Acaricides. Part I. Crystal Structure of Pentac [Synclinal 1,1′,2,2′,3,3′,-4,4′,5,5′-Decachloro-1,1′-bis(cyclopenta-2,4-dienyl)]

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The crystal structure of Pentac has been determined by the symbolic addition procedure from 1 543 reflections collected on a diffractometer. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 854.9(1)$, $b = 1127.9(2)$, $c = 1843.7(4)$ pm, $\beta = 113.38(2)°$. The structure was refined by least-squares to R 0.075. In the molecule the chlorine atoms connected at the 1-positions in the planar cyclopentadiene rings are mutually synclinal. The angle between the normals to these rings is 61.9°.

PENTAC was first made in 1955 [1] by treating hexachlorocyclopentadiene with copper(I) chloride in 80% ethanol at 298 K. In 1964 [2] Pentac was used for the control of normally resistant mites on roses, and was reported to have a low mammalian toxicity and lack of phytotoxicity. It resisted attempts [1] to effect a Diels–Alder reaction with maleic anhydride and other dienophiles and an explanation was given in terms of the steric requirements of the diene. In analysing the various conformers it was felt that the one reported here (synclinal or *cis*-) was probably incapable of existence. A more recent investigation [3] of isomeric polychlorofulvalenes by use of u.v. and ^{35}Cl n.q.r. spectra indicates that the cyclopentadienyl ring fragments probably interact 'face-to-face'. The structure of the title compound was determined in order to obtain further information on the stereochemistry of halogenated hydrocarbons.[4]

The stereochemistry of Pentac is indicated in Figure 1. Bond distances and angles in the cyclopentadiene rings are similar to those found [5] in octachloropentafulvalene [2,2′,3,3′,4,4′,5,5′-octachloro-1,1′-bis(cyclopenta-2,4-dienylidene)]. The rings, including the chlorine atoms, are essentially planar, σ for the equation of the plane being 75 and 59 pm for the two rings. All the chlorine atoms except Cl(4) (14 pm) are directed away from the other cyclopentadiene plane.

As recorded before,[6] the C–Cl distance is influenced by the carbon environment: (*a*) Cl–C link in the planar chlorocyclopentene group in Heptachlor (181.5 pm) is of the same order as that found for Cl(1)–C(1) (180 pm) and Cl(6)–C(6) (181 pm); (*b*) one chlorine connected to an sp^2 carbon atom in heptachlor (170.0 and 171.0), Endrin [7]

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[1] E. T. McBee, J. D. Idol, and C. W. Roberts, *J. Amer. Chem. Soc.*, 1955, **20**, 4375.

[2] W. W. Allen, A. K. Ota, and R. D. Gehring, *J. Econ. Entomol.*, 1964, **57**, 187.

[3] R. M. Smith and R. West, *J. Org. Chem.*, 1970, **35**, 2681.

[4] G. Smith, C. H. L. Kennard, and A. H. White, *J.C.S. Perkin II*, 1976, 614.

[5] H. L. Ammon, G. L. Wheeler, and I. Agranat, *Tetrahedron*, 1973, **29**, 2695.

[6] K. G. Shields and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 1374.

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

(169.4 and 169.5), Aldrin (170.3 and 170.6 pm) is comparable to (170, 172, 168, and 169; 168, 172, 167, and 168 pm) in Pentac. The C–C distances (within each of the two types) are quite similar. Olefinic bonds for Heptachlor (132.9), Endrin (133), Aldrin (131) are of the same order as C(2)–C(3) (128), C(4)–C(5) (134), C(7)–C(8) (131), and C(9)–C(10) (131 pm). Other ring C–C distances in Pentac are similar to those found in the cyclopentene rings of the cyclodiene compounds.

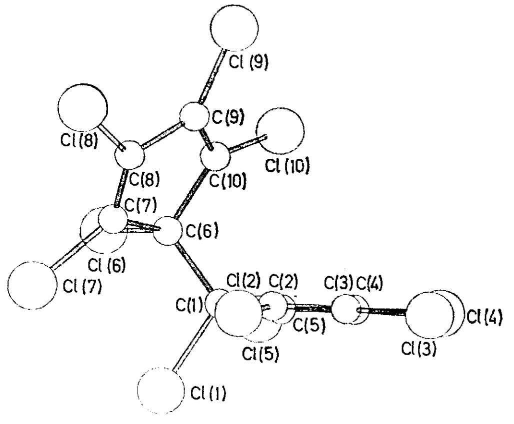

FIGURE 1 The structure viewed perpendicular to the plane C(1), C(6), C(10)

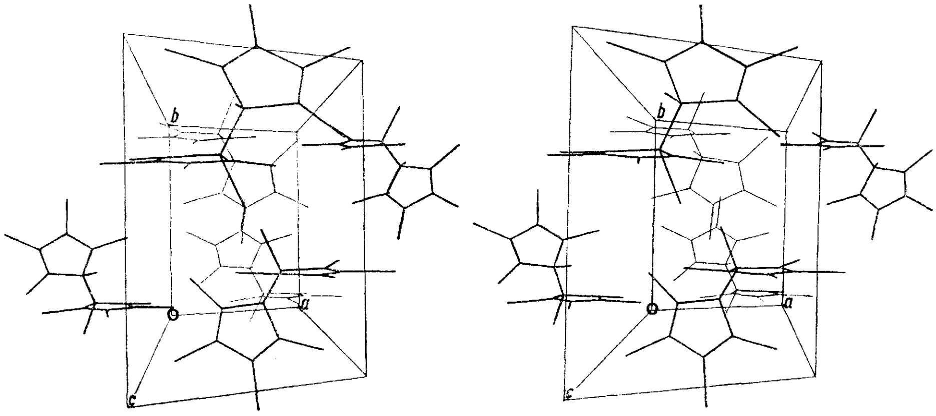

FIGURE 2 Stereoscopic view of the packing viewed perpendicular to the *ab* plane

The internal angles within the cyclopentadiene ring at C(1) and C(6) are compressed [101.2(8) and 102.2(10)°], in order to satisfy requirements of the five-membered diene planar ring. However, of all carbon atoms these have the greatest deviation from the plane of the ring (98 and 88 pm).

The conformation of the chlorine atoms according to the torsion angle about the 1-positions in both rings is synclinal.[8] The angle between the normals to these two rings is 61.9°. The interatomic Cl ··· Cl distances between rings are not less than 325 pm.

The packing of Pentac in the unit cell is indicated in Figure 2.

EXPERIMENTAL

Crystal Data.—$C_{10}Cl_{10}$, $M = 474.6$. Monoclinic, $a = 854.9(1)$, $b = 1\,127.9(2)$, $c = 1\,843.7(4)$ pm, $\beta = 113.38(2)°$, $\mu = 0.1632$ nm^3, $D_m = 1.94$ (by flotation), $Z = 4$, $D_c = 1.931$ g cm^{-3}, $F(000) = 920$. Cu-K_α radiation, $\lambda = 154.18$ pm; μ(Cu-K_α) = 154.5 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}, No. 14). The commercial product was recrystallised as pale yellow crystals from chloroform, m.p. 395—396 K. Intensity data were collected from one crystal up to 2θ 96° by use of a PDP 8 controlled Hilger and Watts four-circle *X*-ray diffractometer, with the Hilger data collection scheme.

1 046 Reflections with $F > 2.5\sigma(F)$ were considered observed out of 1 534 collected. Absorption corrections were applied.

Structure Determination.—The structure was determined by symbolic addition on 250 reflections by use of the FAME, MAGIC, LINK, and SYMPL set of programs. Eight chlorine atoms were located from an *E* map. The first structure-factor calculation gave *R* 0.452, and all the other atoms were found after two cycles of electron-density synthesis–structure-factor calculations. Five full-matrix least-squares refinement cycles reduced *R* from an initial 0.244 to 0.075 and the weighted factor R^1 to 0.067. Plots of

TABLE 1

Interatomic distances (pm) and angles (°), with estimated standard deviations in parentheses. Values in square brackets are taken from ref. 5 for octachloropentafulvalene

(*a*) Distances

Cl(1)–C(1)	180(1)	Cl(6)–C(6)	181(2)
Cl(2)–C(2)	170(2)	Cl(7)–C(7)	169(2) [171.0(3)]
Cl(3)–C(3)	172(1)	Cl(8)–C(8)	172(2) [169.4(3)]
Cl(4)–C(4)	168(2)	Cl(9)–C(9)	167(2) (169.6(3)]
Cl(5)–C(5)	169(2)	Cl(10)–C(10)	168(1) [170.7(2)]
C(1)–C(2)	152(2)	C(6)–C(7)	151(2) [148.0(3)]
C(1)–C(5)	151(2)	C(6)–C(10)	152(2) [146.6(4)]
C(2)–C(3)	128(2)	C(7)–C(8)	131(3) [133.3(4)]
C(3)–C(4)	150(2)	C(8)–C(9)	147(2) [146.5(3)]
C(4)–C(5)	134(2)	C(9)–C(10)	131(2) [134.7(4)]
C(1)–C(6)	154(2)		
		Cl(3)–Cl(6)	347
Cl(1)–Cl(2)	342	Cl(5)–Cl(6)	328
Cl(1)–Cl(5)	340	Cl(6)–Cl(7)	344
Cl(1)–Cl(6)	325	Cl(6)–Cl(10)	339
Cl(1)–Cl(10)	327	Cl(8)–Cl(9)	334
Cl(2)–Cl(3)	335	Cl(9)–Cl(10)	332
Cl(2)–Cl(8)	341		

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[8] Rule E 6.6, *J. Org. Chem.*, 1970, **35**, 2861.

TABLE 1 (*Continued*)

(*b*) Angles

C(1)–C(2)–C(3)	110.1(10)
C(2)–C(3)–C(4)	111.4(10)
C(3)–C(4)–C(5)	106.0(10)
C(4)–C(5)–C(1)	111.2(10)
C(5)–C(1)–C(2)	101.2(8)
C(1)–C(6)–C(10)	116.8(10)
C(1)–C(6)–C(7)	112.7(10)
Cl(1)–C(1)–C(5)	107.7(8)
Cl(1)–C(1)–C(2)	108.3(8)
Cl(1)–C(1)–C(6)	111.5(7)
Cl(2)–C(2)–C(1)	124.8(7)
Cl(2)–C(2)–C(3)	125.0(9)
Cl(3)–C(3)–C(2)	129.5(11)
Cl(3)–C(3)–C(4)	119.0(9)
Cl(4)–C(4)–C(3)	126.1(9)
Cl(4)–C(4)–C(5)	127.8(11)
Cl(5)–C(5)–C(4)	124.5(10)
Cl(5)–C(5)–C(1)	124.3(8)
C(6)–C(7)–C(8)	108.2(11) [109.1(2)]
C(7)–C(8)–C(9)	111.5(11) [108.6(2)]
C(8)–C(9)–C(10)	109.9(9) [108.9(2)]
C(9)–C(10)–C(6)	109.9(9) [108.6(2)]
C(10)–C(6)–C(7)	102.2(10) [104.5(2)]
C(6)–C(1)–C(5)	116.6(9)
C(6)–C(1)–C(2)	111.0(8)
Cl(6)–C(6)–C(10)	106.2(8)
Cl(6)–C(6)–C(7)	108.5(8)
Cl(6)–C(6)–C(1)	109.8(8)
Cl(7)–C(7)–C(6)	124.7(10) [124.8(2)]
Cl(7)–C(7)–C(8)	127.1(10) [123.9(2)]
Cl(8)–C(8)–C(7)	125.1(11) [128.1(2)]
Cl(8)–C(8)–C(9)	123.3(11) [123.1(2)]
Cl(9)–C(9)–C(8)	123.4(8) [123.8(2)]
Cl(9)–C(9)–C(10)	128.5(8) [127.2(2)]
Cl(10)–C(10)–C(9)	125.2(9) [123.4(2)]
Cl(10)–C(10)–C(6)	124.9(8) [126.1(2)]

I_c/I_0 *vs.* I_0 and sin θ/λ showed that three low-angle reflections were seriously affected by extinction and were removed before the last cycle of refinement. A final difference-Fourier synthesis had no unexplainable electron-density concentrations.

Atomic parameters are listed in Table 2. Observed and calculated structure amplitudes and thermal parameters are listed in Supplementary Publication, No. SUP 21643 (8 pp.).*

Scattering factors for chlorine and carbon were taken from ref. 9. No correction was applied for the effects of anomalous dispersion.

TABLE 2

Atomic parameters ($\times$ 10^4), with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cl(1)	5 562(5)	313(3)	3 341(2)
Cl(2)	4 175(5)	1 544(3)	4 676(2)
Cl(3)	7 954(5)	1 605(4)	6 215(2)
Cl(4)	11 080(5)	1 624(4)	5 573(3)
Cl(5)	9 446(6)	1 442(4)	3 613(3)
Cl(6)	5 892(6)	2 723(4)	2 450(2)
Cl(7)	8 333(6)	4 329(4)	4 101(3)
Cl(8)	5 190(8)	5 910(4)	4 242(3)
Cl(9)	1 492(7)	4 511(5)	3 302(3)
Cl(10)	2 161(6)	1 969(5)	2 563(3)
C(1)	6 401(18)	1 672(13)	3 866(8)
C(2)	6 110(18)	1 662(13)	4 627(9)
C(3)	7 542(22)	1 659(14)	5 224(9)
C(4)	9 009(18)	1 645(13)	4 972(10)
C(5)	8 320(19)	1 602(14)	4 183(10)
C(6)	5 571(20)	2 762(15)	3 362(8)
C(7)	6 275(22)	3 913(15)	3 779(9)
C(8)	5 006(25)	4 533(14)	3 810(9)
C(9)	3 366(17)	3 927(12)	3 402(8)
C(10)	3 663(16)	2 919(13)	3 128(7)

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968, p. 202.