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Reuben Rudman [a] [b] & Ben Post [a]

[a] Physics Department, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., 11201

[b] Department of chemistry, Adelphi University, Garden City, New York, 11530

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Polymorphism of the Crystalline Methylchloromethane Compounds†‡

REUBEN RUDMAN§ and BEN POST
Physics Department, Polytechnic Institute of Brooklyn, Brooklyn, N.Y. 11201

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Abstract—Polymorphism of the methylchloromethane compounds, $(CH_3)_nCCl_{4-n}$, where n varies from 0 to 4, has been studied using low-temperature X-ray diffraction techniques. Single crystals of both high and low-temperature phases were grown and crystal data were obtained for the various phases. The crystal structure of the phase of t-butyl chloride which is stable between −54 and −90° was determined. On the basis of the present investigation, the conclusion is reached that the high-temperature modifications are dynamically disordered, in agreement with the results of n.m.r. and dielectric studies.

1. Introduction

Crystals consisting of molecules which are approximately spherical often undergo phase transitions in the solid state and exhibit abnormally low entropies of fusion and unusually high melting points.[1] X-ray studies of the phases stable just below the melting point generally indicate molecular point symmetries greater than the intrinsic molecular symmetries.[2, 3, 4] Phenomena of this sort have been interpreted in terms of either hindered molecular reorientation[5] or static molecular disorder[6] at or about lattice sites.

As the temperature is lowered, crystals of this sort generally undergo transformations to systems of lower symmetry. The soft,

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§ Present Address: Department of Chemistry, Adelphi University, Garden City, New York 11530.

waxy and volatile high temperature forms transform to relatively hard and brittle modifications. In most cases the sum of the entropies of the solid state transitions is considerably greater than the entropy of fusion. The dielectric constants and n.m.r. spectra of the high-temperature phases resemble those of liquids; below the transition temperature they take on characteristics associated with normal solids.

The high temperature phases of these solids are often referred to as "plastic crystals". Although the high- and low-temperature phases of molecular crystals have been studied by many methods, including measurements of heat capacity, dielectric constant and n.m.r. spectra, the number of crystallographic analyses which have been reported is relatively small. Single crystals of the disordered high-temperature modifications are often easily prepared, but it is very difficult to obtain significant amounts of X-ray diffraction data useful for structure determination from these phases. Another difficulty results from the fact that these crystals often shatter as they are cooled through solid phase transitions.

This work was undertaken to investigate the nature of the crystalline disorder in a series of related molecular crystals by single crystal X-ray diffraction methods. The methylchloromethane compounds, $(CH_3)_nCCl_{4-n}$, where n varies from 0 to 4, are relatively simple molecules with similar shapes and sizes, and therefore appear to constitute a suitable series for study. In addition, a large body of data concerning related properties and spectra of these phases is available in the literature.

Neither methyl chloroform nor 2,2-dichloropropane have been studied by X-ray crystallographic methods prior to the present work and only the high-temperature forms of carbon tetrachloride,[2] t-butyl chloride[3] and neopentane[4] have been previously investigated.

2. Experimental

With the exception of neopentane, which is a gas at room temperature, all the methylchloromethane compounds are liquids at room temperature. Commercial grades of these liquids were fractionally distilled and the purity of the distillate was checked by refractive index and vapor phase chromatographic measurements (Table 1).

TABLE 1 Characterization of Methylchloromethane Compounds, $(CH_3)_nCCl_{4-n}$

		Refractive index (n_D^T)			Vapor phase chromatography	
Compound	n	Experimental	Literature	Temperature	% Purity	Column
Carbon tetrachloride[a]	0	1.4630_7	1.46305(7)	15	99.9	Polyglycol D.C. 200 Silicone-oil
Methyl chloroform[b]	1	1.4375	1.4377(8)	21	99.5	Polyglycol
2,2-Dichloropropane	2	1.4154	1.4148(9) 1.4150(10)	20	99.8	Polyglycol Di-isodecyl Phthalate
t-Butyl chloride	3	1.3866	1.3868_6(11)	18	99.7	Polyglycol
Neopentane	4	—	—	—	—	—

[a] The data reported in this article are based on measurements made on spectroscopically pure carbon tetrachloride; reagent grade carbon tetrachloride, used with no further purification, formed the same crystallographic phases as the "pure" material.

[b] Commercially available methylchloroform contains an inhibitor which is difficult to remove by conventional methods. We thank Dow Chemical Co. for supplying a sample without inhibitor; samples with and without inhibitor formed the same crystallographic phases.

A specimen of neopentane was fractionally distilled by slowly warming an ice water bath in which a flask containing the material had been placed. The fraction boiling at 9.5°C was used. No further characterization of the material was attempted.

Dielectric constant and n.m.r. measurements have revealed evidence of rapid decomposition of methyl chloroform stored at room temperature.[12] Although X-ray photographs of samples stored for a number of weeks at -10°C revealed no evidence of decomposition, we used freshly distilled methyl chloroform sealed into 0.2 mm thin-walled glass capillary tubes for our X-ray studies. These were mounted on the arcs of a goniometer head and frozen within 2 hours of the distillation.

PREPARATION OF PHASE I CRYSTALS†

The samples were sealed in thin-walled glass capillary tubes (0.1–0.3 mm i.d.), mounted on the arcs of standard goniometer heads and cooled by blowing streams of cold air across the capillary tubes. Temperature measurements were made using thermocouples immediately adjacent to the samples. The temperature of the cold air stream was maintained 5 to 10° below the melting point of the material. A small hollow needle, flattened at the exit end, was set up perpendicular to and almost touching the sample. Dry air at room temperature was passed through the needle and directed at the specimen, melting a small portion of the sample within the tube. The construction of the X-ray apparatus permitted movement of the goniometer head perpendicular to the warm cross-current stream. As the melted zone passed along the length of the sample tube, a single crystal or a group of single crystals was formed on refreezing the liquid. In the latter case, repeating the entire procedure usually yielded a single crystal of suitable size and quality. The growth of birefringent crystals could be followed conveniently by observation through crossed polaroids.

PREPARATION OF SINGLE CRYSTALS OF THE LOW-TEMPERATURE PHASES

Phase I crystals were grown from the melt as described above. The temperature was then slowly lowered until the crystals shattered at the transition to form opaque Phase II powders. The sample was maintained just below the transition temperature for relatively long periods. After a few hours, observation through

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† In accordance with widely accepted conventions, Phase I refers to the solid phase formed by cooling the melt; other phases, stable at progressively lower temperatures, are designated Phase II, Phase III, etc.

crossed polaroids, supplemented by X-ray diffraction photographs, usually indicated that the specimen had achieved some preferred orientation. Suitable single crystal specimens, ranging in length from 0.5 to 2 mm, formed in the thin-walled glass tubes after periods ranging from 8 hours to 5 days.

This "annealing" technique was used more than twenty times with three methylchloromethane compounds ($n=0$, 1, 3) and in each case suitable single crystals were grown.

X-ray Diffraction Apparatus

X-ray diffraction data were obtained with a 57.3 mm diameter Weissenberg film camera especially constructed for use in low-temperature studies.[13] Powder patterns of all the phases obtained were taken with a standard Debye-Scherrer powder camera using techniques which have been described elsewhere.[14] Nickel-filtered CuKα radiation was used throughout the investigation.

3. Crystal Structure of Phase II of t-Butyl Chloride

Face-centered cubic crystals of t-butyl chloride usually grow from the melt along the [110] direction which upon transformation to the tetragonal phase becomes the [001] direction (Table 2). Examination of single-crystal X-ray patterns of the latter indicated that reflections of the type $h+k$ odd were absent from all $hk0$ reflections and that the intensities of hkl reflections were essentially identical with the corresponding khl reflections, indicating that the most probable space group was $P4/n$ mm (No. 129). The crystal structure was determined from zero, first and second layer Weissenberg photographs of a crystal aligned along [001]. The diameter of the crystal was 0.09 mm; $\mu r = 0.38$ and absorption corrections were not applied. The unit cell contains two molecules. The two-fold atoms (chlorine and one carbon), therefore, lie on four-fold rotation axes parallel to c at $x=y=\frac{1}{4}$ (positions 2c). Molecules of t-butyl chloride do not possess intrinsic four-fold symmetry, but can

TABLE 2 Crystal Data: $(CH_3)_nCCl_{(4-n)}$ [a]

n	0		1	2	3	4
Name	Carbon tetrachloride		Methyl chloroform	2,2-Dichloropropane	t-Butyl chloride	Neopentane
Melting point (°C)	−23		−33	−34	−27	−19
ΔS_f (e.u./mole)	2.4[b]		1.85[c]	3.3[d]	1.9[e]	3.0[f]
Phase I						
Data obtained at (°C)	−35	−44	−38	−45	−45	−40
Crystal system	Cubic[g] (Face-centered)	Rhombohedral[h]	Cubic (Primitive)	Rhombohedral	Cubic (Face-centered)[i]	Cubic (Face-centered)[j]
Unit cell dimensions (Å)	$a = 8.34$	$a = 14.42$ $\alpha = 90.0°$	$a = 14.61$	$a = 14.68$ $\alpha = 90.0°$	$a = 8.62$	$a = 8.82$
# Molecules/unit cell	4	21	21	21	4	4
Volume/molecule ($Å^3$)	145	143	148	151	160	172
Density, calc. (g/cc)	1.76[k]	1.79[k]	1.50	1.25	0.96[k]	0.70
Transition temp. (°C)	−48		−49	−86	−54	−133
ΔS_{tr} (e.u./mole)	4.86[b]		7.92[c]	>4[d]	6.4[e]	4.39[f]
Phase II						
Data obtained at (°C)	−60		−58	−125	−60	−155
Crystal system	Monoclinic		Orthorhombic	Orthorhombic	Tetragonal	Hexagonal
Unit cell dimensions (Å)	$a = 20.3$ $b = 11.6$ $c = 19.9$ $\beta = 111°$		$a = 7.92$ $b = 11.2$ $c = 5.78$	$a = 9.67$ $b = 6.09$ $c = 9.40$	$a = 7.08$ $c = 6.14$	$a = 14.3$ $c = 8.84$
# Molecules/unit cell	32		4	4	2	12
Volume/molecule ($Å^3$)	137		129	138	154	130
Density, calc. (g/cc)	1.87[k]		1.61	1.36	1.00	0.92
Transition temp. (°C)			−68		−90	
ΔS_{tr} (e.u./mole)			0.24[c]		2.3[e]	
Phase III						
Data obtained at (°C)			−110		Note (l)	
Crystal system			Monoclinic			
Unit cell dimensions (Å)			$a = 7.92$ $b = 11.2$ $c = 5.78$ $B = 91.2°$			
# Molecules/unit cell			4			
Volume/molecule ($Å^3$)			129			
Density, calc. (g/cc)			1.61			

[a] Crystal data for phases stable above −70°C obtained from single crystals; powder data used below −70°C.

[b] Ref. 20. [c] Ref. 24. [d] Ref. 27. [e] Ref. 28. [f] Ref. 29. [g] Ref. 2. [h] Ref. 16.

[i] Redetermination; $a = 8.40 \pm 0.05$ Å was reported in original investigation.[3] The newer results lead to good agreement with the experimentally determined density.[30]

[j] Ref. 4.

[k] The following are the only experimentally determined densities which have been found in the literature:[30] CCl_4: 1.774 g/cc at −35°C and 1.882 g/cc at −48.5°C; t-butyl chloride: 0.949 g/cc at −45°C.

[l] Twinned crystals of Phase III were formed when single crystals of Phase II were cooled.

acquire this symmetry if the three methyl groups are randomly oriented or rotating about the molecular axis passing through the chlorine and the central carbon (carbon 1).

A Patterson projection along [001] confirmed that these atoms (Cl and C(1)) were at $x = y = \frac{1}{4}$. Normal C–Cl and C–C intramolecular distances were assumed (1.8 and 1.54 Å) and the problem was reduced to determining the z coordinate of the chlorine atom.

An over-all isotropic temperature factor of 7.2 Å^2 was determined from the slope of a plot of $|F_0|^2/|F_c|^2$ vs $\sin^2\theta/\lambda^2$. Corrections for cylindrical disorder about the four-fold axis were calculated for each of the observed reflections and structure factors were calculated for values of z_{Cl} varying from 0 to 0.5 in steps of 0.1. The residuals

$$R = \frac{\Sigma\,(|F_0| - |F_c|)}{\Sigma\,|F_0|}$$

were plotted as a function of this parameter.

The Busing-Martin-Levy Fortran Crystallographic Least-Squares Program (ORNL-TM-305) adapted for use on the IBM 7040 was modified by modulating the atomic scattering factor by a function describing the cylindrical disorder in the molecule. Six cycles of least squares refinement using 50 observations and 9 parameters (3 scale factors, 3 atomic position parameters and 3 isotropic temperature factors) were calculated.

The final residual was 0.14. Observed and calculated structure factors are listed in Table 3; and the final parameters in Table 4. The C(1)–Cl interatomic distance computed from these parameters is 1.85 Å.

A difference electron density projection along [001] was computed. The contributions of the chlorine atom and carbon (1) were subtracted from the scaled, observed structure factors used as the coefficients of the Fourier series summation. Two rings, with diameters of approximately 3.0 Å, centered about $\pm(\frac{1}{4}, \frac{1}{4})$ were visible. These apparently correspond to the projected "electron density" of the disordered methyl groups.

In this phase molecules are aligned with their molecular axes parallel to [001]. Adjacent molecules are arranged with Cl atoms

TABLE 3 Structure Factors for t-Butyl Chloride, Phase II

hkl	F_{obs}	F_{calc}	$J_0(x)$[a]	*hkl*	F_{obs}	F_{calc}	$J_0(x)$[a]
200	77.0	69.7	−0.0968	221	53.9	48.0	−0.3968
400	40.2	33.2	−0.1140	231	20.2	15.0	−0.2749
600	16.6	16.3	0.2174	241	24.7	24.3	0.0947
110	100.8	108.2	0.3160	251	7.0	2.0	0.3000
130	40.5	38.3	−0.3875	261	8.9	11.2	0.1190
150	30.2	24.8	0.2760	331	29.9	26.9	−0.0088
220	40.0	42.4	−0.3968	341[b]	4.0	2.5	0.2585
240	30.8	30.3	0.0947	351	9.7	13.8	0.2560
260	7.1	13.6	0.1190	441	10.8	14.8	0.2840
330	28.0	31.6	−0.0088	012	47.2	48.7	0.7054
350	16.4	17.8	0.2560	022	9.6	6.8	0.0968
440	28.7	19.3	0.2840	032	24.3	21.6	−0.4018
550	6.9	8.8	−0.1330	042[b]	3.5	7.4	−0.1140
101	41.8	39.4	0.7054	052	11.4	12.9	0.2601
201	61.8	60.2	−0.0968	112	4.2	1.2	0.3160
301	15.7	23.4	−0.4018	122	30.5	28.1	−0.2243
401	25.5	29.8	−0.1140	132	11.3	15.0	−0.3875
501[b]	4.0	2.4	0.2601	142	16.9	16.7	−0.0585
601	9.9	12.9	0.2174	152[b]	4.2	2.2	0.2760
111	60.6	65.1	0.3160	222	24.9	17.1	−0.3968
121	29.5	22.6	−0.2243	232	15.4	18.7	−0.2749
131	43.4	42.4	−0.3875	242[b]	3.7	4.2	0.0947
141[b]	3.5	8.1	−0.0585	252	8.9	11.2	0.3000
151	16.3	18.6	0.2760	332	6.1	5.6	−0.0088
161[b]	4.5	2.3	0.1944	342	11.0	12.9	0.2585

[a] $J_0(x)$ is the zero-order Bessel function which modifies the structure factor to account for the disorder of the three methyl groups about the chlorine–carbon (1) axis; $x = 2\pi r/d_{hkl} \sin \Psi$, where r is the radius of the cylinder and Ψ is the angle between the axis of rotation and the normal to the plane (hkl) of interplanar spacing d_{hkl}.[15]

[b] Not observed; assigned intensity equal to one-half that of the weakest observed reflection.

alternately "up" and "down" relative to carbon 1. Although the methyl groups appear to be highly disordered in the a–b plane, there is no indication of disorder parallel to c. Also, any reasonable assignment of effective radii of atoms and methyl groups rules out the possibility of free molecular rotation about c.

TABLE 4 Atomic Positional Parameters for Phase II of t-Butyl Chloride ($x = y = 0.250$)

Atom	$z(\sigma \times 10^3)$	$B(\sigma)$
Chlorine	0.917 (5)	6.0 (0.5)
Central carbon, C(1)	0.216 (29)	5.6 (1.8)
Pseudo-atom, C(2)[a]	0.276 (11)	8.9 (2.4)

[a] C(2) is the pseudo-atom representing the three disordered methyl carbon atoms centered about $\pm(\frac{1}{4}, \frac{1}{4}, z)$.

The transition from Phase I to II appears to involve primarily a transition from a cubic phase in which each molecule possesses effective crystallographic point symmetry 23 or higher (probably 43 m) to effective molecular symmetry 4 mm in the tetragonal modification.

4. Results and Discussion

Crystal data for the methylchloromethane compounds are listed in Table 2. The high-temperature phases of t-butyl chloride[3] and neopentane[4] have been discussed previously.

In the case of carbon tetrachloride, optically isotropic (face-centered cubic) crystals were formed by carefully freezing the liquid. When crystals of this phase are maintained within the temperature region in which they are reported to be stable,[2] they transform spontaneously, after several hours, to a rhombohedral modification.[16] Crystals of either the cubic or rhombohedral modification, cooled *below* the transition temperature, transform to a monoclinic phase isostructural with corresponding modifications of carbon tetrabromide and carbon tetraiodide.[17] Weissenberg photographs of this monoclinic form revealed systematic absences characteristic of space groups Cc or C2/c. The centrosymmetric C2/c is preferred, based on the negative piezoelectric test reported by Hettich.[18]

Warming the monoclinic crystals above the transition temperature induces a transformation to the *rhombohedral* phase. In no case was the face-centered cubic phase detected when the monoclinic phase was heated above the transition temperature. Identical results were obtained with different types of sample holders.

Single crystals of all three crystalline forms of carbon tetrachloride shatter when they undergo solid-phase transformations. Although the monoclinic phase is strongly birefringent and easily identified, the polycrystalline form of the rhombohedral phase is weakly birefringent and could readily be mistaken for polycrystalline cubic material. Thus, even though the crystals were examined repeatedly with polarized light, the existence of the rhombohedral phase was not suspected until X-ray photographs indicated its presence. In the course of a reinvestigation of the freezing curve of carbon tetrachloride under high pressure, Trappeniers[19] identified a phase which had not been previously reported. It appears likely that this phase corresponds to our rhombohedral modification.

The rhombohedral and monoclinic modifications appear to be simply related, dimensionally, to the face-centered cubic form. The edge of the unit cell of the rhombohedral form is equivalent in length to $\sqrt{3}$ times the cubic unit cell edge (that is, it is equal to the length of the cubic body diagonal). It is, however, difficult on this basis to account for the observed rhombohedral angle of 90°; the body diagonals of a cube meet at angles of 70°32′. The shattering of single crystals of the face-centered cubic phase as they spontaneously transform to the rhombohedral modification may result from the major molecular rearrangements needed to convert the 70°32′ angles of the cubic phase to the 90° angles of the rhombohedral form.

It is useful to discuss the lengths of the axes of the monoclinic unit cell in terms of the face-centered cubic unit cell (approximately 8 Å on edge).

$$d_{101} \simeq 2a_{\text{cubic}}; \quad d_{010} \simeq d_{10\bar{1}} \simeq \sqrt{2}a_{\text{cubic}};$$

and the angle between [101] and [10$\bar{1}$] is 91.4°. The monoclinic axes given in Table 2 were chosen to be consistent with those reported for the isomorphous, low-temperature forms of carbon tetrabromide and carbon tetraiodide.[17]

Although the transition temperature of carbon tetrachloride has been proposed as a fixed point for low-temperature thermometry, a number of workers have reported discrepancies in the measured transition temperatures. These discrepancies were sufficiently large and persistent to prompt Hicks, Hooley and Stephenson[20] to observe that ". . . the differences obtained between the temperature obtained when the equilibrium is approached from the low-temperature phase and the temperature obtained by cooling from the high-temperature phase indicate that equilibrium cannot be reached in a reasonable period of time . . .". Our findings indicate that warming monoclinic carbon tetrachloride through the transition region may involve processes different from those involved in cooling face-centered cubic carbon tetrachloride to form the monoclinic phase. Recent differential thermal analysis studies of carbon tetrachloride, which confirm the existence of all three phases, indicate that the melting point of the face-centered cubic phase is about four degrees lower than that of the rhombohedral phase.[21, 22]

2,2-Dichloropropane is the only member of the methylchloromethane series which does not have at least one three-fold molecular axis, and, although the size and shape of the molecule are similar to those of other members of the series, 2,2-dichloropropane is also the only one for which no cubic phase has been detected. N.m.r. studies show large differences between the spectra of 2,2-dichloropropane and those of the other high-temperature phases of the methylchloromethane series.[23]

If the choice of the crystal system of Phase I of carbon tetrachloride, methyl chloroform, and 2,2-dichloropropane had been based solely on the available X-ray diffraction evidence (Table 2), we might have classified all three as cubic. However, optical examination of the crystals, using polarized light, indicated that only methyl chloroform is optically isotropic. The crystals of carbon tetrachloride and 2,2-dichloropropane are birefringent (the carbon tetrachloride crystals became weakly birefringent when they transformed from the cubic to the rhombohedral modification, as was mentioned above), i.e. they are rhombohedral with *alpha* approximately equal to 90°; the methyl chloroform crystals are cubic.

The latter undergo a major transformation at $-49°C$ (heat of transition = 1780 cal/mole) and a second, relatively minor, transformation at $-68°C$ (heat of transition = 50 cal/mole).[24] Weissenberg photographs of a single crystal aligned along b, taken at $-58°C$ and $-110°C$ showed that an orthorhombic phase is stable between the two transition temperatures; this transformed to a monoclinic phase below $-68°C$. The dimensions of the unit cells of both phases (i.e. the orthorhombic and monoclinic unit cells) are almost identical; the structural transformation involves primarily a shift of the angle between the a and c axes from 90° to 91.2° (Table 2).

Axial relationships similar to those found for carbon tetrachloride are also found in the unit cells of the high- and low-temperature modifications of methyl chloroform and 2,2-dichloropropane. The high-temperature cubic forms of both these compounds have cell edges approximately $\sqrt{3}$ as large as the corresponding dimension of the cubic carbon tetrachloride cell.

Similarly, the unit cell dimensions of the orthorhombic modification of methyl chloroform are simply related to those of an 8 Å cube; the orthorhombic a axis $\simeq$ 8 Å; $b \simeq \sqrt{2}a$; and $c \simeq a/\sqrt{2}$. This unit cell is, therefore, also closely related to the monoclinic form of carbon tetrachloride. In fact, the relationship between the two low-temperature phases is evidenced by the remarkable similarity of Weissenberg photographs of the respective a^*c^* reciprocal-lattice planes.

The unit-cell dimensions of the low-temperature phase of 2,2-dichloropropane were determined by indexing powder patterns (Table 5). Crystal data based on these calculations appear to be physically reasonable (Table 2).

The crystal system (Table 2) and *hkl* indices (Table 5) of the low-temperature phase of neopentane have been deduced from measurements of patterns of polycrystalline specimens. Although all observed d^{*2} values are multiples of 64.0×10^{-4} ($d^* = 1/d$) it was possible to index the complete patterns only on the basis of a

Table 5 Powder Diffraction Data for Phase II of 2,2-Dichloropropane and Neopentane

(a) 2,2-Dichloropropane, Phase II (at −125°C)

I	*d*	*hkl*	d^{*2}_{obs}	d^{*2}_{calc}
VS	4.82	200	430	428
S	4.68	002	457	452
W	4.52	111	489	490
S	3.80	210	693	698
M−	3.05	020 301	1078	1080 1071
M	2.95	212	1146	1150
M	2.90	120 021	1189	1187 1193
W	2.82	013	1260	1287
M	2.74	311	1333	1341
W	2.65	302	1420	1415
W	2.60	220	1485	1508
W	2.40	400 213	1730	1712 1714
M	2.35	004	1805	1808
W	2.26	222	1954	1960
VW	2.178	023	2108	2099
VW	1.975	031	2563	2543
VW	1.953	131	2621	2650
W	1.892	420	2795	2792
W	1.838	231	2960	2971
W	1.789	502	3124	3127
W−	1.765	115	3211	3202
W−	1.730			
W−	1.659			
W−	1.626			
W	1.598			
VW	1.564			

(b) Neopentane, Phase II (at −155°C)

I	*d*	*hkl*	d^{*2}_{obs}	d^{*2}_{calc}
VW	6.26	200	255	256
VW	5.61	111	317	320
W	5.11	201	383	384
VS	4.73	210	447	448
M	4.17	300, 102, 211	576	576
M	3.77	301, 112	703	704
W+	3.48	310	827	832
W	3.35	221	893	896
W−	3.22	311, 312	962	960
W	2.87	320, 103	1212	1216
VW	2.73	113, 410, 321, 312	1337	1344
W	2.67	203	1407	1408
W	2.50	500, 213	1600	1600
W−	2.29	421, 223	1912	1920
VW	2.25	510, 313	1982	1984
VVW	2.184	502, 104, 511	2096	2112
VVW	2.089	600, 422, 204	2292	2304
VVW	2.005	520, 214, 413, 512, 431	2488	2496
VVW	1.952	304, 521	2624	2624
VVW	1.910	610, 503	2741	2752
VVW	1.792	700, 530, 513	3113	3136
VVW	1.693	433	3492	3520
VVW	1.576	315, 514, 541	4027	4032
VVW	1.549	631, 712	4171	4160
VVW	1.312	650, 910, 326, 813	5814	5824

hexagonal unit cell. An estimate of the density of solid neopentane was based on the observation that it sinks in liquid nitrogen. Its density must, therefore, be greater than 0.8 g/cc and the assumption of 12 molecules per hexagonal unit cell leads to a physically reasonable calculated density and volume/molecule.

Some tentative conclusions which may be drawn from the available data are summarized in Table 6. These data indicate that crystalline disorder persists to increasingly lower temperatures as the number of methyl groups per molecule increases. N.m.r. measurements show that the barriers to methyl group reorientations decrease in the same way.[25] Ubbelohde[26] has reached a similar conclusion: "tetrahedral molecules exhibit transformation temperatures which rise as the crystal potential barriers opposing randomization of orientation increase."

TABLE 6 Molecular Volumes of the Methylchloromethane Compounds

			Volume ($Å^3$)		
Compound	Number of methyl groups	Temperature[a] (°K)	Phase I	Low-temperature phase	ΔV (%)
Carbon tetrachloride	0	225	143	137	4
Methyl chloroform	1	205	148	129	13
2,2-Dichloropropane	2	187	151	138	9
t-Butyl chloride	3	183	160	—[b]	—
Neopentane	4	140	172 (at 233°K) 159 (at 140°K)	130	18[c]

[a] Lowest temperature at which phase transition is known to occur.
[b] Not investigated.
[c] Based on volume/molecule at transition temperature (140°K).

Our X-ray diffraction measurements show that in the high-temperature phase the volume/molecule increases steadily with increasing number of methyl groups per molecule. In the low-temperature phases the volume/molecule is apparently independent of the number of methyl groups present. The magnitudes of the decreases in volume/molecule which accompany ordering of the high-temperature phases (with the possible exception of carbon tetrachloride) are in satisfactory agreement with the results of n.m.r. and dielectric constant studies, all of which have been interpreted in terms of the substantially dynamic character of the disorder in the high-temperature phases.

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