The average C—C distances in the phenyl rings *A*, *B*, *C* are 1·383 (3), 1·380 (3) and 1·386 (3) Å respectively. The length N=C(8) = 1·268 Å is in good agreement with that in *N*,*N'*-dibenzylidene-1,2-diphenylethylenediamine (Prelesnik & Nowacki, 1975).

Bond lengths involving H atoms are given in Table 3. The C—H lengths range from 0·88 to 1·12, mean 1·01 (3) Å.

As is shown in Table 2 the positional parameters correspond to the enantiomer of the molecule used to solve the structure. The asymmetric C(15) has an *S* configuration.

Fig. 3 shows the contents of the unit cell projected down *c*. There are no H atom intermolecular contacts <3·5 Å.

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Molecular and Crystal Structure of *meso*-(*RS*)-1,1,1,3,6,8,8,8-Octachlorooctane

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Abstract

1,1,1,3,6,8,8,8-Octachlorooctane, $C_8H_{10}Cl_8$, crystallizes in space group $P2_1/n$ with $Z = 2$ and cell parameters $a = 6{\cdot}269$ (5), $b = 15{\cdot}546$ (16), $c = 7{\cdot}947$ (6) Å, $\beta = 93{\cdot}60$ (7)°. The crystal structure has been determined by X-ray diffraction techniques (857 observed reflections collected by an automatic diffractometer; final *R* value 0·049). The conformation of the molecule is governed by the steric and electrostatic interactions of the Cl atoms. Steric hindrance is minimized by the adoption of a nearly eclipsed conformation around the C_β—C_γ bonds (20° twist) and staggered conformations in other parts of the molecule. Strain is further relieved by slight angular deformations. C—Cl bond distances at tri- and monosubstituted C atoms differ significantly: 1·768 (average) and 1·800 (6) Å, respectively. Similarly, C_α—C_β is shorter [1·499 (7) Å] than other C—C bonds [average 1·528 (5) Å].

Introduction

Recently the addition reaction of carbon tetrachloride to 1,5-hexadiene using a redox-transfer initiating system has led to a highly chlorinated linear biadduct together with a cyclic monoadduct in low yield (Piccardi, Modena & Massardo, 1973). The main reaction product, 1,1,1,3,6,8,8,8-octachlorooctane, (I) has now been subjected to an X-ray crystal structure determination to establish the molecular conformation and to collect evidence for the bond-shortening effects of the electronegative substituents.

Experimental

The space group and preliminary cell parameters of (I) were obtained from Weissenberg photographs. Accurate cell dimensions and the orientation matrix were obtained from a least-squares fit of χ, φ, ω and 2θ values from 12 independent reflections measured on a four-circle diffractometer.

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Crystal data

$C_8H_{10}Cl_8$, $M_r = 389{\cdot}82$, monoclinic, $a = 6{\cdot}269$ (5), $b = 15{\cdot}546$ (16), $c = 7{\cdot}947$ (6) Å, $\beta = 93{\cdot}60$ (7)°, $V = 772{\cdot}96$ Å^3, $Z = 2$, $D_c = 1{\cdot}674$ Mg m^{-3}, $F(000) = 388$, μ(Mo $K\alpha$) = 1·41 mm^{-1}; space group $P2_1/n$ from systematic absences: $0k0$ for k odd, $h0l$ for $h + l$ odd.

A needle-shaped colourless crystal (dimensions 0·2 × 0·3 × 0·4 mm) was chosen for intensity-data collection on a Picker FACS-1 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ 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 the $K\alpha_1$–α_2 splitting at different 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, varied by no more than 3% and were used for scaling purposes. Of the 1363 independent reflections measured, 857 were considered observed according to the criterion $I > 2{\cdot}0\sigma$ $\{\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, 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 reflections. All intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the multi-solution tangent-refinement method *MULTAN* (Germain, Main & Woolfson, 1971). The correct solution was selected unambiguously by the program. Positional and isotropic thermal parameters of the non-hydrogen atoms were refined to $R = (\sum |k|F_o| - |F_c||)/\sum k|F_o| = 0{\cdot}14$ by full-matrix least squares, minimizing the function $\Delta = \sum w(k|F_o| - |F_c|)^2$ 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). Cruickshank's (1965) weighting scheme $1/w = A + B|F_o| + C|F_o|^2$ was adopted, where $A = 2F_o(\text{min.})$, $B = 1{\cdot}0$ and $C = 2/F_o(\text{max.})$. H atoms with coordinates defined on stereochemical grounds were introduced when the heavy atoms had settled down and were constrained to those of C with $B = 5$ Å^2. Anisotropic refinement of the heavy atoms then converged to $R = 0{\cdot}049$ for the 857 non-zero reflections ($R' = 0{\cdot}090$, including unobserved reflections). The final shifts of the atomic parameters were all well below the corresponding σ value.

Table 1. *Final fractional coordinates with estimated standard deviations in parentheses*

	x	*y*	*z*
C(1)	0·4353 (8)	0·6751 (3)	0·5734 (6)
C(2)	0·3854 (10)	0 6567 (3)	0·7519 (7)
C(3)	0·3878 (9)	0·5607 (3)	0·7985 (6)
C(4)	0·4920 (10)	0·5472 (4)	0·9748 (7)
Cl(1)	0·1182 (3)	0·5203 (1)	0·7898 (2)
Cl(2)	0·4304 (3)	0·7887 (1)	0·5437 (2)
Cl(3)	0·2490 (3)	0·6278 (1)	0·4262 (2)
Cl(4)	0·6920 (3)	0·6385 (1)	0·5299 (3)
H(21)	0·227	0·681	0·774
H(22)	0·502	0·689	0·837
H(3)	0·479	0·527	0·708
H(41)	0·401	0·581	1·064
H(42)	0·653	0·573	0·979

The final fractional coordinates and the corresponding standard deviations of the atoms of the independent unit are listed in Table 1.* All calculations were performed on the Univac 1110/20 computer of this Institute using a local program set.

Table 2. *Geometrical parameters of the independent unit*

Primes indicate atoms related by the inversion centre.

(*a*) Bond lengths (Å)

Cl(1)–C(3)	1·800 (6)	C(1)–C(2)	1·499 (7)
Cl(2)–C(1)	1·782 (6)	C(2)–C(3)	1·537 (7)
Cl(3)–C(1)	1·761 (5)	C(3)–C(4)	1·523 (7)
Cl(4)–C(1)	1·761 (5)	C(4)–C(4′)	1·523 (10)

(*b*) Bond angles (°)

Cl(1)–C(3)–C(2)	109·6 (2)	Cl(2)–C(1)–Cl(4)	107·6 (1)
Cl(1)–C(3)–C(4)	109·5 (2)	Cl(3)–C(1)–Cl(4)	108·1 (1)
Cl(2)–C(1)–C(2)	108·1 (2)	C(1)–C(2)–C(3)	114·4 (2)
Cl(3)–C(1)–C(2)	112·3 (2)	C(2)–C(3)–C(4)	110·7 (2)
Cl(4)–C(1)–C(2)	111·8 (2)	C(3)–C(4)–C(4′)	113·1 (3)
Cl(2)–C(1)–Cl(3)	108·7 (1)		

(*c*) Non-bonded distances (Å)

Cl(1)···Cl(3)	3·480 (2)	Cl(4)···H(22)	2·90
Cl(1)···C(4′)	3·162 (7)	Cl(4)···H(3)	2·65
Cl(1)···H(21)	2·60	C(1)···H(3)	2·55
Cl(1)···H(41)	2·88	C(2)···H(41)	2·74
Cl(1)···H(42′)	2·68	C(2)···H(42)	2·72
Cl(2)···H(21)	2·84	C(3)···H(41′)	2·76
Cl(2)···H(22)	2·81	C(3)···H(42′)	2·75
Cl(3)···C(3)	3·205 (5)	C(4)···H(22)	2·46
Cl(3)···H(21)	2·90	C(4)···H(3′)	2·77
Cl(4)···C(3)	3·188 (5)	H(22)···H(42)	2·30

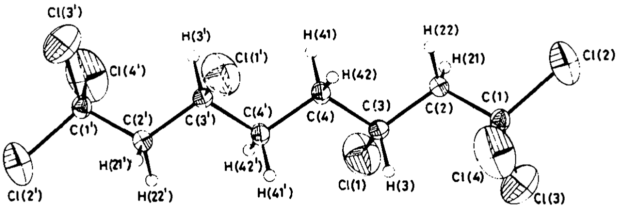

Fig. 1. The molecule of *meso*-(*RS*)-1,1,1,3,6,8,8,8-octachlorooctane showing the atom-labelling scheme and 30% probability thermal-vibration ellipsoids.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34623 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

The molecular and crystal structures of 1,1,1,3,6,8,8,8-octachlorooctane are given in Figs. 1 and 2, as derived by the *ORTEP* computing and drawing program (Johnson, 1970). Bond data are reported in Table 2 and Fig. 3.

The molecular structure of (I) is best described in terms of torsion angles τ and non-bonded interactions. The crystallographically imposed molecular symmetry C_i leads to a *trans* arrangement around the central bond C(4)–C(4′). As a result of the inversion centre, the configuration of the asymmetric atoms C(3) and C(3′) in (I) is (*RS*) and the compound has a *meso* configuration. Non-bonded interactions are also minimized across the C(1)–C(2) and C(3)–C(4) links by the adoption of staggered conformations (Fig. 3). This is different to the situation around C(2)–C(3) which assumes a nearly eclipsed conformation (20° twist). Consequently only part of the carbon chain, namely C(2,3,4,4′,3′,2′), is planar. This plane is represented by the equation $-0\cdot8893X + 0\cdot0888Y + 0\cdot4486Z + 2\cdot1803 = 0$ (r.m.s. deviation 0·021 Å), as referred to the a^*, b, c orthogonal axis system. As a result of the conformation assumed by atoms linked to C(2) and C(3), the C(3)–Cl(1), C(3)–C(4) and C(1)–C(2) bonds are nearly eclipsed with respect to the C–H bonds. The minimum 1,2 (vicinal) interactions H···Cl,

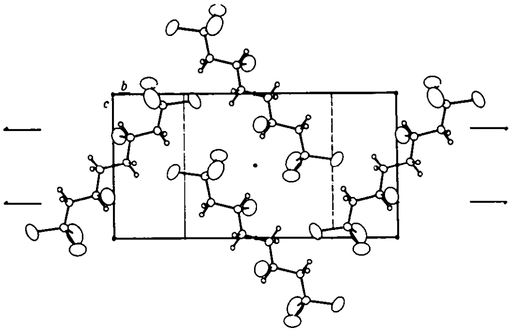

Fig. 2. Structure of *meso*-(*RS*)-1,1,1,3,6,8,8,8-octachlorooctane viewed down the *a* axis.

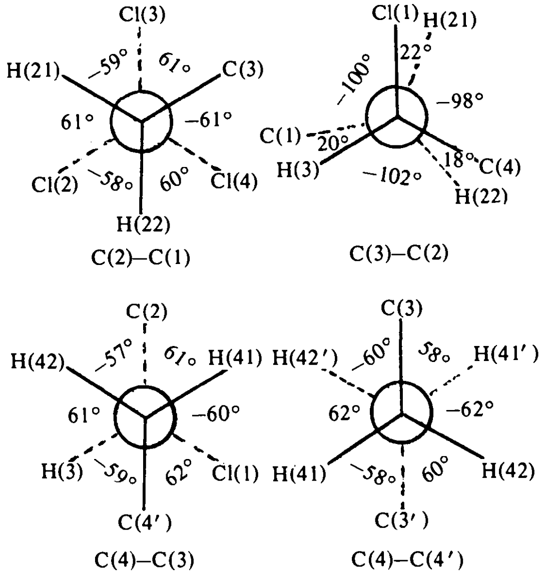

Fig. 3. Newman projections along the C(1)–C(2), C(2)–C(3), C(3)–C(4) and C(4)–C(4′) bonds of *meso*-(*RS*)-1,1,1,3,6,8,8,8-octachlorooctane.

Table 3. *Structural data of (poly)chloroalkanes*

Compound	⟨C–Cl⟩	Substitution*	Method†	References
CH_3Cl	1·784 (3) Å	1	E	(*a*)
CH_3Cl (148 K)	1·805 (14)	1	X	(*b*)
CH_3Cl	1·781 (1)	1	M	(*c*)
CD_3Cl	1·781 (1)	1	M	(*d*)
C_2H_5Cl	1·7785 (3)	1	E	(*e*)
C_2H_5Cl	1·788 (2)	1	M	(*f*)
CH_2DCH_2Cl	1·777 (n.d.)	1	M	(*g*)
$(CH_3)_3CCl$	1·80 (4)	1	E	(*h*)
$(CH_3)_3CCl$	1·765 (30)	1	E	(*i*)
(*RS*)-1,2,5,6-Tetrachlorohexane	1·794 (4)	1	X	(*j*)
(*RRSS*)-2,3,6,7-Tetrachlorooctane	1·810 (5)	1	X	(*j*)
CH_2Cl_2	1·772 (5)	2	M	(*k*)
CH_2Cl_2	1·768 (13)	2	X	(*l*)
CH_2ClF	1·759 (3)	2	M	(*m*)
$CH_3CCl_2CH_3$	1·776 (20)	2	E	(*h*)
$CHCl_3$	1·758 (1)	3	M	(*n*)
$CHCl_3$	1·767 (n.d.)	3	M	(*o*)
$CHCl_3$	1·767 (n.d.)	3	M	(*p*)
$CHCl_3$ (185 K)	1·750 (15)	3	X	(*q*)
$C_{16}H_{14}CoN_2O_2.CHCl_3$	1·772 (8)	3	X	(*r*)
CH_3CCl_3	1·775 (20)	3	E	(*h*)
CH_3CCl_3	1·7712 (8)	3	M	(*s*)
CH_3CCl_3(128 K)	1·782 (16)	3	X	(*t*)
Cl_3CCCl_3	1·763 (10)	3	E	(*u*)
Cl_3CCCl_3	1·765 (n.d.)	3	X	(*v*)
FCl_2CCCl_2F	1·760 (10)	3	E	(*w*)
$F_2ClCCClF_2$	1·745 (15)	3	E	(*w*)
FCl_2CCF_2Cl	1·747 (27); 1·758 (20)	3	E	(*w*)
$Cl_3COC(O)OCCl_3$	1·766 (7)	3	X	(*x*)
CCl_4	1·770 (10)	4	E	(*y*)
CCl_4	1·766 (3)	4	E	(*z*)
CCl_2F_2	1·775 (6)	4	E	(*aa*)
$CClF_3$	1·751 (4)	4	E	(*a*)

References: (*a*) Bartell & Brockway (1955); (*b*) Burbank (1953); (*c*) Miller, Aamodt, Dousmanis, Townes & Kraitchman (1952); (*d*) Costain (1958); (*e*) Wagner & Dailey (1957); (*f*) Schwendeman & Jacobs (1962); (*g*) Wagner & Dailey (1955); (*h*) Coutts & Livingston (1953); (*i*) Bowen, Gilchrist & Sutton (1955); (*j*) Bassi & Scordamaglia (1974); (*k*) Myers & Gwinn (1952); (*l*) Kawaguchi, Tanaka, Takeuchi & Watanabé (1973); (*m*) Muller (1953); (*n*) Jen & Lide (1962); (*o*) Townes & Schawlow (1955); (*p*) Ghosh, Trambarulo & Gordy (1952); (*q*) Fourme & Renaud (1966); (*r*) Schaeffer & Marsh (1969); (*s*) Holm, Mitzlaff & Hartmann (1968); (*t*) Silver & Rudman (1972); (*u*) Morino & Hirota (1958); (*v*) Sasada & Atoji (1953); (*w*) Iwasaki (1959); (*x*) Sørensen (1971); (*y*) Karle & Karle (1949); (*z*) Bartell, Brockway & Schwendeman (1955); (*aa*) Livingston & Lyon (1956).

* Number of halogen atoms attached to the same C atom.

† E: electron diffraction; M: microwave spectroscopy; X: X-ray diffraction.

C···Cl, H···C and H···H around the C(2)–C(3) bond are 2·60, 3·62, 2·46 and 2·73 Å respectively. These values may be compared to the average staggered H···Cl, C···Cl, H···C and H···H interactions of 2·87, 3·18, 2·75 and 2·45 Å, respectively, in the same molecule.

It appears that the conformation adopted by the molecule is due to a complex interplay of non-bonded substituent repulsions rather than to intermolecular forces. For a staggered conformation around C(2)–C(3), *i.e.* a completely planar carbon skeleton, the Cl(1)···Cl(3) non-bonded distance of 3·48 Å would decrease to about 2·6 Å, corresponding to an interaction energy of 27·9 kJ mol^{-1} (Eliel, Allinger, Angyal & Morrison, 1965). On the other hand, a perfectly eclipsed conformation would lead to decreases of Cl(4)···C(4) (4·08 Å), and Cl(4)···H(42) (3·74 Å) to about 3·7 and 3·1 Å; further, the energy would increase by means of shorter Cl(1)···H(21), C(4)···H(22) and C(1)···H(3) non-bonded distances.

The non-bonded distances (Table 2) result from both angular and conformational distortions. The major deformation from the standard tetrahedral value is at C(2), thus relieving the repulsions between the electronegative substituents at C(1) and C(3). The C–C–Cl angles average 110·2° (range 108·1–111·8°) while Cl–C–Cl angles in (I) are slightly smaller than tetrahedral values and range from 107·6 to 108·7° (av. 108·1°); the latter geometrical effect has also been noticed for F–C–F angles (Bart, Piccardi & Bassi, 1979).

Apart from the C(1)–C(2) bond distance, the average C–C length in 1,1,1,3,6,8,8,8-octachlorooctane is 1·528 (5) Å, close to the normal C(sp^3)–C(sp^3) single-bond length of 1·537 (5) Å (Sutton, 1965). The shorter C(1)–C(2) bond, 1·499 (7) Å, is noteworthy and is just significantly different both from the other C–C bond lengths in (I) and from the standard value. The effect may be due to the asymmetric substitution of electronegative groups in the molecule. In fact, it is well established that without steric interference, replacement in a structure B–A–C of C by a more electronegative atom causes the adjacent B–A bond to become shorter (Bent, 1960*c*). These variations in bond lengths are not accounted for in Schomaker & Stevenson's (1941) rule. The bond-shortening effect of electronegative substituents (Bent, 1960*b*,*c*,*d*) is such that halogen (X) derivatives show a progressive decrease in bond length C–X with increasing halogenation. Peters (1963) suggests that charge transfer from C to the electronegative substituent(s) is the primary cause of the observed progressive shortening of *all* bonds from a given C atom as the number of electronegative substituents on this atom increases. Although the effect is well documented in the case of F (Bent, 1960*a*,*c*; Peters, 1963; Hughes & Small, 1972), it is much less so for Cl. An average C–Cl bond distance of 1·767 (2) Å is given by Sutton (1965). However, this figure includes distances in many compounds containing two or more Cl atoms attached to the same C atom. The more representative structural data of saturated aliphatic compounds with extensive Cl substitution have been collected in Table 3. Available data suggest paraffinic C–Cl bond lengths for mono-, di-, tri- and tetrasubstituted C of 1·788, 1·772, 1·767 and 1·768 Å respectively. As expected, even lower values are found in each category in the presence of more highly electronegative substituents, such as F atoms (*cf.* CH_2Cl_2 and CH_2ClF; Cl_3CCCl_3 and fluorochloroethanes; $CClF_3$ and CCl_4). Duncan (1972), in a theoretical study of CH_3Cl, calculated a C–Cl distance of 1·778 (2) Å. Admittedly, considerably longer C–Cl distances are also known, as in the case of 2,6,11,15-tetrachloro-2,6,11,15-tetramethylhexadecane, 1·857 (7) Å (Mo & Sørum, 1968), and *trans*-2,5-dichloro-1,4-dioxane, 1·845 (6) Å for axial C–Cl (Altona, Knobler & Romers, 1963), which are, to date, unexplained. Also the C–halogen distances in allyl halides are unusually long (Bowen, Gilchrist & Sutton, 1955). As to 1,1,1,3,6,8,8,8-octachlorooctane, C–Cl bond distances at tri- and monosubstituted C differ significantly, namely 1·768 Å (average) (range 1·761–1·782 Å) and 1·800 (6) Å, respectively, and confirm the trend displayed in Table 3 for a variety of small molecules determined by various techniques, mainly in the gas phase. Further X-ray diffraction work seems appropriate here, in particular with regard to compounds such as (I), containing both mono- and polysubstituted C atoms.

The shortest non-bonded C···Cl, C···H, Cl···Cl, Cl···H and H···H distances (excluding 1,3 contacts) correspond to interaction energies of 0·0, 5·9, −1·7, 0·0 and −0·0 kJ mol^{-1}, respectively, as calculated by the method given by Eliel *et al.* (1965).

The arrangement of the chlorocarbon (I) in the unit cell is shown in Fig. 2. The shortest intermolecular distances for C···Cl, C···C, C···H, Cl···Cl, Cl···H and H···H are 3·76, >4·0, 3·81, 3·64, 2·79 and 3·43 Å as compared to the expected van der Waals distances of 3·50, 3·40, 2·90, 3·60, 3·00 and 2·40 Å, respectively. Noteworthy is the absence of C···C, C···H and H···H contacts, indicating that the packing arrangement is mainly governed by Cl and H atoms.

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Prediction of the Bilayer Packing in the Orthorhombic Phases of Deoxycholic Acid Molecules by van der Waals Energy Calculations

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Abstract

The orthorhombic crystal structures of the deoxycholic acid (DCA) canal complexes so far studied belong to the space group $P2_12_12_1$ and are characterized by the association through hydrogen bonds of the DCA molecules into pleated bilayers. The size and shape of the canals, covered by hydrophobic interior surfaces, and of the guest molecules which can be accommodated depend on the mutual positions along **b** and on the separation along **a** of two adjacent antiparallel bilayers. The van der Waals energy was com-

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