# Insecticides. Part IV.† Crystal Structure of Heptachlor (Racemic 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene)

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The crystal structure of Heptachlor was determined by the symbolic addition procedure from three-dimensional diffractometer data with 1239 reflections. $Z = 8$ in the orthorhombic unit cell, space group, $Pbca$, $a = 1580 \cdot 0(1)$, $b = 1421 \cdot 5(1)$, and $c = 1266 \cdot 6(1)$ pm. The structure was refined by least squares to $R$ $0 \cdot 047$. The major difference between Aldrin, Endrin, and Heptachlor is that the nonchlorinated methanocyclohexane ring in the first two is replaced by a chlorocyclopentene system.

As part of an investigation to determine possible molecular criteria for the mode of action of cyclodiene insecticides,[1] the crystal structure of an active compound, heptachlor, has been determined.
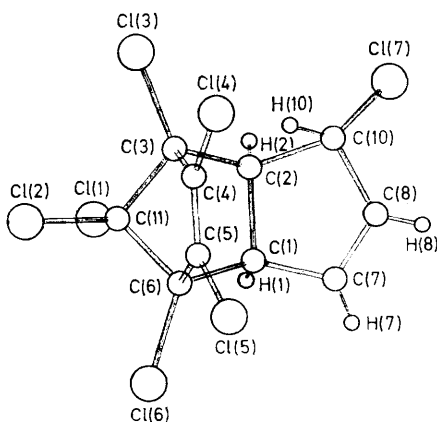


FIGURE 1 The structure viewed perpendicular to the plane of the gross molecule

## DISCUSSION

The molecule has an *endo*-configuration and is shown in Figures 1 and 2 where it is viewed perpendicular and parallel to the plane of the gross molecule.

The molecule has no symmetry, yet it crystallises out in a centric space group. Consequently both optical

isomers are present. The geometry of the hexachloro-cyclopentene ring about the C(1)–C(2) bond is similar to
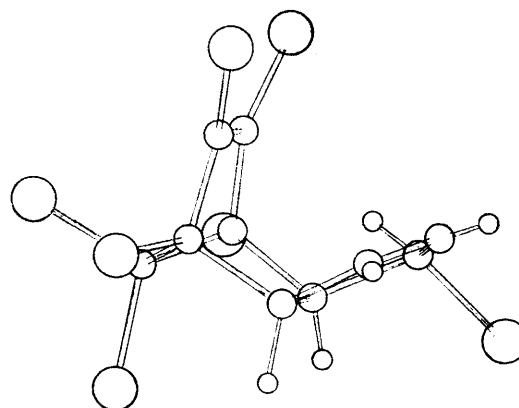


FIGURE 2 The structure viewed parallel to the plane of the gross molecule

that found in Endrin and Aldrin.[2] However, the major difference is that the non-chlorinated methanocyclo-hexane ring in Endrin (*endo*-) and methanocyclohexene in Aldrin (*exo*-) is replaced by the planar chlorocyclo-pentene group.

The interatomic distances (Table 1) are of the same order as for the other two cyclodienes. The C–Cl distance is influenced by the carbon environment (in

† Part III, ref. 2.

1 S. B. Solway, *Adv. Pest Control. Res.*, 1965, **6**, 85.

2 T. P. DeLacy and C. H. L. Kennard, *J.C.S. Perkin II*, 1972, 2153.

TABLE 1

Interatomic distances (pm) and angles (deg.) with
estimated standard deviations in parentheses

(a) Distances

| | | | |
|---|---|---|---|
| Cl(1)–C(11) | 177·6(5) | C(2)–C(10) | 157·2(7) |
| Cl(2)–C(11) | 177·4(5) | C(2)–H(2) | 97 |
| Cl(3)–C(3) | 174·8(5) | C(3)–C(4) | 151·9(8) |
| Cl(4)–C(4) | 171·0(5) | C(3)–C(11) | 156·0(7) |
| Cl(5)–C(5) | 170·0(6) | C(4)–C(5) | 132·9(8) |
| Cl(6)–C(6) | 176·5(5) | C(5)–C(6) | 152·2(7) |
| Cl(7)–C(10) | 181·5(5) | C(6)–C(11) | 156·2(7) |
| C(1)–C(2) | 157·3(7) | C(7)–C(8) | 132·4(8) |
| C(1)–C(6) | 156·0(7) | C(7)–H(7) | 80 |
| C(1)–C(7) | 149·8(8) | C(8)–C(10) | 148·4(8) |
| C(1)–H(1) | 113 | C(8)–H(8) | 82 |
| C(2)–C(3) | 155·4(7) | C(10)–H(10) | 88 |

(b) Angles

| | | | |
|---|---|---|---|
| C(2)–C(1)–C(6) | 102·2(3) | C(1)–C(6)–C(11) | 100·8(3) |
| C(2)–C(1)–C(7) | 103·8(3) | C(1)–C(6)–Cl(6) | 114·5(2) |
| C(2)–C(1)–H(1) | 107 | C(5)–C(6)–C(11) | 99·2(3) |
| C(6)–C(1)–C(7) | 114·8(3) | C(5)–C(6)–Cl(6) | 115·7(3) |
| C(6)–C(1)–H(1) | 113 | C(11)–C(6)–Cl(6) | 116·6(3) |
| C(7)–C(1)–H(1) | 114 | C(1)–C(7)–C(8) | 112·6(3) |
| C(1)–C(2)–C(3) | 103·4(3) | C(1)–C(7)–H(7) | 119 |
| C(1)–C(2)–C(10) | 105·8(3) | C(8)–C(7)–H(7) | 127 |
| C(1)–C(2)–H(2) | 116 | C(7)–C(8)–C(10) | 114·2(3) |
| C(3)–C(2)–C(10) | 114·9(3) | C(7)–C(8)–H(8) | 112 |
| C(3)–C(2)–H(2) | 115 | C(10)–C(8)–H(8) | 133 |
| C(10)–C(2)–H(2) | 102 | C(2)–C(10)–C(8) | 103·6(3) |
| C(2)–C(3)–C(4) | 107·7(3) | C(2)–C(10)–Cl(7) | 110·8(3) |
| C(2)–C(3)–C(11) | 100·6(3) | C(2)–C(10)–H(10) | 63 |
| C(2)–C(3)–Cl(3) | 115·1(3) | C(8)–C(10)–Cl(7) | 110·2(3) |
| C(4)–C(3)–C(11) | 98·6(3) | C(8)–C(10)–H(10) | 120 |
| C(4)–C(3)–Cl(3) | 115·9(3) | Cl(7)–C(10)–H(10) | 129 |
| C(11)–C(3)–Cl(3) | 116·7(3) | Cl(1)–C(11)–C(3) | 113·5(3) |
| Cl(4)–C(4)–C(3) | 124·5(3) | Cl(1)–C(11)–C(6) | 113·8(3) |
| Cl(4)–C(4)–C(5) | 126·8(3) | Cl(1)–C(11)–Cl(2) | 107·5(2) |
| C(3)–C(4)–C(5) | 108·4(3) | C(3)–C(11)–C(6) | 92·9(3) |
| Cl(5)–C(5)–C(4) | 128·5(3) | C(3)–C(11)–Cl(2) | 114·3(3) |
| Cl(5)–C(5)–C(6) | 123·7(3) | C(6)–C(11)–Cl(2) | 114·7(3) |
| C(4)–C(5)–C(6) | 107·3(3) | | |
| C(1)–C(6)–C(5) | 108·0(3) | | |

decreasing length): (a) 181·5 pm; the only C–Cl link in
the planar chlorocyclopentene group Cl(7)–C(10), is
significantly longer than the normal value (172 pm);
(b) 177·3 pm (mean); two chlorines connected to the
same carbon atom (177·4, 177·6, Heptachlor; 176·6,
177·5, Endrin; 176·5, 178·4, Aldrin); (c) 175·7 pm
(mean); one chlorine connected to an $sp^3$ carbon atom
174·8, 176·5, Heptachlor; 176·2, 176·5, Endrin; 174·8,
175·3, Aldrin); (d) 170·1 pm (mean); one chlorine
connected to an $sp^2$ carbon atom (170·0, 171·0, Hepta-
chlor; 169·4, 169·5, Endrin; 170·3, 170·6, Aldrin).

Figure 3 shows the packing arrangement of the racemic
Heptachlor molecules in the crystal.

EXPERIMENTAL

*Crystal Data.*—$C_{10}H_5Cl_7$, $M = 373·3$. Orthorhombic,
$a = 1580·0(1)$, $b = 1421·5(1)$, $c = 1226·6(1)$ pm, $U =$
2·755 nm³, $D_m = 1·82$ (by flotation), $Z = 8$, $D_c = 1·80$,
$F(000) = 1472$. Mo-$K_\alpha$ radiation, $\lambda = 71·07$ pm;
$\mu$(Mo-$K_\alpha$) = 14·01 cm⁻¹. Space group, $Pbca$ ($D_{2h}^{15}$, No. 61).

* See note about Supplementary Publications in Notice to
Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

³ H. C. Freeman, J. M. Guss, C. E. Nockolds, R. Page, and
A. Webster, *Acta Cryst.*, 1970, *A*, **26**, 149.
⁴ A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.
⁵ A. D. Rae and A. B. Blake, *Acta Cryst.*, 1966, **20**, 566.
⁶ ' International Tables for *X*-Ray crystallography,' vol. III,
Kynoch Press, Birmingham, 1962.

Intensity data ($h0$—$12l$; $hk0$—$10$) were collected from
two crystals by use of a PDP 8/S controlled Supper equi-
inclination diffractometer.³ Intensities were measured by
the ω scan method at a rate dependent on peak intensity to
give constant counting statistics. After correcting for
Lorentz and polarisation factors, the two data sets were
scaled together ⁴·⁵ to give 2570 independent reflections, of
which 1239 were considered observed, having $I > 2·5\sigma(I)$.
Corrections were made for absorption on the two crystals by
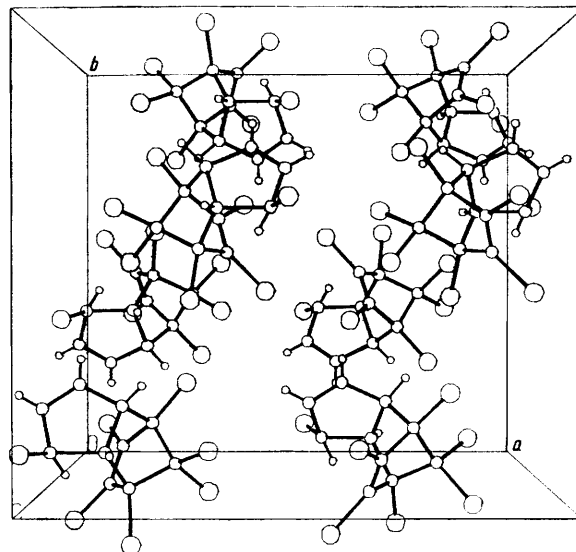use of Gaussian integration with grid size $4 \times 4 \times 4$.



FIGURE 3 Packing in a unit cell viewed perpendicular
to $c$

*Structure Determination.*—The structure was determined
by symbolic addition on three hundred reflections using the
FAME, MAGIC, LINK, and SYMPL set of programs. All
non-hydrogen atoms were located from the $E$ map. Full-
matrix least-squares refinement reduced the residual
$R$ from an initial value of 0·238 to 0·066. A difference-
Fourier synthesis revealed the positions of the hydrogen
atoms. Further refinement reduced $R$ to 0·047, and the
weighted $R'$ [$= \Sigma w ||F_o| - |F_c||^2 / \Sigma w |F_o|^2]^{\frac{1}{2}}$ to 0·031. A
plot of $I_c/I_o$ vs. $I_o$ indicated that no reflections were
seriously affected by extinction. A final difference-Fourier
synthesis did not reveal any unexplainable electron density.
The atomic and thermal parameters are listed in Table 2.
Observed and calculated structure factor amplitudes are
listed in Supplementary Publication No. SUP 20716 (7 pp.,
1 microfiche).* The scattering factors used were those for
chlorine, carbon,⁶ and hydrogen.⁷ No correction was
applied for anomalous dispersion. All calculations were
carried out with local versions of standard programs ⁸ on a
CDC 3600 computer.

*X*-Ray data were recorded at the University of Sydney
on an automated diffractometer which is supported by a grant

⁷ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem.
Phys.*, 1965, **42**, 3175.
⁸ FAME, MAGIC LINK, SYMPL, Symbolic addition pro-
grams, Dewar and Stone, modified by R. C. Seccombe, 1970;
PREDAP, Structure factor; FORDAP, A. Zalkin and R. J.
Dellaca; ORFLS, Full-matrix least-squares, W. R. Busing,
K. O. Martin, and H. A. Levy, 1964; PTPEDIT, Editing of
data, and absorption correction, University of Sydney.

TABLE 2

Atomic and thermal parameters, with their estimated standard deviations in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ | $B/Å^2$ |
|---|---|---|---|---|
| Cl(1) | 0·1628(1) | −0·1148(1) | 0·3631(1) | * |
| Cl(2) | 0·1730(1) | −0·0012(1) | 0·1708(1) | |
| Cl(3) | 0·3041(1) | 0·0755(1) | 0·3762(1) | |
| Cl(4) | 0·4376(1) | 0·0616(1) | 0·1682(1) | |
| Cl(5) | 0·3897(1) | −0·1330(1) | 0·0174(1) | |
| Cl(6) | 0·2201(1) | −0·2355(1) | 0·1228(1) | |
| Cl(7) | 0·4846(1) | −0·1288(1) | 0·5196(1) | |
| C(1) | 0·3286(3) | −0·2015(3) | 0·2986(4) | |
| C(2) | 0·3524(3) | −0·1131(3) | 0·3696(4) | |
| C(3) | 0·3152(3) | −0·0296(3) | 0·3035(4) | |
| C(4) | 0·3638(3) | −0·0229(4) | 0·1907(5) | |
| C(5) | 0·3447(3) | −0·0974(4) | 0·1363(4) | |
| C(6) | 0·2812(3) | −0·1560(3) | 0·2003(4) | |
| C(7) | 0·4127(4) | −0·2445(4) | 0·2712(5) | |
| C(8) | 0·4769(4) | −0·1972(4) | 0·3134(5) | |
| C(10) | 0·4517(3) | −0·1140(4) | 0·3789(4) | |
| C(11) | 0·2322(3) | −0·0751(3) | 0·2589(4) | |
| H(1) † | 0·286 | −0·248 | 0·351 | 3·0 |
| H(2) | 0·335 | −0·115 | 0·446 | 3·0 |
| H(7) | 0·414 | −0·296 | 0·246 | 3·0 |
| H(8) | 0·522 | −0·225 | 0·306 | 3·0 |
| H(10) | 0·429 | −0·065 | 0·347 | 3·0 |

* Anisotropic thermal parameters $(\times 10^4)$ in the form: $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.
† These parameters were not refined.

TABLE 2 (Continued)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Cl(1) | 23(1) | 80(1) | 67(1) | −1(1) | 12(1) | 7(1) |
| Cl(2) | 32(1) | 60(1) | 62(1) | 17(1) | −11(1) | 3(1) |
| Cl(3) | 47(1) | 39(1) | 66(1) | 16(1) | −10(1) | −22(1) |
| Cl(4) | 39(1) | 44(1) | 96(1) | −19(1) | 5(1) | 18(1) |
| Cl(5) | 43(1) | 60(1) | 43(1) | 11(1) | 14(1) | −2(1) |
| Cl(6) | 35(1) | 51(1) | 75(1) | −12(1) | −20(1) | −8(1) |
| Cl(7) | 41(1) | 47(1) | 60(1) | −2(1) | −21(1) | 4(1) |
| C(1) | 21(2) | 28(3) | 39(5) | 5(2) | −6(3) | −7(3) |
| C(2) | 28(3) | 29(3) | 32(4) | −4(2) | −1(3) | 2(3) |
| C(3) | 26(3) | 35(3) | 39(5) | 3(2) | 6(3) | −3(3) |
| C(4) | 24(3) | 27(3) | 58(5) | 2(2) | −5(3) | 9(3) |
| C(5) | 28(3) | 28(3) | 46(5) | 2(3) | −5(3) | 3(3) |
| C(6) | 32(3) | 13(3) | 38(4) | −11(2) | 1(3) | −12(3) |
| C(7) | 37(3) | 38(3) | 52(5) | −4(3) | −22(3) | −6(3) |
| C(8) | 40(3) | 44(3) | 47(4) | 31(2) | 0(3) | 16(4) |
| C(10) | 24(3) | 44(3) | 49(4) | 21(2) | −22(3) | 4(3) |
| C(11) | 20(3) | 47(3) | 31(4) | 3(3) | 1(3) | 2(3) |