal data are summarized in Table 1.

Table 1. Crystal data

Compound	methylene dichloride, CH_2Cl_2
MW	84.83
Bp	39.95°C
Mp	−96.8°C
Exp. temp.	−120°C
Orthorhombic; $D_{2h}^{14}-Pbcn$	
Z	$= 4$
a	$=4.249\pm0.001$ Å
b	$=8.138\pm0.020$
c	$=9.492\pm0.002$
V	$=328.21$ Å³
D_x	$=1.718$ g/cm³
D_m	$=1.327$ (at 20°C) 1.761 (at −194°C)
μ	$=153.2$ cm⁻¹ (for Cu*Kα* radiation)

Integrated intensities of reflections, taken from six layers between the zeroth and the fifth layers around the [010] axis, were collected by means of the multiple-film method and the equi-inclination Weissenberg technique. The X-rays used were Ni-filtered Cu*Kα* radiations. The intensities were measured visually and were corrected for Lorentz-polarization and absorption effects by cylindrical approximation, followed by bringing them into a common scale by considering with different time exposures. Inorder to determine the structure, 226 independent reflections were used.

Structure Determination

Since the crystal has the symmetry *Pbcn*, each molecule should be located on the C_2 site in the tetramolecular cell. Approximate co-ordinates of the chlorine and carbon atoms were immediately found with the aid of the three-dimensional Patterson function. A least-squares refinement was made for these co-ordinates with isotropic temperature factors. The reliability factors, $R=\sum||F_o|-|F_c||/\sum|F_o|$, decreased from 0.25 to 0.17.

Further refinement was made for the relative scales of the intensities from the six different layers, followed

---

[*] To whom all correspondence should be addressed. Present address: Department of Research and Development, Nippon Crucible Co., Ltd., 925 Inada, Higashi-Osaka, 577.

[1] T. Kawaguchi, K. Takashina, T. Tanaka, and T. Watanabé, *Acta Crystallogr. B* **28**, 967 (1972).

[2] Y. Iwata, M. Oyama, T. Kawaguchi, 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. Phys.*, **45**, 1400 (1966); M. P. Marzocchi, P. Manzelli, V. Schettino, and S. Califano, *ibid.*, **49**, 5438 (1968).

[5] M. P. Marzocchi and P. Manzelli, *ibid.*, **52**, 2630 (1970).

[6] T. Kawaguchi, A. Wakabayashi, M. Matsumoto, T. Takeuchi, and T. Watanabé, This Bulletin, **46**, 57 (1973).

[7] W. Blitz and A. Sapper, *Z. Anorg. Allgem. Chem.*, **203**, 277 (1932).

Table 2. Observed and calculated structure factors

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	2	31.47	33.97	4	1	3	23.07	25.60
0	0	4	129.18	144.96	4	1	5	25.10	29.29
0	0	6	53.53	42.37	4	1	6	18.71	22.82
0	0	8	104.17	100.29	4	1	7	14.19	15.19
0	0	10	19.86	16.48	4	1	8	4.48	6.45
1	0	2	164.40	181.95	5	1	0	12.61	21.20
1	0	4	33.91	26.19	5	1	1	9.25	14.66
1	0	6	116.63	105.66	5	1	3	13.11	15.25
1	0	8	29.04	21.93	5	1	4	8.76	9.77
1	0	10	57.10	54.87	5	1	5	2.24	7.95
1	0	12	16.39	19.62	0	2	2	33.91	38.79
2	0	0	90.15	81.60	0	2	3	113.46	125.83
2	0	2	33.83	26.12	0	2	4	80.29	75.74
2	0	4	98.42	89.10	0	2	5	74.85	65.68
2	0	6	8.74	7.79	0	2	6	10.11	10.27
2	0	8	41.96	36.52	0	2	7	86.64	87.04
2	0	10	24.47	25.07	0	2	8	24.76	20.61
3	0	2	34.26	28.01	0	2	9	37.84	35.30
3	0	4	9.71	9.45	0	2	10	10.36	9.90
3	0	6	22.86	18.42	0	2	11	43.94	47.29
3	0	8	16.09	14.22	1	2	1	104.33	121.45
3	0	10	11.09	10.61	1	2	2	58.39	55.05
4	0	4	13.28	10.72	1	2	3	88.39	86.06
4	0	6	12.78	12.39	1	2	5	92.80	87.08
5	0	2	14.56	13.85	1	2	6	32.62	29.00
1	1	0	83.86	86.84	1	2	7	46.32	38.94
1	1	1	56.20	54.98	1	2	8	8.24	5.24
1	1	2	34.42	31.16	1	2	9	54.00	57.49
1	1	3	43.11	38.90	1	2	10	16.62	19.51
1	1	4	13.35	10.84	1	2	11	16.08	15.70
1	1	5	29.42	25.37	2	2	0	39.19	38.74
1	1	6	17.97	17.22	2	2	1	56.33	48.42
1	1	7	29.42	28.00	2	2	2	17.89	12.44
1	1	8	28.58	28.38	2	2	3	72.19	67.59
1	1	9	16.77	17.06	2	2	4	5.18	7.45
1	1	11	12.07	14.21	2	2	5	41.75	36.17
1	1	12	3.70	5.11	2	2	6	15.59	12.90
2	1	1	64.45	61.44	2	2	7	45.88	42.86
2	1	2	56.96	50.94	2	2	8	20.91	20.09
2	1	3	57.67	50.18	2	2	9	11.91	9.87
2	1	4	8.52	7.15	2	2	10	3.18	2.78
2	1	5	54.89	46.88	2	2	11	21.24	31.12
2	1	6	41.48	38.24	3	2	1	24.00	21.98
2	1	7	30.72	29.68	3	2	2	9.11	1.57
2	1	8	6.05	3.82	3	2	3	13.80	13.25
2	1	9	28.16	31.31	3	2	5	25.53	22.23
2	1	10	18.86	20.25	3	2	9	17.09	17.48
2	1	11	13.17	15.60	4	2	0	16.42	13.96
3	1	0	42.86	37.10	4	2	2	5.90	6.80
3	1	1	51.38	43.67	4	2	4	4.35	1.08
3	1	2	12.94	11.82	4	2	5	7.45	7.81
3	1	3	53.30	49.74	4	2	6	3.41	3.87
3	1	4	54.41	48.20	4	2	7	2.70	4.62
3	1	5	36.44	35.26	4	2	8	5.53	9.18
3	1	7	32.68	35.72	4	2	1	4.82	7.69
3	1	8	18.27	20.29	5	2	2	5.88	8.12
3	1	9	14.51	17.98	5	2	3	6.55	8.95
3	1	10	7.47	11.52	1	3	0	42.57	42.50
4	1	1	28.35	31.42	1	3	1	19.04	17.75
4	1	2	26.26	29.67	1	3	2	25.72	21.88

Table 2. (Cont.)

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
1	3	4	67.60	64.06	1	4	8	21.40	20.35
1	3	5	5.07	4.41	1	4	9	26.71	19.14
1	3	6	8.24	6.72	1	4	10	31.59	35.82
1	3	7	12.64	11.49	1	4	11	10.23	14.04
1	3	8	26.50	23.31	2	4	0	72.81	68.71
1	3	9	4.38	5.45	2	4	1	40.13	35.44
1	3	10	9.22	9.35	2	4	3	16.08	16.30
2	3	1	18.01	11.81	2	4	4	46.83	42.17
2	3	2	84.06	81.32	2	4	5	9.90	9.17
2	3	3	12.76	8.54	2	4	6	22.15	20.81
2	3	4	5.77	3.57	2	4	7	24.12	26.27
2	3	5	14.72	10.08	2	4	8	35.80	36.86
2	3	6	62.02	56.15	2	4	9	10.39	13.05
2	3	8	9.98	8.47	2	4	10	9.94	10.32
2	3	9	9.73	7.87	3	4	1	8.61	3.72
2	3	10	34.35	36.30	3	4	2	28.73	25.05
3	3	0	82.81	78.82	3	4	4	9.25	7.65
3	3	1	6.93	3.64	3	4	6	20.51	18.59
3	3	2	7.85	3.75	3	4	7	4.60	0.15
3	3	3	21.31	18.29	3	4	8	8.91	9.39
3	3	4	57.64	55.47	3	4	9	2.07	3.81
3	3	5	13.62	11.26	4	4	1	15.81	12.78
3	3	6	16.01	14.25	4	4	2	5.20	6.45
3	3	7	10.20	6.68	4	4	3	4.01	2.23
3	3	8	40.75	48.11	4	4	4	6.48	7.59
4	3	1	12.08	10.34	4	4	5	5.49	4.05
4	3	2	41.79	45.25	4	4	7	3.79	7.50
4	3	3	10.82	8.25	5	4	1	4.86	9.12
4	3	4	7.36	5.93	5	4	2	1.58	4.65
4	3	5	11.18	9.15	1	5	0	23.44	20.47
4	3	6	30.18	35.54	1	5	1	21.61	18.93
4	3	7	4.33	3.19	1	5	2	10.06	9.39
5	3	0	11.74	18.78	1	5	3	42.97	39.80
5	3	1	7.16	8.54	1	5	5	34.14	30.25
5	3	2	3.23	6.27	1	5	7	17.08	15.49
5	3	3	3.33	5.12	1	5	8	12.87	11.18
0	4	2	24.60	26.76	1	5	9	7.43	6.89
0	4	3	66.74	71.11	1	5	10	5.02	5.01
0	4	4	96.80	102.74	2	5	1	49.24	45.48
0	4	5	54.53	52.00	2	5	2	16.48	13.31
0	4	6	14.34	11.47	2	5	3	41.23	38.04
0	4	7	36.20	35.76	2	5	5	43.44	41.01
0	4	8	48.96	48.68	2	5	6	13.29	11.61
0	4	9	17.88	19.20	2	5	7	26.16	25.23
0	4	10	22.90	24.49	2	5	9	30.75	29.06
0	4	11	24.99	30.78	3	5	1	49.48	48.51
1	4	1	46.35	53.07	3	5	3	32.36	34.97
1	4	2	90.61	92.76	3	5	4	11.82	12.44
1	4	3	44.20	42.41	3	5	5	24.91	23.40
1	4	4	16.50	13.59	3	5	7	33.61	39.38
1	4	5	47.04	44.30	4	5	1	23.50	29.58
1	4	6	61.84	60.97	4	5	3	20.47	23.33
1	4	7	27.74	27.61	4	5	5	25.42	29.38

by the least-squares refinement, where the anomalous dispersion effect was taken into consideration for the chlorine atom. The difference Fourier synthesis indicated the probable coordinates of the hydrogen atoms. Successive refinement with anisotropic temperature factors for the chlorine and carbon atoms and with an isotropic temperature factor for hydrogen atom finally decreased the R value to 0.109.

Results

The observed and calculated structure factors are

TABLE 3. POSITIONAL AND THERMAL PARAMETERS WITH THEIR e.s.d.'s (IN PARENTHESES)

* The temperature factors are of the form $\exp[-B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)]$ for the chlorine and carbon atoms, and of the form $\exp[-B(\sin\theta/\lambda)^2]$ for the hydrogen atom.

Parameter	Cl	C	H
X	0.1846 (8)	0 (—)	0.1747 (266)
Y	0.1522 (6)	0.0307 (28)	−0.0369 (199)
Z	0.1195 (3)	1/4 (—)	0.2859 (109)
B_{11}	0.0529 (19)	0.0384 (97)	0.2 (27)
B_{22}	0.0095 (10)	0.0060 (50)	...
B_{33}	0.0053 (3)	0.0053 (15)	...
B_{12}	−0.0164 (21)	0 (—)	...
B_{23}	0.0034 (8)	0 (—)	...
B_{31}	−0.0077 (12)	0.0065 (65)	...

listed in Table 2, while the final set of the positional and thermal parameters of the atoms is summarized in Table 3. It is found that the bond distances and angles of the molecule calculated by using these coordinates are much closer to those of the gas molecule obtained by a microwave study.[8] A comparison between the two is shown in Table 4.

TABLE 4. COMPARISON OF THE MOLECULAR STRUCTURES

	Microwave study[8]	Present work
C–H	1.068 ±0.005 Å	0.99 ±0.13 Å
C–Cl	1.7724±0.0005	1.768±0.013
Cl...Cl	2.935[a]	2.932±0.004
∠Cl–C–Cl	112.0±0.3°	112±1°
∠H–C–H	118.8 (C–H=C–D, ass.)	112±7

a) calculated by the authors.

The crystal structure is illustrated in Figs. 1 and 2. Figure 1 shows the projection along the b axis, and Fig. 2, the projection along the a axis. In these figures, several interatomic distances between neighboring molecules are also shown. Here, the e.s.d.'s are about 0.005 for Cl···Cl and 0.1 Å for Cl···H. The intermolecular atomic distances were found to be close to the sums of the van der Waals radii.

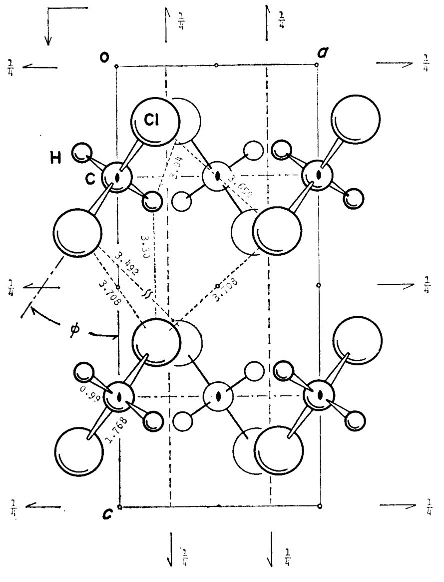

Fig. 1. Projection of the crystal structure along the b axis.

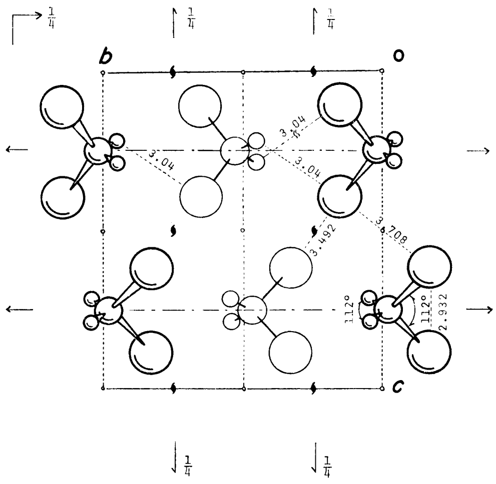

Fig. 2. Projection of the crystal structure along the a axis.

Lattice-energy Calculations

In this section, it will be described how the same conclusion was obtained by means of lattice-energy calculations, given the unit-cell dimensions and the symmetry of the crystal.

If the molecular structure of methylene dichloride and the symmetry and dimensions of the crystal are

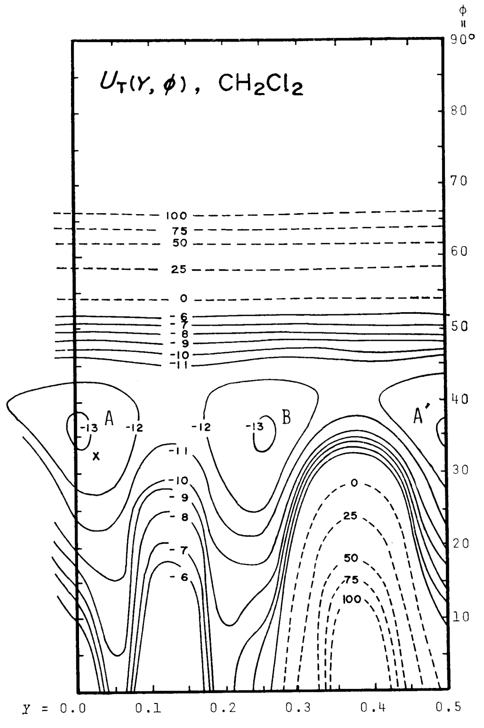

Fig. 3. Potential map, $U(Y,\phi)$. Contours with solid lines are at 1 kcal/mol intervals and contours with dashed lines show positive energy region, being at 25 kcal/mol intervals. Sign **X** indicates the crystal structure determined by the X-ray analysis.

---

[8] R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952).

TABLE 5. CALCULATED LATTICE ENERGIES FOR METHYLENE DICHLORIDE AND ITS RELATED COMPOUNDS, IN kcal/mol.

Compound	Note	Total	Dispersion	Exchange repulsion	Dipole-coupling	Induction
CH_2Cl_2	**A**[a]	−13.07	−13.35	3.08	−2.51	−0.29
	B[a]	−13.03	−13.23	2.95	−2.47	−0.29
	X-ray	−12.74	−13.22	3.04	−2.27	−0.29
CH_2Br_2	*C2/c*	−14.41	−20.57	7.24	−0.82	−0.26
CH_2I_2	*C2/c*	−14.26	−23.06	9.35	−0.40	−0.15

a) **A** and **B** denote the structures obtained by the lattice energy calculations.

given, one can describe the crystal structure, by using two structural parameters, Y and ϕ, where Y is the co-ordinate of the carbon atom, and ϕ, the angle of tilt of the reference molecule located on the two-fold axis, as is shown in Fig. 1. Lattice-energy calculations were made by using four kinds of molecular interactions; the dispersion, the exchange repulsion, the dipole-dipole coupling, and the induction effects, using the constants cited in the previous paper,[1] together with a dipole moment of 1.62 Debye and a molecular polarizability of 6.48×10^{-24} cm^3. Calculations of the dipole-dipole interaction were carried out for every pair of molecules within a range of 40 Å, while those of the other three interactions were carried out for every pair of atoms within a range of 20 Å. The dipole-dipole interactions between eight nearest neighboring molecules were substituted for interactions between the divided bond moments (referred to 2.3 for $C^{(+)}-Cl^{(-)}$ bond and 0.4 debye for $C^{(+)}-H^{(-)}$ bond[9]).

A potential map, $U(Y,\phi)$, was obtained; it is given in Fig. 3. Contours with solid lines are located at 1 kcal/mol intervals, while contours with dashed lines show the positive energy region, being at 25 kcal/mol intervals. Two stable structures were found as deep ravines, **A** and **B**, in the map, (Ravine **A**′ is crystallographically equivalent to **A**): $U_A(Y=0.0,\ \phi=35°)=-13.08$ and $U_B(Y=0.25,\ \phi=35°)=-13.03$ kcal/mol. The present X-ray analysis gives a structure which is very close to Structure **A**, corresponding to $Y=0.030_7\pm0.003$ and $\phi=32.3\pm0.1°$, as is indicated by **X** in the map.

The lattice energy for the structure obtained by the X-ray analysis, together with those for Structures **A** and **B**, are given in Table 5. In this table, the lattice energies calculated for the crystals of methylene dibromide and methylene diiodide are also summarized for the sake of comparison.

Discussion

On the basis of an infrared spectroscopic study,[5] Marzocchi and Manzelli reported that all the observed data on methylene dichloride are consistent with an orthorhombic *Pbcn* unit cell, in which four molecules are located on C_2 sites and tilt their symmetrical planes at 29±2° from one of the crystal axes. These spectroscopic conclusions, except for the mutual molecular arrangement, are in excellent agreement with those of the present work.

The potential map, $U(Y,\phi)$ in Fig. 3, suggests another probable crystal structure corresponding to the ravine, **B**. This structure can be derived from Structure **A** by a translation (0.25) of Y, while keeping ϕ constant. This structure can also be looked upon as being derived by orienting every molecule inversely along the b axis. It might be possible to obtain crystals with this structure by means of different procedures of crystallization.

The crystal structures of methylene dibromide and methylene diiodide, which are isomorphous with the symmetry *C2/c*, are quite different from that of methylene dichloride. The lattice energies calculated for the two crystals are added in Table 5. It is noticeable that the contribution of the dipole-dipole interactions in the crystal of methylene dichloride is much larger than those in the crystals of methylene dibromide and methylene diiodide. This suggests that the dipole-dipole interactions play an important role upon solidification, leading to a different crystal structure from those of methylene dibromide and methylene diiodide.

The authors are indebted to the Kwansei Gakuin University Computing Center for calculations.

---

9) R. Daudel, R. Lefebver, and C. Moser, "Quantum Chemistry, Methods and Applications," Interscience Publishers, Inc., New York (1959), p. 206.