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The Crystal Structure of Methyl Chloride at −125°[1]

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The crystal structure of methyl chloride has been investigated by X-ray diffraction at −125°. The arrangement of the molecules is equivalent to that in the chlorine structure if the methyl groups are replaced by chlorine atoms. The chlorine–carbon bond distance is 1.805 Å. Several possible orientations of the methyl group have been considered and an orientation in which the intermolecular chlorine-hydrogen distances are all 3 Å. or more is in best agreement with the X-ray data.

Introduction

Methyl chloride, m.p. −98°, b.p. −24°, is one of the many simple aliphatic compounds which has not been studied in the crystalline state by X-ray diffraction. The initial and very limited objective of the present work was to determine the number of molecules in the asymmetric unit of the crystal structure. This was a quantity which Dr. Ralph Livingston of the Oak Ridge National Laboratory wished to know in conjunction with an investigation of pure quadrupole spectra in solids. When it was found that the asymmetric unit consisted of one molecule situated on a mirror plane it appeared that the experimental data at hand would be quite adequate for a structure analysis.

Experimental

A sample of methyl chloride was sealed in a fluorothene capillary about 0.5 mm. in diameter and about 1.5 cm. long by Messrs. A. V. Faloon and W. B. Kenna of this Laboratory. The material was under sufficient pressure to remain a liquid at room temperature. On placing the capillary in a cold gas stream the liquid froze immediately into a single crystal suitable for X-ray work. Diffraction patterns were recorded at −125° using a precession camera and low temperature apparatus which has been described previously.[2]

The system proved to be orthorhombic with the following cell constants: $a = 6.495 \pm 0.01$ Å.; $b = 5.139 \pm 0.01$ Å.; $c = 7.523 \pm 0.01$ Å; λ for Mo-Kα = 0.7107 Å.

With a precession angle of $\mu = 30°$ and the c-axis of the crystal parallel to the dial axis of the camera the $0kl$, $h0l$ and hhl reflections were recorded. Intensities were measured by visual observation using a series of timed exposures which varied by a factor of 4 from one exposure to the next. The intensities were corrected for the Lorentz and polarization factors by the method developed by Waser.[3] No corrections were made for absorption effects.

Structure Analysis

Extrapolation of the density of methyl chloride to −125° leads to 4 molecules per unit cell and an X-ray density of 1.335 g. cm.$^{-3}$. The systematic extinctions show that the space group symmetry is Cmcm = D_{2h}^{17}, Cmc2_1 = C_{2v}^{12} or C2cm = C_{2v}^{16}. The $0kl$ data were used in the Patterson function P(vw) to select the correct space group. For the fourfold positions (a), (b) and (c) in Cmcm or (a) and (b) in C2cm the w component of any vector must be a multiple of $^1/_4$. The vectors arising from chlorine–carbon interactions have w components of ± 0.174 or $^1/_2 \pm 0.174$ and therefore we have one chlorine atom and one carbon atom in fourfold position (a) of Cmc2_1. Defining the origin by setting $z_{\mathrm{Cl}} = {}^1/_4$ we have a preliminary structure in which $y_{\mathrm{Cl}} \cong {}^1/_8$, $y_{\mathrm{C}} \cong {}^3/_8$ and $z_{\mathrm{C}} = 0.424$.

Refinement of the structure was limited to the non-centrosymmetric a-axis projection. The three parameters defining the chlorine and carbon positions are available on this projection and the preliminary structure indicates ideal resolution with no projected distances involving chlorine or carbon of less than 1.8 Å. The initial synthesis of $\rho(yz)$ utilized 18 of the 31 $0kl$ reflections available while the subsequent syntheses used all the terms. Structure factor calculations were made with Hartree scattering factors modified by an isotropic temperature correction with B = 2.8 Å.^{2}. The correlation function $R = \Sigma||F_{\mathrm{obsd}}| - |F_{\mathrm{calcd}}||/\Sigma|F_{\mathrm{obsd}}|$ dropped to 9.2% after the second synthesis and the contribution of hydrogen atoms was then considered.

Space group symmetry permits two possible orientations of the methyl group. In either case we have an atom, H_1, in fourfold position (a) and an atom, H_2, in the general eightfold position (b) of Cmc2_1. We assume that the C–H bond distance is 1.09 Å. and that the H–C–H bond angle is the tetrahedral 109°28′. If we let T denote the tetrahedral angle and α the angle between the Cl–C bond and the b axis of the crystal, then the hydrogen parameters in Å. are

Orientation 1

$$\left.\begin{aligned} y_{\mathrm{H}_1} &= y_c + 1.09\cos(\pi - T - \alpha) \\ z_{\mathrm{H}_1} &= z_c - 1.09\sin(\pi - T - \alpha) \\ x_{\mathrm{H}_2} &= 1.09\sin {}^1/_2\, T \\ y_{\mathrm{H}_2} &= y_c - 1.09\cos {}^1/_2\, T\cos(\pi - {}^1/_2T - \alpha) \\ z_{\mathrm{H}_2} &= z_c + 1.09\cos {}^1/_2T\sin(\pi - {}^1/_2T - \alpha) \end{aligned}\right\} \quad (1)$$

Orientation 2

$$\left.\begin{aligned} y_{\mathrm{H}_1} &= y_c - 1.09\cos(T - \alpha) \\ z_{\mathrm{H}_1} &= z_c + 1.09\sin(T - \alpha) \\ x_{\mathrm{H}_2} &= 1.09\sin {}^1/_2T \\ y_{\mathrm{H}_2} &= y_c + 1.09\cos {}^1/_2T\cos({}^1/_2T - \alpha) \\ z_{\mathrm{H}_2} &= z_c - 1.09\cos {}^1/_2T\sin({}^1/_2T - \alpha) \end{aligned}\right\} \quad (2)$$

The methyl group has a threefold axis of symmetry so that one orientation is derived from the other by a 60° rotation about the Cl–C bond axis.

Structure factor calculations were made for both cases using the Hartree scattering factor for hydrogen with a temperature correction of B = 2.8 Å.^{2}. The correlation function R decreased by about 1% for case 1 and increased by about 1% for case 2. For the moment we will accept the parameters given by eq. (1) as correct and resume the question of orientation of the methyl group in a subsequent section.

The refinement was continued through four more syntheses in which the hydrogen atoms for orientation 1 were included in calculating phase angles. Termination of series corrections were made at each

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[1] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company at Oak Ridge, Tennessee.

[2] R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, in press.

[3] J. Waser, *Rev. Sci. Instruments*, **22**, 567 (1951).

step by the method described by Booth.[4] The maxima of peaks in the electron density were located by the method of Carpenter and Donohue.[5] The Cl–C bond distance remained fixed at 1.80_5 Å. during the last three refinements and only intermolecular distances were altered.

The final map of $\rho(yz)$ synthesized from observed structure factors and calculated phase angles is illustrated in Fig. 1. There are regions of electron density at the base of the chlorine and carbon peaks which appear to correlate with the hydrogen positions of orientation 1. However, these densities have improbable magnitudes and may represent a chance accumulation of random error in the observed structure factors. The final parameters obtained from the Fourier syntheses are

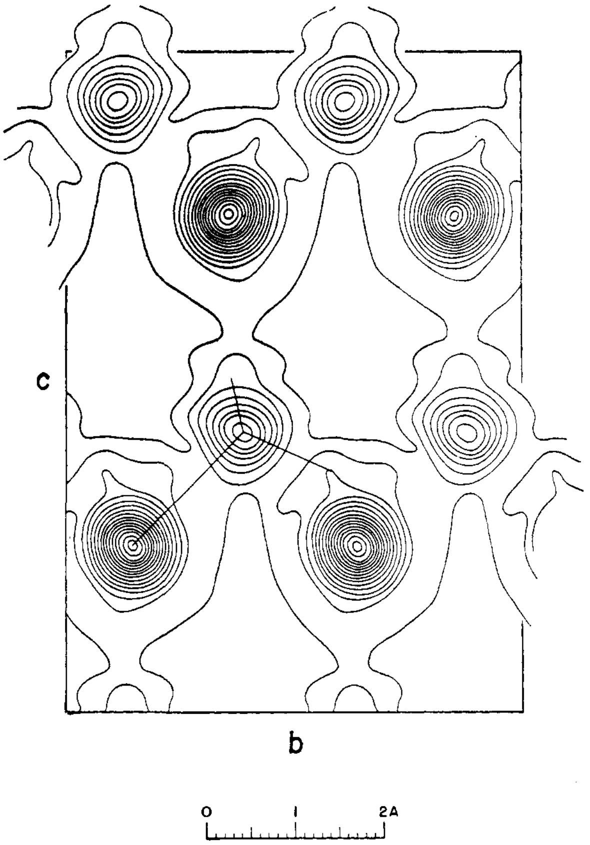

Fig. 1.—Electron density projected along *a*-axis. Lowest contours at 1, 2 and 3 e.A.$^{-2}$, then at intervals of 1 e.A.$^{-2}$ on carbon and at intervals of 2 e.A.$^{-2}$ on chlorine.

	x	*y*	*z*
Cl	0	0.1351	$^1/_4$
C	0	.3799	0.4221

while Eqs. (1) were used to calculate the hydrogen positions.

	x	*y*	*z*
H_1	0	0.573	0.362
H_2	0.137	.3575	.504

The structure factors calculated with these parameters for the 0*kl*, *h*0*l* and *hhl* reflections are compared with the magnitudes of the observed structure factors in Table I.

The standard errors in the parameters were calculated from the usual formula[6] involving the differences between F_{obsd} and F_{calcd} and the curvatures of electron density at peak centers. A factor of $n = 2$ was included in the calculation to take account of the fact that nearly all the 0*kl* structure factors are complex.[7] The following errors were obtained: $\sigma(y)_{Cl} = 0.0055$ Å.; $\sigma(y)_C = 0.0142$ Å.; $\sigma(z)_C = 0.0115$ Å. Thus the standard error in any Cl–C distance is ~ 0.014 Å.

The observed Cl–C bond length of 1.80_5 Å. is 0.024 Å. longer than the value of 1.781 Å. observed in the vapor phase by microwave spectroscopy.[8] The standard error in the X-ray determination is large enough so that we cannot say that there is a significant difference between the two lengths which is not attributable to random errors in the experiment.[6]

Description of Structure with Methyl Group in Orientation 1.—We still assume that the hydrogen positions given by Eq. (1) are correct in the account of the structure which follows.

The *a*-axis projection is illustrated in Fig. 2. Each molecule makes contacts of 3 Å. with six neighboring molecules and longer contacts with eight additional molecules. Each hydrogen atom makes one short contact and three long contacts with chlorine atoms while each chlorine atom makes three short contacts and nine long contacts with hydrogen atoms. These contacts are summarized in Table II. The numerals I, II, III and IV designate molecules located at 0*yz*; 0, $\bar{y}$, $^1/_2 + z$; $^1/_2$, $^1/_2 + y$, *z*; and $^1/_2$, $^1/_2$-*y*, $^1/_2 + z$, respectively. Other molecules in adjacent unit cells are designated by the same numerals but a subscript is added to indicate the lattice translation involved in translating a molecule from the origin cell to an adjacent cell. To distinguish between H_2 atoms in the same molecule the convention has been used for all molecules that the atom with the larger *x* coördinate along the positive *a* axis direction is designated H_2, while the other atom is designated H_2'. The notation is adhered to in Figs. 2, 3 and 4.

The closest contacts link up molecules of types I and IV in one three dimensional array, while molecules of types II and III are linked in a second similar array. The contacts between the two arrays are those listed in part B of Table II. For the closest contacts the hydrogen atoms lie almost on straight lines from carbon to chlorine while the coördination of chlorine by hydrogen approximates to a threefold axis of symmetry as is indicated in Table III. These contacts are illustrated in Fig. 3 where the view is along the Cl–C bond axis of molecule I and the van der Waals radii have been shaded in.

The structure becomes equivalent to that found for chlorine[9] with respect to space group symmetry if the methyl groups are replaced by chlorine atoms

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(4) A. D. Booth, *Proc. Roy. Soc.* (*London*), **A188**, 77 (1946).

(5) G. B. Carpenter and J. Donohue, *ibid.*, **72**, 2315 (1950).

(6) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

(7) D. P. Shoemaker, J. Donohue, V. Schomaker and R. B. Corey, THIS JOURNAL, **72**, 2328 (1950).

(8) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes and J. Kraitchman, *J. Chem. Phys.*, **20**, 1112 (1952).

(9) R. L. Collin, *Acta Cryst.*, **5**, 431 (1952).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS

0kl	$\lvert F_0\rvert$	$\lvert F_c\rvert$	$\alpha(°)$	*h0l*	$\lvert F_0\rvert$	$\lvert F_c\rvert$	$\alpha(°)$	*hhl*	$\lvert F_0\rvert$	$\lvert F_c\rvert$	$\alpha(°)$
002	42.0	40.3	202.4	200	67.5	64.0	0	220	2.9	3.0	180
4	29.4	30.9	347.3	2	39.3	36.4	196.8	1	28.0	29.9	168.0
6	24.2	25.0	181.6	4	26.4	25.4	346.6	2	3.8	4.2	347.6
8	10.0	10.9	11.6	6	24.2	23.0	181.7	3	40.2	33.2	1.7
10	7.1	6.7	166.2	8	8.5	10.0	11.0	4	3.7	3.2	183.6
020	4.0	4.3	180	10	6.6	6.3	165.3	5	16.4	16.4	192.7
1	40.7	37.0	162.0	400	35.6	34.0	0	6	2.5	1.9	0.0
2	4.3	4.2	340.7	2	25.6	24.3	193.6	7	12.1	12.4	345.5
3	41.6	37.3	4.9	4	15.5	17.9	345.7	8	<0.8	1.4	175.9
4	3.9	4.1	184.2	6	17.1	17.7	181.9	9	8.6	9.2	183.1
5	16.8	18.3	189.4	8	7.4	7.4	10.9	330	14.8	16.1	180
6	1.9	1.8	0.0	600	17.7	20.9	0	1	14.7	14.4	192.0
7	12.8	13.5	346.7	2	12.3	13.6	193.6	2	17.6	18.9	351.8
8	1.5	1.5	176.2	4	11.9	11.9	346.5	3	7.3	7.3	356.9
9	9.2	10.2	182.8	6	11.9	11.1	181.5	4	14.7	15.3	189.0
10	1.1	0.8	7.1	800	8.7	11.0	0	5	9.1	10.2	167.6
040	29.0	26.5	180	2	6.0	7.2	193.7	6	7.7	8.1	357.2
1	4.3	5.3	358.9	4	6.1	6.3	346.2	7	6.2	6.2	17.0
2	16.5	16.8	13.4					8	6.9	7.1	173.6
3	4.3	4.2	178.6	*hhl*				440	16.1	17.4	180
4	13.4	14.9	166.1					1	3.3	3.7	6.2
5	3.9	3.9	354.1	110	17.7	18.8	0	2	11.8	12.0	13.0
6	12.9	13.5	2.1	1	48.8	43.2	194.5	3	3.3	2.9	176.1
7	2.4	2.4	187.1	2	34.9	36.0	165.7	4	9.2	9.9	165.4
8	5.4	5.9	191.7	3	19.8	20.9	353.4	5	2.6	2.6	357.8
060	4.0	3.3	0	4	27.1	21.7	11.7	6	9.2	9.6	2.4
1	8.4	8.5	345.0	5	24.1	20.9	173.4	7	1.2	1.7	186.7
2	3.5	3.6	173.7	6	8.8	10.1	187.7	550	2.0	2.2	180
3	9.0	10.3	181.7	7	12.4	12.5	10.6	1	7.5	8.2	7.0
4	3.1	3.1	5.5	8	8.2	9.5	350.9	2	3.9	4.8	344.2
5	5.2	5.3	13.0	9	4.3	5.4	174.7	3	4.6	5.5	179.0
				10	4.6	4.6	193.7	4	3.3	3.7	198.9

TABLE II

INTERMOLECULAR CONTACTS

From Cl atom on molecule I To H atom	On molecule a		Equivalent contact[a] to molecule b		Distance in Å.
A. Closest contacts					
H_1	I	$0\bar{1}0$	I	010	3.01
H_2	IV	$\bar{1}0\bar{1}$	IV		3.00
H_2'	IV	$00\bar{1}$	IV	$\bar{1}00$	
B. Other contacts shorter than 3.5 Å.					
H_1	II	$00\bar{1}$	II		3.29
H_1	III	$0\bar{1}0$	III	$\bar{1}00$	3.37
H_1	III	$\bar{1}\bar{1}0$	III		
H_2	II	$0\bar{1}\bar{1}$	II	$0\bar{1}0$	3.26
H_2'	II	$0\bar{1}\bar{1}$	II	$0\bar{1}0$	
H_2	II	$00\bar{1}$	II		3.32
H_2'	II	$00\bar{1}$	II		
H_2	III	$\bar{1}\bar{1}0$	III		3.36
H_2'	III	$0\bar{1}0$	III	$\bar{1}00$	

[a] The equivalent contact is from H atom on molecule I to Cl atom on molecule b.

TABLE III

ANGLES DEFINED BY CLOSEST INTERMOLECULAR CONTACTS

Contact	Angle
C–H_1–Cl	171° 46′
C–H_2–Cl	172° 32′
C–H_2'–Cl	
H_1–Cl–H_2	100° 36′
H_1–Cl–H_2'	
H_2–Cl–H_2'	103° 50′

to form diatomic molecules. The space group then alters from $Cmc2_1$ to Cmca. Defining an origin at the mid-point of the molecule the parameters for atoms in eightfold position (*f*) of Cmca are $y = 0.122$, $z = 0.086$, as compared with the values $y = 0.130$, $z = 0.100$ found in the actual chlorine structure.

Possible Orientations of Methyl Group.—The complete environment of chlorine atoms about the methyl group of molecule I is illustrated in Fig. 4 where the view again is along the Cl–C bond axis of molecule I. The methyl group is shown in orientation 1 which gives the loosely packed structure described above with no hydrogen–chlorine distances less than 3 Å. As the methyl group is rotated around the Cl–C axis the distances to type I and IV chlorine atoms increase until they are about 3.6 Å. after a 60° rotation to orientation 2. At the same time the distances to type II and III chlorine atoms decrease from about 3.4 Å. at orientation 1 to about 3 Å. after a 25° rotation and finally to 2.63 and 2.73 Å. at orientation 2.

It is of considerable interest to investigate whether orientations of the methyl group which do not conform to the requirements of space group symmetry will give better agreement with the experimental data. The *0kl* structure factors were calculated for several possibilities using the final chlorine and carbon parameters. In addition to

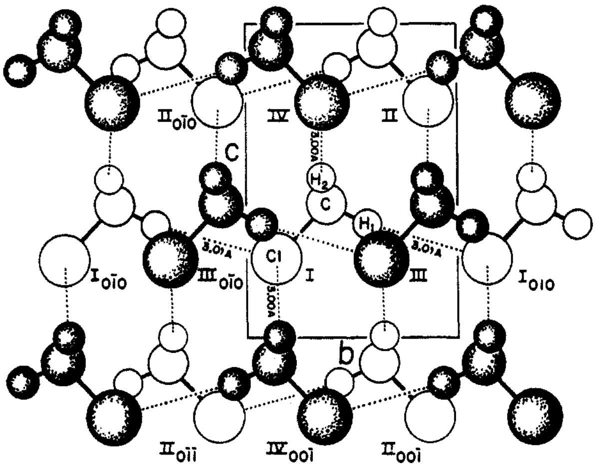


Fig. 2.—Crystal structure of methyl chloride with methyl group in orientation 1. Positive direction of a-axis points out of plane of figure.

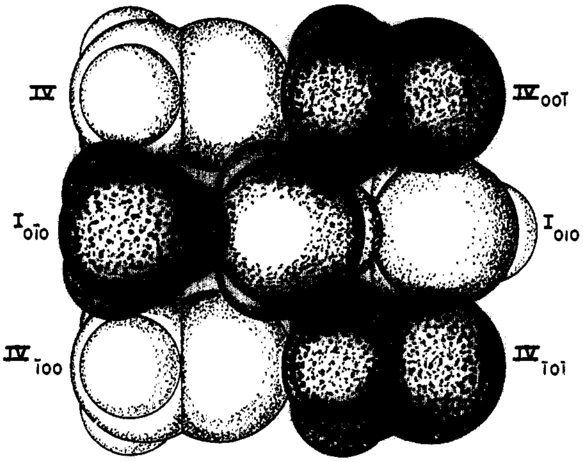
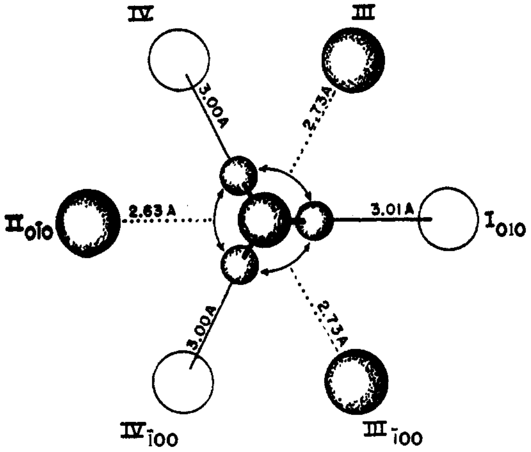


Fig. 3.—Closest hydrogen-chlorine contacts to molecule I with methyl group in orientation 1. Viewed along Cl–C axis of molecule I. Van der Waals radii shaded in.

orientations 1 and 2 the cases were considered where the methyl groups are distributed at random over both these orientations and where the methyl groups are in free rotation. For the case of free rotation the calculation followed that of Bijvoet and Ketelaar[10] with the Hartree scattering factor for hydrogen used without an isotropic temperature correction. Finally, the structure factors for orientations 1 and 2 were evaluated for the *h0l* and *hhl* reflections. The values of the correlation function R obtained for these various cases are listed in Table IV. It is seen that orientation 1 gives the best result and orientation 2 gives the poorest result, while other cases including that of ignoring the hydrogen atoms give intermediate results. We conclude that orientation 1 gives the most satisfactory structure so far as our X-ray data are concerned. However, we cannot eliminate the possibility that the methyl groups undergo oscillations about the Cl–C axis with orientation 1 as the mid-point of oscillation. To determine the magnitude of such an oscillation appears to be a problem which can be examined most profitably by neutron diffraction.



· Fig. 4.—Environment of chlorine atoms around methyl group of molecule I. Viewed along Cl–C axis of molecule I.

TABLE IV

VALUES OF CORRELATION FUNCTION R FOR VARIOUS ORIENTATIONS OF THE METHYL GROUP

Orientation	0*kl*	*h*0*l*	*hhl*	All reflections
1	7.0%	7.3%	9.0%	7.9%
Omit H atoms	7.5	8.0	9.5	8.6
Random 1 and 2	7.8			
Free rotation	7.9			
2	8.9	8.2	9.6	9.0

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OAK RIDGE, TENNESSEE

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[10] J. M. Bijvoet and J. A. A. Ketelaar, THIS JOURNAL, **54**, 625 (1932).