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Polymorphism of the Crystalline Methylchloromethane Compounds. VI.* The Crystal and Molecular Structure of Ordered Carbon Tetrachloride

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Abstract

The structure of phase II of CCl_4 has been determined from single-crystal diffractometer data at 195 K. In this phase, crystals of CCl_4 are monoclinic with $a = 20.181$ (8), $b = 11.350$ (4), $c = 19.761$ (6) Å, $\beta = 111.46$ (3)°, $Z = 32$, and space group $C2/c$. There are four molecules per asymmetric unit with four C–Cl bonds per molecule for a total of sixteen crystallographically unique C–Cl distances. Within the limits of experimental error, the molecules are regular tetrahedra, with average C–Cl and intramolecular Cl···Cl distances, uncorrected for thermal motion, of 1.751 (13) and 2.859 (6) Å, respectively. These same distances, corrected for thermal motion using a rigid-body treatment, are 1.773 and 2.889 Å. The average of the four shortest intermolecular Cl···Cl distances is 3.582 (7) Å, thus indicating a van der Waals radius for Cl of 1.79_1 Å.

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* Part V: Rudman (1977).

Introduction

The methylchloromethane (MCM) molecules $(CH_3)_n$-CCl_{4-n}, where n varies from 0 to 4, are nearly spherical and form orientationally disordered, or plastic, crystals. These compounds undergo a number of solid–solid phase transitions, with the highly-disordered crystalline phase closest to the melting point exhibiting molecular motion characteristic, in many ways, of that of a liquid. The identification and characterization of these transitions in the MCM compounds, using low-temperature differential-scanning calorimetry (Silver & Rudman, 1970) and X-ray diffraction (Rudman & Post, 1968) techniques, have been reported previously. Single-crystal structure analyses of the crystallographic phases formed by the MCM compounds between their melting points and 110 K (at atmospheric pressure) are now underway in this laboratory.

Crystalline carbon tetrachloride, CCl_4 ($n = 0$), is orientationally disordered between its melting point (250 K) and 225 K (Post, 1959). Below 225 K, it forms an ordered phase II (CCl_4-II) which is isostructural with the room-temperature (phase II) modification of CBr_4 (Rudman & Post, 1968).

Experimental

Spectroscopic grade (Mallinckrodt Chemical Works) CCl_4 was fractionally distilled twice. A drop of the fraction boiling at 348·8 K was sealed in a thin-walled glass capillary tube of diameter 0·1 mm, which was then mounted on a goniometer head located on a Syntex $P2_1$-F diffractometer equipped with a locally modified Syntex low-temperature system.

A single crystal of the low-temperature phase of CCl_4 was grown using techniques developed in this laboratory (Rudman, 1970, 1976; Lippman, Cohen & Rudman, 1979); rotation photographs were used to check the quality of the crystals. The orientation matrix and unit-cell parameters were determined from 15 carefully centered reflections. The existence of C centering and a c glide plane were confirmed by fast data collection in the 2θ range 18–35°. Crystal data are given in Table 1.

Data were collected at 195 K, using a θ–2θ scan ($2\theta_{max} = 95°$) with Ni-filtered Cu K radiation ($\lambda = $

Table 1. *Crystal data for* CCl_4 *at* 195 K

Monoclinic	Space group $C2/c$
$a = $ 20·181 (8) Å	$F(000) = 2560$
$b = $ 11·350 (4)	$\mu = 19·03$ mm^{-1}
$c = $ 19·761 (6)	$Z = 32$
$\beta = 111·46$ (3)°	$D_c = 1·940$ Mg m^{-3}
	$D_m{}^* = 1·927$

* Calculated from molar volume of CCl_4 at 195 K (Higgins, Ivor, Staveley & Virden, 1964).

1·54051 Å). The scan range was 2° (2θ) plus the α_1–α_2 separation, with the background measured for one quarter of the total scan time at each of the two extremes of the scan range. The scan rate was 2° (2θ) min^{-1} for counting rates less than 150 counts min^{-1} and 5° (2θ) min^{-1} for rates greater than 2500 counts min^{-1}, with proportional scan rates between these two limits.

During the data collection, the crystal was automatically recentered every 500 reflections. A total of six centering sets obtained during the measurement of 2287 reflections, and three monitor reflections which were checked after every 47, indicated minimal motion and reasonable stability of the crystal during data collection.

Crystals of CCl_4-II can only be grown by annealing the polycrystalline sample that invariably occurs as crystals of CCl_4-I are cooled through the transition. The single crystals of CCl_4-II that eventually form are accompanied by minute crystallites. Since absorption corrections must account for the large absorption coefficient (cylindrical sample, $\mu R = 0·95$), thin-walled glass capillary tube, and miscellaneous crystallites in the vicinity of the single crystal, empirical absorption corrections, based on the ψ scans of ten reflections distributed over the 2θ range, were applied. The ψ scans showed up to 40% variation in intensity.

Structure determination

Since CCl_4-II and CBr_4-II are isostructural, the parameters reported for CBr_4-II (More, Baert & Lefebvre, 1977; Powers, 1978) were used as starting parameters in the refinement of the CCl_4-II data. Three cycles of full-matrix least-squares refinement of 1105 unique structure factors greater than $3\sigma(F)$ and using isotropic temperature factors produced an R factor of 0·118; two additional cycles using anisotropic temperature factors reduced R to 0·0650. Further refinement with an anomalous-scattering factor for Cl and an isotropic extinction factor (0·2150) resulted in $R(F) = 0·061$ and $R_w(F) = 0·080$.

These parameters were then refined using all the 1928 unique structure factors [including those with $F < 3\sigma(F)$] and 162 variables. The intramolecular distances and angles obtained from the refinement of all the data agreed to within 0·001 Å and 0·1° with the results of the previous refinement, but the e.s.d.'s dropped by about 25% as the final agreement factors rose to $R(F) = 0·088$ and $R_w(F) = 0·086$.

The fractional coordinates* (Table 2) and molecular geometry reported here are based on the refinement of

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* Lists of structure factors, anisotropic thermal parameters, intramolecular distances and angles, and **TLS** tensors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34378 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

all 1928 reflection data. The weighting scheme used was based on the counting statistics as described in Eilerman & Rudman (1979) and the standard deviation for an observation of unit weight was 2·1. The C atom peaks in the three-dimensional electron-density map ranged from 6·3 to 7·7 e Å^{-3}, while the Cl peaks were between 18·2 and 20·2 e Å^{-3}. The difference map showed no features, with a maximum of 1 e Å^{-3}. The computer programs used in this crystal structure determination were: SYNBUR, a local program which reads the data tape produced by the Syntex $P2_1$-F diffractometer and converts it to the format used on the Burroughs 6700 computer; EMABS, empirical absorption correction program based on ψ-scan data [adapted from the Syntex program TAPER by Powers (1978)]; EQUIV, program for averaging equivalent reflections; AULP, program for plotting standard reflections and applying Lp corrections; NUCLS, modification of the ORFLS least-squares program (Busing, Martin & Levy, 1962); FORDAP, modification of the Zalkin Fourier summation program; ORFFE, function and error program (Busing, Martin & Levy, 1964); and TLS6 modified version of the Schomaker & Trueblood (1968) program, obtained from Brookhaven National Laboratory. The atomic scattering factors for C and Cl are from Table 2.2A and the anomalous-dispersion corrections are from Table 2.3.1 of International Tables for X-ray Crystallography (1974); $R(F) = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w(F) = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

Table 2. Atomic positional parameters in fractional coordinates ($\times 10^5$, for C $\times 10^4$) for carbon tetrachloride at 195 K

Numbers in parentheses are e.s.d.'s in the units of the least significant digits of the preceding number.

	x	y	z
Cl(1)	34650 (20)	79244 (36)	79905 (19)
Cl(2)	26969 (17)	76639 (35)	89463 (20)
Cl(3)	42093 (17)	73629 (39)	94954 (18)
Cl(4)	33034 (21)	56418 (31)	85418 (20)
Cl(5)	70520 (17)	10531 (36)	64381 (20)
Cl(6)	63058 (21)	27208 (39)	69881 (19)
Cl(7)	55386 (18)	08942 (34)	60083 (21)
Cl(8)	61645 (18)	28067 (32)	54912 (17)
Cl(9)	45633 (16)	−14834 (35)	64086 (20)
Cl(10)	38750 (21)	02128 (35)	69790 (18)
Cl(11)	30536 (16)	−15783 (33)	60280 (20)
Cl(12)	36691 (18)	02568 (35)	54719 (18)
Cl(13)	60300 (19)	53518 (38)	80178 (19)
Cl(14)	67330 (16)	48861 (36)	95234 (17)
Cl(15)	52298 (16)	52439 (33)	89506 (18)
Cl(16)	58197 (21)	31498 (33)	85888 (21)
C(1)	3415 (6)	7155 (11)	8749 (7)
C(2)	6271 (6)	1869 (12)	6231 (7)
C(3)	3802 (6)	−0648 (11)	6219 (6)
C(4)	5928 (6)	4655 (11)	8750 (6)

Discussion

Molecular structure

The asymmetric unit of CCl$_4$-II contains four independent molecules and thus affords the opportunity to compare the intramolecular geometries of four crystallographically unique molecules. More, Baert & Lefebvre (1977) reported that the molecules in isostructural CBr$_4$-II 'show departures from regular tetrahedral symmetry'. However, from a redetermination of the structure of CBr$_4$-II (Powers, 1978) it was concluded that these molecules are regular tetrahedra within the limits of experimental error.

Table 3. Ranges and average values of intramolecular distances in each of the four crystallographically independent CCl$_4$ molecules at 195 K

Molecule	C–Cl (Å)		Cl···Cl (Å)	
	Uncorrected	Corrected*	Uncorrected	Corrected*
(1) C(1)	1·733–1·768	1·752–1·790	2·850–2·875	2·885–2·915
Cl(1)–Cl(4)	1·753 (12)	1·774	2·864 (6)	2·878
(2) C(2)	1·743–1·768	1·765–1·789	2·861–2·880	2·896–2·918
Cl(5)–Cl(8)	1·757 (13)	1·778	2·870 (6)	2·902
(3) C(3)	1·726–1·767	1·750–1·790	2·838–2·861	2·883–2·898
Cl(9)–Cl(12)	1·746 (12)	1·769	2·850 (5)	2·888
(4) C(4)	1·726–1·796	1·746–1·819	2·838–2·864	2·873–2·900
Cl(13)–Cl(16)	1·748 (13)	1·769	2·853 (6)	2·888
Overall ranges and averages	1·726–1·796 / 1·751 (13)	1·746–1·819 / 1·773	2·838–2·880 / 2·859 (6)	2·873–2·918 / 2·889

* Based on the rigid-body treatment of Schomaker & Trueblood (1968).

A similar analysis of the present data reveals that the molecules in CCl_4-II are also regular tetrahedra. The C—Cl distances and the Cl—C—Cl angles for each molecule are within 3σ of the average value (Table 3).* However, the empirical absorption corrections (which had to compensate for the wall thickness of the glass capillary tube and for small fragments of crystalline CCl_4-II attached to the sides of the capillary tube, in addition to the diffraction path through the CCl_4-II single crystal) may not have been sufficient to allow for the accurate refinement of four C atom positions in the presence of 16 Cl atoms, resulting in 3σ values of 0·39 Å and 2·1°, respectively.

A better assessment of the tetrahedral character of the CCl_4 molecules can be obtained by considering the more accurately determined Cl atom positions independently of the central C atoms. Each molecule has six unique Cl···Cl distances and twelve Cl···Cl···Cl angles forming four faces which, in a regular tetrahedron, are equilateral triangles. In CCl_4-II, the 48 individual angles (with one exception) are within 3σ (0·45°) of 60° and all 24 Cl···Cl distances fall within 3σ (0·18 Å) of the average values, thus indicating that the Cl atoms in each molecule are located at the corners of a regular tetrahedron.

The centers of these tetrahedra (the average of the Cl atom fractional coordinates for each molecule) are displaced between 0·014 and 0·050 Å from their respective C atom positions as determined by the least-squares refinement. The fact that the C atom positions are not all at the ideal centers of the tetrahedra lends credence to our supposition that this deviation is due to an artifact of the calculations rather than to a physical feature of the molecule.

A rigid-body analysis (Schomaker & Trueblood, 1968) of these data revealed that each of the four crystallographically unique CCl_4 molecules acts as a

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* See deposition footnote.

Table 4. *Comparison of intramolecular distances reported for* CCl_4

Physical state	C—Cl (Å)	Cl···Cl (Å)	Method*	Reference
Crystalline	1·773 (13)	2·889 (6)	X-ray	This work
Liquid	1·767 (3)	2·886 (3)	X-ray	a
Liquid	1·766 (3)	2·884	X-ray, n.d.	b
Gaseous	1·760 (2)	2·884 (1)	e.d.	c
Gaseous	1·769 (2)	2·887 (4)	e.d.	d
Gaseous	1·765 (2)	2·886 (2)	e.d.	e
Liquid	1·768 (6)	2·889 (2)	X-ray	f

References: (a) Reichelt, Weidner & Zimmermann (1974). (b) Narten (1976). (c) Haase & Zeil (1965). (d) Bartell (1960). (e) Morino, Nakamura & Iijima (1960). (f) Nishikawa & Murata (1979).

* X-ray: X-ray diffraction; n.d.: neutron diffraction; e.d.: electron diffraction.

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rigid body.* When corrected for thermal motion the C—Cl distances increase by between 0·019 and 0·024 Å (Table 3), with the average C—Cl distance equal to 1·773 Å as compared with 1·751 (13) Å for the uncorrected value; corresponding values for the intramolecular Cl···Cl distances are 2·889 and 2·859 (6) Å.

If one assumes that the e.s.d.'s for the corrected distances are similar to those for the uncorrected distances, it is to be noted that the C—Cl and Cl···Cl distances corrected for rigid-body thermal motion fall within one e.s.d. of the values found in the investigations of liquid and gaseous CCl_4 (Table 4).

The CCl_4 molecule was part of at least two other substances whose structures were determined using single-crystal X-ray diffraction methods (Hardy, McKendrick & MacNicol, 1976; Huber, Post & Siiman, 1978). However, in both cases the CCl_4 moiety was highly disordered and not completely resolved.

Crystal structure

The crystal structure of CCl_4-II is isostructural with that of CBr_4-II (More, Baert & Lefebvre, 1977) and fits the analytical treatment describing the structural relationship between CCl_4-II and MCF-II [phase II of the adjacent member of this series, methylchloroform (CH_3CCl_3) (Rudman, 1977)]. The unusual distribution of reflection intensities [in hkl, for layers with $k = 4n$ all $h \neq 4n$ are exceptionally weak as are reflections with $h \neq 4n + 2$ in layers with $k = 4n + 2$; I_{hkl} $(k = 2n) \gg I_{hkl}$ $(k = 2n + 1)$] and the observed structure verify the fact that one unit cell of MCF-II (with $Z = 4$) is the asymmetric unit of CCl_4-II. A detailed description of the structural relationships between CCl_4-II, CBr_4-II and MCF-II, as well as a description of the pseudo-polymorphism in CCl_4 and CBr_4, will be published elsewhere (Powers & Rudman, 1979).

The orientationally disordered form of CCl_4 is face-centered cubic, with $Z = 4$ and is essentially a cubic close-packed arrangement of the nearly spherical molecules (Post, 1959). This is typical of orientationally disordered molecules in general. The residual effects of this close packing can be seen in CCl_4-II as well as in the molecular structure of the ordered phases of many other tetrahedral molecules (Rudman, 1979).

The only intermolecular contacts in CCl_4-II are Cl···Cl interactions. Since the Cl atoms are all covalently bonded and are evenly distributed on the surfaces of spheres (at the corners of regular tetrahedra) which are essentially close packed, the shortest intermolecular distance should correspond to the van der Waals radius of a Cl atom. The shortest Cl···Cl distance observed is 3·555 (6) Å and the average of the four shortest Cl···Cl distances is 3·582 (7) Å, thus

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* See deposition footnote.

indicating a van der Waals radius of 1·791 (7) Å. This is in good agreement with the value of 1·75 Å that is usually quoted (*e.g.* Bondi, 1968).

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