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The Structure of 1,1,3,5,7,7-Hexachloroheptane

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Abstract

The structure of a monoclinic modification of 1,1,3,5,7,7-hexachloroheptane, $C_7H_{10}Cl_6$, has been determined by X-ray diffraction techniques (911 observed reflections collected by an automatic diffractometer; final R value 0·043). Crystal data are: $C2/c$, $a = 12·599$ (9), $b = 10·320$ (6), $c = 9·994$ (8) Å, $\beta = 107·02$ (5)°, $Z = 4$. The molecule adopts staggered conformations throughout and is composed of a planar carbon skeleton. The two asymmetric C atoms of the molecule have the same configuration. Strain is relieved by considerable angular deformations. Chlorine bonds to di- and mono-substituted C atoms differ significantly, namely 1·772 (7) (average) and 1·802 (4) Å, respectively.

Introduction

In a recent paper (Bart, Bassi & Calcaterra, 1979) evidence has been given for a genuine effect concerning the C—Cl bond lengths in polychloro-substituted paraffins. In order to substantiate further the observed bond-shortening effects due to electronegative substituents we have now subjected 1,1,3,5,7,7-hexachloroheptane, (I), to an X-ray crystal structure determination. The product, which is an intermediate in the synthesis of flame retardants, had originally been obtained by telomerization of vinyl chloride and chloroform in the presence of ferrous chloride (Razuvaev, Bobinova, Zvezdin & Egorochkin, 1970).

Experimental

1,1,3,5,7,7-Hexachloroheptane crystallizes in at least two polymorphic modifications (orthorhombic and

monoclinic). Space-group and preliminary unit-cell parameters of the orthorhombic form were obtained from Weissenberg photographs [$P2_12_12$, $Z = 2$, $a = 14.801$ (21), $b = 7.941$ (10), $c = 5.460$ (8) Å]. A small colourless monoclinic crystal, obtained by crystallization after storage, was mounted on a four-circle computer-controlled diffractometer equipped with a scintillation counter and pulse-height analyser, and accurate cell dimensions and orientation matrix were obtained from a least-squares fit of χ, φ, ω and 2θ values from 12 independent reflections.

Crystal data

$C_7H_{10}Cl_6$, $M_r = 306.90$. Monoclinic, $a = 12.599$ (9), $b = 10.320$ (6), $c = 9.994$ (8) Å, $\beta = 107.02$ (5)°. $V = 1242$ Å^3, $Z = 4$, $D_c = 1.640$ Mg m^{-3}, m.p. 405 K. $F(000) = 616$, μ(Mo $K\alpha$) = 1.30 mm^{-1}. Space group $C2/c$ from systematic absences: hkl for $h + k$ odd, $h0l$ for h and l odd, $0k0$ for k odd.

A needle-shaped crystal (dimensions $0.3 \times 0.3 \times 0.8$ mm) was chosen for intensity-data collection on a Picker FACS-1 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) in the range $3° < 2\theta < 50°$. The moving-crystal–moving-counter technique was used with a 2θ scan rate of $1°$ min^{-1} and a scan range of 2.0–$2.5°$ in order to account for $K\alpha_1$ and $K\alpha_2$ peaks at various 2θ values. Background counts were measured for 10 s at each end of every 2θ scan. Three standard reflexions, measured at regular intervals of 50 reflexions, showed a steady decrease in intensity up to 12% and were used for scaling purposes. Out of the 1095 independent reflexions measured, 911 were considered observed according to the criterion $I > 2.5\sigma$ { $\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, where N_s is the total peak count during the time of scanning t_s, and t_b is the time spent in measuring the N_b background counts}. An arbitrary intensity equal to 0.5 times the observable limit was assigned to the non-significant reflexions. All intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the multisolution tangent refinement method *MULTAN* (Germain, Main & Woolfson, 1971) after the observed structure factors were converted into normalized structure factor amplitudes $|E|$. All $|E| > 1.34$ (200 reflexions) were introduced into the calculations together with 50 weak reflexions for the definition of the ψ_0 figure of merit. The total number of phase relationships found was 1379. The automatically chosen starting set is reported in Table 1. Among the four possible solutions generated by *MULTAN*, according to the values ($\pi, 2\pi$) of the phase angles A and B, the correct one was characterized by a high value of ABS FOM and low values of ψ_0 and of RESID. The corresponding phase angles A and B were both π. Positional and isotropic thermal parameters of the non-hydrogen atoms were refined to

Table 1. *Tangent formula results*

(a) Tangent formula input

$h \ k \ l$	$|E|$	Phase angle	
12 2 3	3.52	2π }	Origin-fixing
$\bar{1}$ 3 3	2.44	π }	reflexions
2 2 7	2.45	A	
$\bar{3}$ 1 2	1.86	B	

(b) Tangent formula output

No. of set	ABS FOM	ψ_0	Resid	Combined FOM
1	1.0202	1603	21.41	0.000
2	1.0683	1111	18.35	2.011
3	1.0245	1280	21.02	0.667
4	1.0947	1004	15.80	3.000

Table 2. *Final fractional coordinates with estimated standard deviations in parentheses*

	x	y	z
C(1)	0.5000	0.4406 (5)	0.2500
C(2)	0.3919 (2)	0.5173 (3)	0.2099 (3)
C(3)	0.2956 (3)	0.4236 (3)	0.1689 (4)
C(4)	0.1806 (2)	0.4842 (3)	0.1234 (3)
Cl(1)	0.08050 (7)	0.3574 (1)	0.0841 (1)
Cl(2)	0.15649 (8)	0.5833 (1)	0.2555 (1)
Cl(3)	0.38639 (7)	0.6238 (1)	0.0652 (1)
H(1)	0.500	0.380	0.162
H(2)	0.387	0.574	0.299
H(3)	0.306	0.365	0.084
H(31)	0.301	0.362	0.258
H(4)	0.173	0.541	0.030

R [$= (\sum |k|F_o| - |F_c||)/\sum k|F_o|] = 0.17$ by various cycles of full-matrix least squares minimizing the function $\Delta = \sum w(|F_o| - |F_c|)^2$ with the program of Immirzi (1967). Atomic scattering factors were calculated from the expression given by Vand, Eiland & Pepinsky (1957) with the parameter values according to Moore (1963). The Cruickshank (1965) weighting scheme $1/w = A + B|F_o| + C|F_o|^2$ was adopted, where $A = 2F_o(\text{min})$, $B = 1.0$ and $C = 2/F_o(\text{max})$. The positions of the H atoms were defined on stereochemical grounds (C—H, 1.09 Å) and were introduced in the calculations when the heavy atoms had settled down. Anisotropic refinement then converged to $R = 0.043$ for the 911 non-zero reflexions ($R' = 0.053$, including unobserved reflexions). The final shifts of the atomic parameters were all well below the corresponding σ value.

The final fractional coordinates and the corresponding standard deviations of the atoms of the independent unit are listed in Table 2.* All calculations

were performed on the Univac 1100/20 computer of this Institute using a local program set.

Results and discussion

The molecular and crystal structures of 1,1,3,5,7,7-hexachloroheptane are given in Figs. 1 and 2, as derived by the *ORTEP* computing and drawing program (Johnson, 1965). Bond data are reported in Table 3.

The crystallographically imposed molecular symmetry of (I) is C_2, whereas the configuration of the asymmetric C atoms C(2) and C(2') is *RR* (Cahn, Ingold & Prelog, 1956). The individual molecule is therefore optically active, whereas in the crystal both *RR* and *SS* molecules are present due to the inversion centres contained in the unit cell.

The molecular structure is best understood in terms of torsional angles and nonbonded interactions. The latter are minimized across all C—C links by the adoption of staggered conformations with torsion
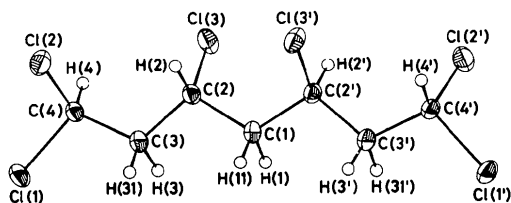

Fig. 1. The molecular structure of 1,1,3,5,7,7-hexachloroheptane showing the atom-labelling scheme and 30% probability thermal vibration ellipsoids.
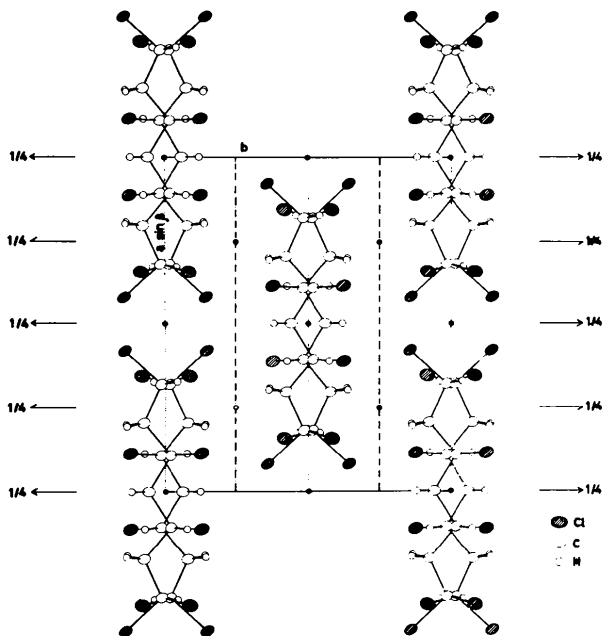

Fig. 2. The crystal structure of 1,1,3,5,7,7-hexachloroheptane viewed down the *c* axis.

Table 3. *Geometrical parameters of the independent unit*

Standard deviations are given in parentheses as units in the last place. A prime indicates an atom related to that of the independent unit by the twofold axis.

(*a*) Bond lengths (Å)

C(1)—C(2)	1·524 (5)	C(2)—Cl(3)	1·802 (4)
C(2)—C(3)	1·512 (5)	C(4)—Cl(1)	1·779 (3)
C(3)—C(4)	1·520 (5)	C(4)—Cl(2)	1·765 (3)

(*b*) Bond angles (°)

C(2')—C(1)—C(2)	117·4 (2)	Cl(1)—C(4)—Cl(2)	109·0 (1)
C(1)—C(2)—C(3)	108·9 (1)	Cl(2)—C(4)—C(3)	111·8 (1)
C(2)—C(3)—C(4)	115·9 (1)	Cl(3)—C(2)—C(1)	110·5 (1)
Cl(1)—C(4)—C(3)	108·4 (1)	Cl(3)—C(2)—C(3)	109·5 (2)

(*c*) Non-bonded distances (Å)

Cl(2)—H(2)	2·81	Cl(1)—H(31)	2·82
Cl(3)—H(4)	2·74	Cl(1)—H(3)	2·84
Cl(3')—H(2)	2·83	H(1)—H(3)	2·34

angles in the range 56·7–63·6°. The carbon chain is planar; this plane, defined by C(1,2,3,4), is represented by the equation $-0·0258X - 0·0271Y + 0·9993Z - 0·3809 = 0$ (r.m.s. deviation 0·011 Å, maximum displacement 0·006 Å), as referred to the a^*, b, c orthogonal-axis system. The out-of-plane deviation of Cl(1) is 0·037 Å. The minimal 1,2 (vicinal) interactions H$\cdots$Cl, C$\cdots$Cl, H$\cdots$C and H$\cdots$H are 2·82, 3·17, 2·64 and 2·42 Å, respectively, and may be compared with the corresponding average H$\cdots$Cl, C$\cdots$Cl, H$\cdots$C and H$\cdots$H interactions of 2·87, 3·18, 2·75 and 2·45 Å, respectively, in 1,1,1,3,6,8,8,8-octachloro-octane (Bart, Bassi & Calcaterra, 1979).

The non-bonded distances given in Table 3 partly result also from angular rather than conformational distortions. In view of the predominantly one-sided chlorine substitution of the carbon chain with consequent repulsions between the electronegative substituents, it is not surprising to notice considerable deformations from the standard tetrahedral value at C(1) and C(3) (up to 117·4°), at variance with the almost regular bond angles at C(2) and C(4). The C—C—Cl angles average 110·1° (range 108·4–111·8°), while the Cl—C—Cl angle measures 109·0 (1)°.

The average C—C length in 1,1,3,5,7,7-hexachloroheptane is 1·519 (5) Å, close to the normal C(sp^3)—C(sp^3) single-bond length of 1·537 (5) Å (Sutton, 1965). No effect on C—C bond lengths is observed which can be interpreted in connexion with the asymmetric substitution of electronegative groups in the molecule. However, this bond-shortening effect (Bent, 1960*a,b,c*) is more readily noticed in progressive shortening of the C—Cl bonds with increasing halogenation of the C atom. The effect has recently been expressed in quantitative terms. Available struc-

tural data of saturated aliphatic compounds with extensive Cl substitution have suggested paraffinic C—Cl bond lengths for mono- and di-substituted carbon of 1·788 and 1·772 Å, respectively (Bart, Bassi & Calcaterra, 1979). The C—Cl bond distances in (I) differ significantly, namely 1·802 (4) and 1·772 (7) Å on average (range 1·765–1·779 Å) for mono- and di-substituted C atoms, respectively, and confirm the trend for the aforementioned variety of small molecules determined by various techniques, mainly in the gas phase.

The shortest intermolecular distances for C···Cl, C···C, C···H, Cl···Cl, Cl···H and H···H are 3·61, >4·0, 3·87, 3·40, 2·94 and 3·01 Å as compared with the expected van der Waals distances of 3·55, 3·60, 3·00, 3·50, 2·95 and 2·40 Å, respectively. Noteworthy is the absence of C···C, C···H and H···H contacts, indicating that the crystal packing is mainly governed by Cl atoms, as is also clearly visible in the arrangement of the chlorocarbon (I) in the unit cell (Fig. 2).

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Structures of Polyether Complexes.

XI.* A Pseudo-Binuclear Complex Formed by a Linear Oligoether and a Neutral Guest Molecule: Bis[(8-quinolyloxy)ethoxyethyl] Ether–Thiourea

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Abstract

$C_{26}H_{28}N_2O_5.CH_4N_2S$ is monoclinic, $P2_1/c$, with $a = 13.291$ (3), $b = 13.080$ (4), $c = 16.075$ (5) Å, $\beta = 103.20$ (9)°, $M_r = 524.64$, $Z = 4$, $d_c = 1.281$, m.p. = 415 K, $\mu = 1.389$ mm^{-1}. The thiourea molecule is hydrogen bonded through two N–H–N and one N–H–O(ether) interaction with three of the seven hetero-atoms of the ligand. The remaining four O atoms interact only weakly with the thiourea. The ligand displays an S-like configuration with each S loop wrapping around one N atom of the thiourea. This is similar to a binuclear linear oligoether complex.

Introduction

The ability of linear polyethers to form stable complexes with alkali- and alkaline-earth-metal cations is well known (Tümmler, Maass, Weber, Wehner & Vögtle, 1977; Vögtle & Sieger, 1977). With polar neutral guest molecules, however, complexes are mostly observed with cyclic crown ethers (Knoechel, Kopf, Oehler & Rudolph, 1978; Goldberg, 1975).

In a stoichiometric complex of quinol and urea (Mahmoud & Wallwork, 1975), the rather acidic OH groups are involved in hydrogen bridges, but hydrogen bonds to O atoms of linear polyethers have only seldom been reported (Suh & Saenger, 1978).

Since the structure of a complex of the title ligand with RbI has been published previously (Saenger & Brand, 1979) and since the distances Rb⁺···O (2·87