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Neutron Structure Refinement of Orthorhombic Hexachloroethane

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Abstract

The structure of orthorhombic hexachloroethane has been refined at 294 and 140 K. At room temperature 983 symmetry-independent reflections were measured on a four-circle neutron diffractometer. The final $R(F)$ was 0·066 including an isotropic extinction parameter. At 140 K 793 symmetry-independent reflections refined to $R(F) = 0.056$. The temperature parameters have been analyzed in terms of the tensors T, L and S describing the rigid-body movement of the C_2Cl_6 molecule. The temperature variation of the T and L tensors can be understood with the assumption of strong anharmonic contributions. There is, however, no indication of rotational disorder in the orthorhombic phase.

Introduction

Hexachloroethane is known in three modifications:

$$\text{orthorhombic} \xleftrightarrow{318\ K} \text{'monoclinic'} \xleftrightarrow{344\cdot4\ K} \text{cubic (plastic)}$$

(Sasada & Atoji, 1953; Atoji, Oda & Watanabé, 1953; Koga & Miŭra, 1978). The cubic modification shows the characteristics of a plastic phase: high symmetry and Bragg intensities which rapidly decrease with the scattering angle. Crystallographic data for the monoclinic (or perhaps triclinic) phase are not known. Neutron powder diagrams of all three phases together with neutron and X-ray single-crystal photographs (Gerlach, Hohlwein & Prandl, 1978) have shown considerable diffuse scattering in the intermediate and even in the low-temperature orthorhombic phase. The investigation reported here was started, therefore, with the aim of finding out whether the crystals are rotationally or otherwise disordered at room temperature.

A structure determination at room temperature based on visually estimated intensities from X-ray film data has been reported (Sasada & Atoji, 1953). Only positional parameters could be refined at that time. Therefore, four-circle measurements on a neutron diffractometer were performed to obtain precise data for a full structure refinement. Neutrons are advantageous for the study of soft materials because the scattering length does not decrease with sin θ/λ. Also, the difference in the scattering lengths of C and Cl is less pronounced. The relatively large librations of the molecules at room temperature are the reason for a second measurement at 140 K.

Experimental

Crystals were grown from solution (acetone + methyl alcohol). The large crystal faces were (210) planes, giving a plate-like appearance. The crystals are very volatile and were kept in a closed aluminum cylinder during the measurements.

The experiments were performed at the FR2-reactor in Karlsruhe on the P110 (294 K) and P32 (140 K)

Table 1. *Crystal data for* C_2Cl_6 *at 294 K*

$a = 11.568 (4)$ Å	Space group *Pnma*
$b = 10.198 (3)$	$Z = 4$
$c = 6.409 (2)$	$\mu = 0.090$ mm^{-1}
$V = 756$ Å^3	
$\lambda = 0.920$ Å	

Table 2. *Crystal data for* C_2Cl_6 *at 140 K*

$a = 11.28$ Å	Space group *Pnma*
$b = 10.06$	$Z = 4$
$c = 6.39$	$\mu = 0.098$ mm^{-1}
$V = 725$ Å^3	
$\lambda = 1.024$ Å	

automatic four-circle diffractometers. The reflections were measured in ω-step scans. The integrated intensities were corrected for absorption by a Gaussian grid method with the program *ABSORB* (XRAY system, 1976), giving correction factors between 1.13 and 1.29.

Crystal data for the measurements at 294 K are given in Table 1. The lattice constants were determined by Guinier X-ray powder measurements (Gerlach, 1979). In the range up to $2\theta_{max} = 75°$ (sin $\theta/\lambda = 0.66$ Å^{-1}) 983 symmetry-independent reflections were measured, 376 of which had intensities less than $3\sigma(I)$. The absorption coefficient was determined by transmission measurements.

Data for the measurements at 140 K are given in Table 2. The crystal was mounted with its longest dimension (4.2 mm, c axis) vertical on the cold end of a DISPLEX closed-cycle refrigerator. The volume of the crystals used was approximately 17 mm^3 in both cases. From the 793 symmetry-independent reflections with $2\theta_{max} = 76°$ (sin $\theta/\lambda = 0.60$ Å^{-1}) 199 had intensities less than $3\sigma(I)$. The absorption coefficient was calculated from the value of Table 1, a linear λ dependence being assumed.

Structure refinement

Full-matrix refinements were carried out with the program *CRYLSQ* (XRAY system, 1976). The starting parameters were the atomic positions given by Sasada & Atoji (1953) together with isotropic temperature factors. The weights were $w = 1/\sigma^2(F_o)$ with $\sigma^2(F_o) = \sigma_c^2(F_o) + (0.03F_o)^2$; $\sigma_c(F_o)$ was given by the counting statistics. The quantity minimized was $\sum w(F_o - F_c)^2$. The values of the scattering lengths were $b_C = 0.633 \times 10^{-11}$ and $b_{Cl} = 0.958 \times 10^{-11}$ mm (*International Tables for X-ray Crystallography*, 1974).

The isotropic extinction parameter g was refined using the mean path lengths TBAR calculated with the *ABSORB* program (Larson, 1967).

(A) 294 K *data*

With isotropic temperature parameters the refinement stopped at $R(F) = 0.18$; anisotropic refinement yielded a final $R(F) = 0.10$. With an isotropic extinction parameter, $R(F) = 0.066$ was obtained for all reflections. The refined extinction parameter was $g = 23.0 \pm 0.6 \times 10^{-3}$, which is relatively large and probably prevents a further refinement with only one extinction parameter. A difference Fourier map did not give evidence for disordered molecules. Table 3 shows the positional parameters with their standard deviations in parentheses.*

(B) 140 K *data*

With isotropic temperature factors the refinement stopped at $R(F) = 0.12$; anisotropic refinement converged at $R(F) = 0.095$, and with an isotropic extinction parameter at $R(F) = 0.056$ for all reflections. The extinction parameter refined to $g = 11.8 \pm 0.4 \times 10^{-3}$. Table 4 shows the final positional parameters with their standard deviations.*

Structure and bonding

Bond distances and angles within the molecule are shown in Fig. 1 and Table 5. The C atoms have nearly

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* Lists of structure factors and anisotropic thermal parameters obtained at 294 and 140 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34719 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Fractional coordinates* ($\times 10^4$) *at 294 K*

	Lattice position in *Pnma*	x	y	z
C(1)	4(*c*)	1109 (3)	2500	−2156 (5)
C(2)	4(*c*)	1405 (3)	2500	231 (5)
Cl(1)	4(*c*)	2410 (2)	2500	−3608 (4)
Cl(2)	4(*c*)	93 (2)	2500	1663 (4)
Cl(3)	8(*d*)	300 (2)	3920 (2)	−2747 (3)
Cl(4)	8(*d*)	2221 (2)	1082 (2)	828 (3)

Table 4. *Fractional coordinates* ($\times 10^4$) *at 140 K*

	x	y	z
C(1)	1095 (3)	2500	−2142 (4)
C(2)	1415 (3)	2500	271 (4)
Cl(1)	2411 (2)	2500	−3641 (3)
Cl(2)	90 (2)	2500	1781 (3)
Cl(3)	259 (1)	3940 (2)	−2747 (2)
Cl(4)	2255 (2)	1065 (2)	887 (2)

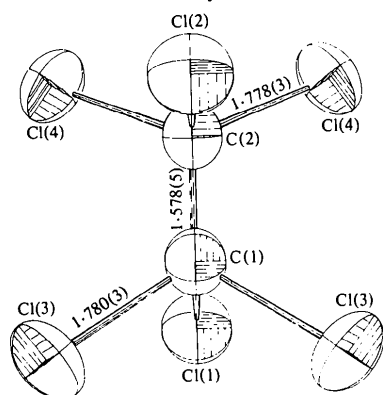Fig. 1. *ORTEP* plot (Johnson, 1965) of the C_2Cl_6 molecule at 294 K. The thermal ellipsoids are at the 50% probability level.

Table 5. *Distances* (Å) *and angles* (°) *within the molecule* (294 K) *with values corrected for libration*

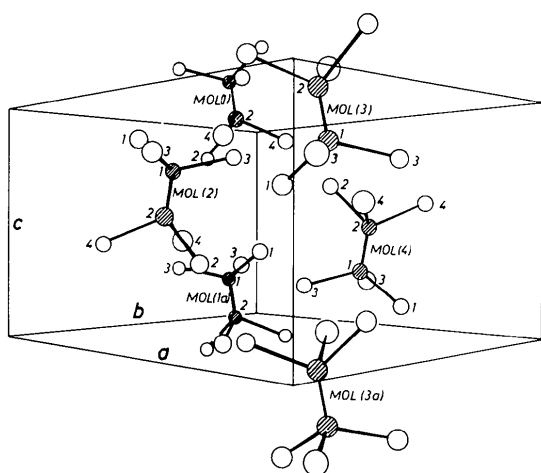|	Uncorrected	Corrected
C(1)—C(2)	1·567 (5)	1·578
C(1)—Cl(1)	1·769 (4)	1·782
C(1)—Cl(3)	1·765 (3)	1·780
C(2)—Cl(2)	1·774 (4)	1·787
C(2)—Cl(4)	1·769 (3)	1·778
C(2)—C(1)—Cl(1)	109·1 (2)	109·0
C(2)—C(1)—Cl(3)	109·0 (2)	109·0
C(1)—C(2)—Cl(2)	108·5 (2)	108·5
C(1)—C(2)—Cl(4)	109·1 (2)	109·2

Fig. 2. Perspective drawing of the molecular packing with the unit cell outlined at 294 K. Molecules are numbered as in Table 6. Carbon atoms are hatched.

ideal tetrahedral bonds. The Cl atoms form an elongated antiprism rather than an octahedron, with an elongation in the C—C direction of 0·12 Å.

The arrangement of the molecules in the crystal is given in Fig. 2. The C—C bonds are parallel to the *ac* plane, alternately inclined to the **c** direction by ±12·5°.

Table 6. *The shortest* Cl—Cl *distances* (Å) *between different molecules* (*molecules numbered as in Fig.* 2)

Molecule (1a)—Molecule (4)		Molecule (1)—Molecule (1a)	
Cl(1)—Cl(2)	3·670 (2)	Cl(2)—Cl(3)	3·872 (3)
Cl(1)—Cl(3)	3·745 (3)	Cl(4)—Cl(1)	3·854 (3)

Molecule (1)—Molecule (2)		Molecule (1)—Molecule (4)	
Cl(4)—Cl(1)	3·696 (2)	Cl(4)—Cl(2)	3·964 (3)
Cl(4)—Cl(3)	3·731 (3)	Cl(4)—Cl(3)	4·211 (3)

The shortest Cl—Cl distances between different molecules are in the range 3·6 to 4·21 Å (Table 6).

Rigid-body analysis of the thermal motion

The thermal parameters were analyzed in terms of the three tensors **T**, **L** and **S** describing the translations, librations and correlated translations–librations (Schomaker & Trueblood, 1968) of the C_2Cl_6 molecule. The program *TLS* 6 (Trueblood & Gantzel, 1977) was used.

Table 7 shows the results for **T**, **L** and **S** with reference axes parallel to the crystal axes and the origin at the center of gravity of the molecule. The largest difference between a thermal parameter U_{ij} and the value calculated from the rigid-body parameters is 0·004 Å².

The principal axes of **T** are parallel to the crystal axes. The movement along the *b* axis is smaller than that in the other two directions.

One of the principal axes of **L** is parallel to **b**. The other two are in the *ac* plane but inclined to the **c** direction by 19 ± 8°. In this way, one is (within σ) parallel to the C—C bond, which is turned away from the **c** direction by 12·5°. The librational movement around this axis is the largest. This is also the axis with the smallest rotational inertia.

Table 7. *Rigid-body analysis of the thermal motion* (*translation, libration and cross tensors* **T**, **L** *and* **S** *relative to the crystal axes*)

T (Å² × 10³)

	T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
294 K	41 (1)	30 (1)	45 (1)	0 (1)	0 (1)	0 (1)
140 K	14 (0·4)	7 (0·4)	11 (0·4)	0 (0·3)	0 (0·7)	0 (0·7)

L (deg²)

	L_{11}	L_{22}	L_{33}	L_{12}	L_{13}	L_{23}
294 K	25 (2)	22 (2)	30 (2)	0 (1)	−2 (1)	0 (1)
140 K	8 (0·5)	7 (0·5)	11 (0·5)	0 (2·5)	0 (0·3)	0 (2·5)

S (rad Å × 10⁴)

	S_{12}	S_{21}	S_{23}	S_{32}
294 K	−4 (4)	33 (4)	12 (4)	15 (4)
140 K	−3 (1)	12 (1)	−1 (1)	3 (1)

The cross tensor **S** has only four elements S_{12}, S_{21}, S_{23} and S_{32} not equal to zero because the molecule is lying on a mirror plane vertical to **b**. Only the element S_{21} is considerably larger than the standard deviations. The intramolecular distances and angles corrected for the librational motion are given in Table 5.

In the harmonic approximation one would expect **U**, **T**, **L**, and **S** to be proportional to the temperature. In our case this would mean: U (294 K) $\simeq$ 2 U (140 K). From Tables 3–5, however, one arrives rather at a factor of 3 between the 140 K and the 294 K values. The inclusion of zero-point oscillations cannot explain this discrepancy because this works in the opposite direction: the low-temperature amplitude would be above a line $\sim T$. This observation seems to indicate a fairly strong anharmonic contribution. The numerical relation between U (294 K) and U (140 K) might be an artefact due to the extinction correction. The refinements without an extinction parameter show, however, essentially the same relation among them.

Conclusion

The structure refinements did not give evidence of disordered molecules. The origin of the diffuse scattering mentioned in the *Introduction* is therefore probably due to the thermal motion of the atoms, which could be analyzed well in terms of the rigid-body parameters **T**, **L** and **S**.

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The Crystal Structure and Absolute Configuration of (−)-Dihydroergotamine Methanesulfonate Monohydrate

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Abstract

(−)-Dihydroergotamine methanesulfonate monohydrate, $C_{33}H_{38}N_5O_5^+ \cdot CH_3O_3S^- \cdot H_2O$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. The unit-cell dimensions are $a = 38 \cdot 732$ (4), $b = 12 \cdot 518$ (2), $c = 7 \cdot 103$ (1) Å. The structure was determined by direct methods and refined by a full-matrix least-squares procedure to an R value of $0 \cdot 058$ for 2667 statistically significant observed reflexions. The absolute configuration was found to be $5(R)$, $9(R)$, $11(S)$, $21(R)$, $26(S)$, $40(S)$, $41(S)$. The rotation about

the peptide link is partly restricted due to steric hindrance and an intramolecular hydrogen bond $O(42)-H(42)\cdots O(19)$. The center of the benzene ring attached to the peptide moiety is at a maximum distance from the ring system of this part of the molecule. Intermolecular hydrogen bonds hold the structure together in the *b* direction.

Introduction

Hydrogenation in positions 10 and 11 (Fig. 1) of the double bond C(10)=C(11) in the lysergic acid moiety