The Crystal and Molecular Structure of *cis*-1,2-Dichloroacenaphthene

By G. Bernardinelli and R. Gerdil*

*Départment de Chimie organique, Université de Genève, 30 quai de l'Ecole-de-Médecine,
1211 Geneva, Switzerland*

The crystal structure of *cis*-1,2-dichloroacenaphthene has been determined by the heavy-atom method and has been refined to $R = 0.049$. Space group $P2_1/c$, $Z = 4$, $a = 15.502$, $b = 6.247$, $c = 10.173$ Å, $\beta = 97.00°$. The naphthalene ring system is planar and the five-membered ring is twisted owing to the strong steric interaction between the *cis* Cl atoms. The short intramolecular $Cl\cdots Cl$ distance is only 3.126 Å and might be the cause of the unexpected difference observed in the ^{35}Cl n.q.r. frequencies between the *cis* and *trans* isomers.

Introduction

The configuration of isomeric vicinal dichloro derivatives of carbocyclic molecules has in general only a small effect on the ^{35}Cl quadrupole resonance frequencies, with the exception of *cis*- and *trans*-1,2-dichloroacenaphthene whose frequencies differ by 2.4 MHz (Ardalan, Lucken & Masson, 1973). Only the crystal structure of the *trans* isomer was known (Le Bihan & Perucaud, 1972) at the time of the n.q.r. measurements. The question of interest was whether the difference in the n.q.r. frequencies could be explained on the basis of the conformation of the *cis* isomer whose X-ray investigation is reported here. The atom-numbering system used is as follows:
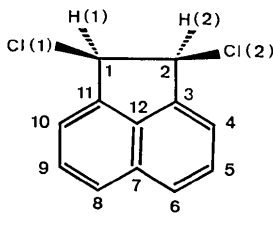
* Author to whom correspondence should be addressed.

The hydrogen atoms (not all shown) are labelled according to the numbering of the carbon atoms to which they are attached.

Experimental

The crystals are colourless tabular prisms with well developed {100} faces. The sample selected for X-ray analysis ($0.2 \times 0.2 \times 0.16$ mm) was sealed in a Lindemann capillary to prevent loss by sublimation. The lattice parameters and the intensities were measured at room temperature on an automatic four-circle Philips PW1100 diffractometer with a graphite monochromator and Mo $K\bar{\alpha}$ radiation ($\lambda = 0.7107$ Å).

Crystal data

$C_{12}H_8Cl_2$. Monoclinic; space group $P2_1/c$.
$a = 15.502$ (4), $b = 6.247$ (1), $c = 10.173$ (3) Å
$\beta = 97.00$ (4)°
$U = 977.8$ Å^3; $Z = 4$
$D_m = 1.510$; $D_x = 1.516$ g cm^{-3}.

2454 independent reflexions were scanned in the θ–2θ mode (scan speed 0.02° s^{-1}) within a parallelepiped limited by $h_{max} = 16$, $k_{max} = 6$, $l_{max} = 10$, and $\sin \theta/\lambda <$
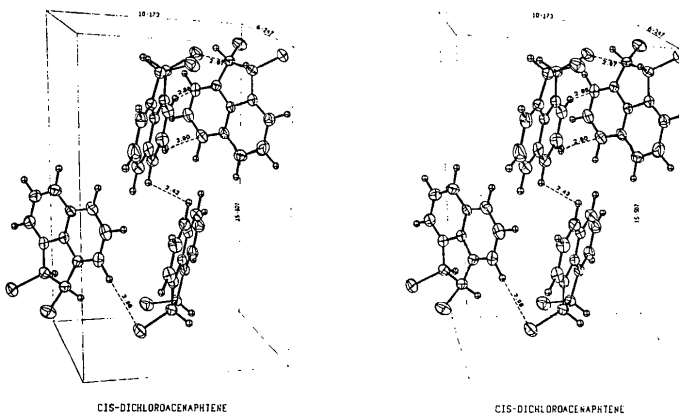

Fig. 1. Stereoscopic view of the unit cell showing the molecular packing. The origin is in the upper-right, rear corner. The upper-right molecule is the basic molecule with positions x, y, z. The thermal ellipsoids are plotted at 50% probability level and the distances are in Å.

0.8 Å^{-1}. A preliminary background measurement allowed the skipping of the unobserved reflexions, rated so when $I_{top} - 2\sqrt{I_{top}} < I_{bg}$, where I_{top} was the intensity (counts s^{-1}) measured at the top of the reflexion and I_{bg} was the mean intensity (counts s^{-1}) of both background measurements. Three monitor reflexions, measured at average intervals of 20 reflexions, were used to correct for intensity variations. No significant signs of crystal degradation were noticed. 1325 intensities were recorded of which 1320 were greater than 2σ in $|F|$. Lorentz and polarization corrections were applied as usual. The linear absorption coefficient μ is 6.1 cm^{-1} ($\mu R \sim 0.06$) and spherical absorption corrections only were applied.
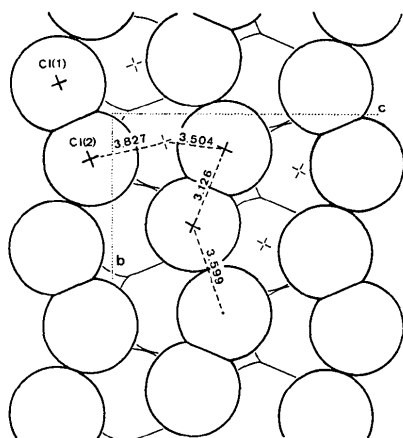

Fig. 2. Orthogonal (100) projection of the close packing of the chlorine atoms, showing the shortest Cl$\cdots$Cl distances in Å. The atoms are distributed in layers lying parallel to, and located 1.297 Å above and below the (100) planes. The interference radius of the atoms is equal to the van der Waals radius of Cl (1.80 Å). Strong non-bonded intramolecular interaction is evident from the overlapping of the circles. The hydrocarbon residues, attached to the chlorine atoms of the upper layer (thick lines), point upwards from the plane of the paper. The hydrocarbon residues of the adjacent lower layer point downwards. The centre of each of the chlorine atoms contained in one unit cell is depicted by a cross. The b and c axes are in the plane of the paper.

Determination and refinement of the structure

A sharpened Patterson function with the complete set of data revealed the positions of the two independent Cl atoms. An electron density map phased on the Cl atoms allowed the location of the C atoms. The structure was refined by full-matrix least-squares analysis with anisotropic temperature factors for the non-hydrogen atoms. Hydrogen atoms were located from a difference map and were included in the model during the latter stages but their positions were not refined. The condition for inclusion of a reflexion in a cycle of refinement was: $|F_o| > 2\sigma(F_o)$; if $|F_c| > |F_o|$ when $2\sigma(F_o) < |F_o| < 3\sigma(F_o)$. The final R, based on 1318 reflexions, was 0.049 with the weighting scheme: $\omega = 1.0$ for $F < 48$, $\omega = 0.67$ for F in the range 48–64, and $\omega = 0.25$ for $F > 64$. The final values of the positional and vibrational parameters are listed in Tables 1 and 2; the structure factors are listed in Table 3.

Table 2. *Positional parameters of the hydrogen atoms* ($\times 10^4$)

B is equal to the isotropic thermal parameter of the carbon atom to which H is bonded.

	x	y	z	B (Å^2)
H(1)	1198	2676	419	3.3
H(2)	904	−719	1147	3.5
H(4)	2168	−4051	2137	3.4
H(5)	3680	−4361	2782	3.5
H(6)	4720	−1822	1866	3.5
H(8)	4833	1499	678	3.0
H(9)	4101	4496	−675	3.4
H(10)	2563	4550	−1257	2.9

Thermal vibration analysis

The thermal vibration of the molecule was analysed in terms of the rigid-body tensors of translation (T), libration (L) and screw motion (S) (Schomaker & Trueblood, 1968). The fit of the rigid-body model including all atoms is fairly good with $\langle (\Delta U_{ij})^2 \rangle^{1/2} = 0.0046$ Å^2. The translational motion is small with

Table 1. *Final positional and thermal parameters (both $\times 10^4$) with standard deviations in parentheses*

Thermal parameters are given in the form $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cl(1)	837 (1)	1793 (2)	−1803 (1)	35 (1)	306 (4)	72 (1)	14 (2)	−16 (1)	47 (3)
Cl(2)	848 (1)	−2799 (2)	−580 (1)	38 (1)	207 (4)	118 (2)	−28 (2)	−22 (1)	−54 (3)
C(1)	1409 (3)	1502 (7)	−187 (4)	25 (2)	169 (12)	71 (4)	12 (6)	1 (4)	−11 (11)
C(2)	1303 (3)	−707 (7)	509 (4)	24 (2)	212 (13)	66 (4)	−24 (7)	14 (4)	−19 (11)
C(3)	2217 (3)	−1312 (7)	1085 (4)	26 (2)	181 (12)	57 (4)	−5 (6)	14 (4)	−7 (10)
C(4)	2536 (3)	−2980 (8)	1870 (4)	45 (2)	208 (14)	60 (5)	−2 (8)	13 (5)	31 (11)
C(5)	3448 (3)	−3123 (8)	2218 (5)	49 (3)	234 (15)	77 (5)	45 (9)	−14 (5)	42 (12)
C(6)	4016 (3)	−1665 (8)	1796 (5)	32 (2)	268 (15)	75 (5)	30 (9)	−7 (5)	−14 (13)
C(7)	3699 (3)	63 (7)	976 (4)	28 (2)	221 (13)	53 (4)	9 (7)	−4 (4)	−28 (11)
C(8)	4191 (3)	1710 (8)	447 (5)	25 (2)	264 (15)	79 (5)	−29 (8)	8 (4)	−57 (13)
C(9)	3784 (3)	3263 (8)	−343 (5)	38 (2)	228 (15)	89 (5)	−44 (8)	19 (5)	3 (13)
C(10)	2866 (3)	3345 (7)	−663 (4)	40 (2)	166 (12)	74 (5)	−21 (8)	5 (5)	15 (11)
C(11)	2378 (3)	1797 (7)	−151 (4)	31 (2)	172 (12)	57 (4)	5 (7)	7 (4)	−3 (10)
C(12)	2797 (3)	175 (7)	645 (4)	28 (2)	165 (12)	50 (4)	7 (6)	6 (4)	−10 (10)

r.m.s. amplitudes in the range 0·13–0·17 Å. The molecular libration is equally small; the main r.m.s. amplitude is 4·2° and the direction of its axis almost coincides with the orientation of the central bond C(7)–

C(12), making an angle of 4·8° with the latter. The next librational motions with r.m.s. amplitudes of 3·5° and 3·1°, are about axes that make angles of 17° with the respective axes of the inertial frame. The C–C and C–Cl

Table 3. *Observed and calculated structure factors*

Columns are *h*, *k*, *l*, $10|F_o|$, $10|F_c|$; reflexions removed from the final refinement are indicated by *.

[Table of structure factors: a large multi-column numerical listing of *h*, *k*, *l*, $10|F_o|$, $10|F_c|$ values — individual figures not legibly resolvable.]

bond lengths corrected for the effect of libration are on the average 0·006 (1) Å longer than the values in Table 4. The averaged absolute value of the correction for the bond angles is 0·21°, the largest correction being 0·35°.

Table 4. *Molecular parameters with the estimated standard deviations given in parentheses*

Bond distances (Å)			Bond angles (°)	
C(1)—Cl(1)	1·780 (4)		Cl(1)—C(1)—C(2)	116·0 (3)
C(1)—C(2)	1·569 (6)		Cl(1)—C(1)—C(11)	113·1 (3)
C(1)—C(11)	1·509 (5)		C(11)—C(1)—C(2)	104·8 (3)
C(2)—Cl(2)	1·801 (5)		Cl(2)—C(2)—C(1)	114·5 (3)
C(2)—C(3)	1·514 (5)		Cl(2)—C(2)—C(3)	109·6 (3)
C(3)—C(4)	1·368 (6)		C(1)—C(2)—C(3)	104·4 (4)
C(3)—C(12)	1·403 (5)		C(2)—C(3)—C(4)	132·1 (4)
C(4)—C(5)	1·419 (7)		C(2)—C(3)—C(12)	108·5 (4)
C(5)—C(6)	1·371 (7)		C(4)—C(3)—C(12)	119·4 (4)
C(6)—C(7)	1·416 (7)		C(3)—C(4)—C(5)	118·1 (4)
C(7)—C(8)	1·424 (6)		C(4)—C(5)—C(6)	122·6 (5)
C(7)—C(12)	1·400 (5)		C(5)—C(6)—C(7)	120·1 (5)
C(8)—C(9)	1·365 (7)		C(6)—C(7)—C(8)	127·6 (4)
C(9)—C(10)	1·421 (6)		C(8)—C(7)—C(12)	116·0 (4)
C(10)–C(11)	1·369 (6)		C(7)—C(8)—C(9)	120·4 (5)
C(11)–C(12)	1·406 (6)		C(8)—C(9)—C(10)	122·6 (5)
			C(9)—C(10)—C(11)	118·1 (4)
C(1)—H(1)	1·037 (4)		C(1)—C(11)—C(10)	132·2 (4)
C(2)—H(2)	0·950 (4)		C(1)—C(11)—C(12)	108·3 (4)
C(4)—H(4)	0·941 (5)		C(10)–C(11)–C(12)	119·4 (4)
C(6)—H(6)	1·089 (4)		C(3)—C(12)—C(7)	123·4 (4)
C(8)—H(8)	1·004 (4)		C(3)—C(12)—C(11)	113·1 (4)
C(9)—H(9)	0·994 (5)		C(7)—C(12)—C(11)	123·5 (4)
C(10)–H(10)	1·041 (5)			

Torsion angles (°)

Cl(1)–C(1)—C(2)—Cl(2)	14·8
C(11)–C(1)—C(2)—C(3)	9·1
C(1)—C(2)—C(3)—C(12)	−6·8
C(2)—C(3)—C(12)–C(11)	1·6
C(3)—C(12)–C(11)–C(1)	4·6
C(12)–C(11)–C(1)—C(2)	−8·5

Discussion

The bond lengths and angles are given in Table 4. The *cis* configuration produces a strong steric interaction between the chlorine atoms whose intramolecular approach, 3·126 Å, is much shorter than a normal van der Waals contact. Such a strong steric interaction has its equivalent only in a severely overcrowded molecule such as octachloronaphthalene (Gafner & Herbstein, 1963). The molecular strain is partially relieved by the splaying apart of the chlorine atoms,

which involves a twisting of the five-membered ring about an axis approximately oriented along the C(7)–C(12) direction. This distortion shifts C(1) by 0·131 Å from the best plane through the naphthalene ring system, whereas C(2) is displaced 0·028 Å in the opposite direction. Part of the strain is also reflected in the lengthening of the aliphatic C(1)–C(2) bond to 1·57 Å, compared with 1·50 Å in the *trans* isomer (Le Bihan & Perucaud, 1972). The aromatic part of the molecule is planar; the mean deviation of the ring atoms from the best plane is 0·005 (3) Å. The aromatic bond lengths are similar to those found in ace-naphthene and naphthalene (Ehrlich, 1957). Unfortunately a meaningful comparison of the remaining bond lengths with those of the *trans* isomer and those of *cis*-1,2-acenaphthenediol (Trotter & Mak, 1963) is impaired by the magnitude of the standard errors in the latter determinations.

A stereoscopic view of the packing is shown in Fig. 1, with a few short intermolecular contacts indicated. The chlorine atoms form layers parallel to (100), which itself belongs to the most developed form of the crystal. The distance between two adjacent layers is 2·593 Å and the shortest interatomic distance between layers is smaller than that expected for a van der Waals contact. The atomic arrangement within the layers and the relevant interatomic distances are shown in Fig. 2. The mean plane of the naphthalene ring system makes an angle of 86° with the layer of chlorine atoms.

It is possible that the difference in the ^{35}Cl n.q.r. frequencies between the *cis* and *trans* isomers resides in the strong non-bonded interaction between the chlorine atoms, rather than a hyperconjugative effect between the C–Cl bond and the aromatic residue [for a discussion see Ardalan & Lucken (to be published)].

References

ARDALAN, Z., LUCKEN, E. A. C. & MASSON, S. (1973). *Helv. Chim. Acta*, **56**, 1720–1724.
EHRLICH, H. W. W. (1957). *Acta Cryst.* **10**, 699–705.
GAFNER, G. & HERBSTEIN, F. H. (1963). *Nature, Lond.* **200**, 130–132.
LE BIHAN, M. T. & PERUCAUD, M. C. (1972). *Acta Cryst.* **B28**, 629–634.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
TROTTER, J. & MAK, T. C. W. (1963). *Acta Cryst.* **16**, 1032–1037.