Insecticides. Part V.[1] Crystal Structures of β-(*eeeeee*)-1,2,3,4,5,6-Hexachlorocyclohexane and γ-(*aaaeee*)-1,2,3,4,5,6-Hexachlorocyclohexane (Lindane) (Redeterminations)

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The crystal structure of β-1,2,3,4,5,6-hexachlorocyclohexane was redetermined from three-dimensional visually estimated data (285 reflections). Crystals are cubic, space group *Pa*3, with $Z = 4$, $a = 1\ 008(1)$ pm. The structure was refined by least squares to *R* 0.108. The crystal structure of the γ-isomer was redetermined from three-dimensional diffractometer data (995 reflections). Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 850.2(1)$, $b = 1\ 025.1(1)$, $c = 1\ 391.4(2)$ pm, $\beta = 121.26\ (1)°$. The structure was refined by least-squares to *R* 0.045. The determinations reconfirmed the assignments of (*eeeeee*) to the β- and (*aaaeee*) to the γ-isomer.

As a further extension of an investigation of the stereochemistry of polychlorinated insecticides, the crystal structures of two isomers β- and γ-1,2,3,4,5,6-hexachlorocyclohexane were redetermined in order to provide more accurate information about their molecular conformation.

The isomers are members of a series of seven known configurational isomers and were prepared by the chlorination of benzene in the presence of u.v. light.[2] The crystal structure of the β-form was determined in 1928.[3] The γ-isomer is well known as lindane[4] or Gammexane and is the only member of the isomeric series possessing useful insecticidal properties.[5] The structure was first determined in 1950,[6] and although a redetermination was reported at a meeting,[7] there was no published record.

DISCUSSION

In the 1928 determination[3] of the β-isomer, only the chlorine parameters were found with any degree of certainty. If the most symmetrical arrangements are considered, the (*aaaaaa*) would have three chlorine atoms above and three below the chair cyclohexane ring. However, the 1,3,5- and 2,4,6-triaxial arrangements are sterically unstable and this conformation would undergo ring inversion into (*eeeeee*).

The major differences between the current results and the 1950 determination[6] of the γ-isomer (structure) are: (1) the regularity of the Cl–C and C–C bond distances [however mean distances compare favourably, Cl–C, 179.1(7), 178; C–C 152.9(9), 155 pm]; (2) the regularity of the Cl–C–C angles and the other C–C–C angles; (3) the decrease in C(1)–C(2)–C(3) from 123 to 116.0(3)° [The cause of the apparent deviation from the regular tetrahedral angle is due to the close proximity of Cl(1) to Cl(3), because of the 1,2,3-triaxial arrangement. Van Vloten *et al.*[6] suggested that the desirability of a three-dimensional structure determination to confirm the existence of this effect.]; and (4) the location of hydrogen atoms.

Both the structures of the δ-(*aeeeee*)[8] and ε-(*aeeaee*)[9] isomers have been reported. No co-ordinates or bond distances were given for the δ-isomer. Probably before comparing results for the ε-isomer with the current results, it would be necessary to refine its atomic parameters.

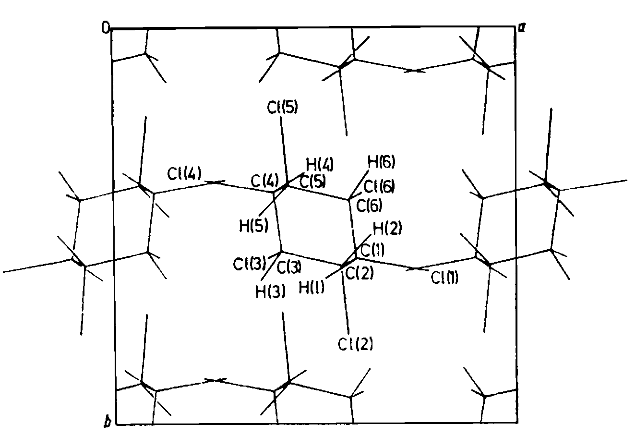

FIGURE 1. Packing of the β-isomer in a unit cell

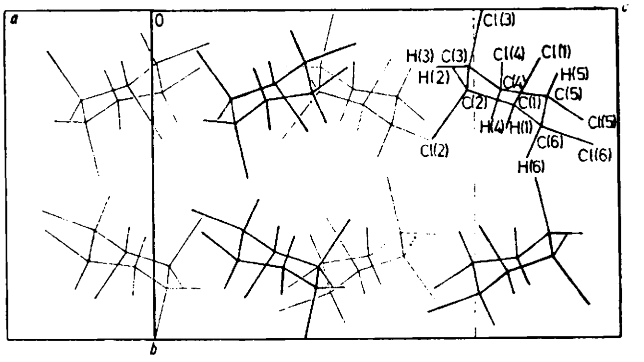

FIGURE 2 Packing of the γ-isomer in a unit cell viewed perpendicular to the *a* axis

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[6] G. W. van Vloten, Ch. A. Kruissink, B. Strijk, and J. M. Bijvoet, *Acta. Cryst.*, 1950, **3**, 139.

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The Cl–C distance in both the β- and γ-isomers are 179(1) and 179.1(7) pm respectively. In previous studies [1] of chlorinated cyclodienes it was found that this distance is influenced by the carbon environment. The distance found is greater than that for one chlorine connected to an sp^3 carbon atom in a boat conformation of a cyclohexane ring (175.7 pm mean).

Figures 1 and 2 show the packing arrangement of the two isomers. In both cases only van der Waals interactions appear to hold the molecules together in the crystal.

EXPERIMENTAL

β-(eeeeee)-1,2,3,4,5,6-*Hexachlorocyclohexane*.— *Crystal data*. $C_6H_6Cl_6$, $M = 290.8$, Cubic. $a = 1\,008(1)$ pm.,[10] $U = 1.024$ nm^3, $D_m = 1.87$ (by flotation), $Z = 4$, $D_c = 1.89$ g cm^{-3}, $F(000) = 576$. Cu-K_α radiation, $\lambda = 154.18$ pm; μ(Cu-K_α) = 147.7 cm^{-1}. Space group $Pa3$ (T_h^6, No. 205).

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

(*a*) β-Isomer

	This work			From ref. 3		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Cl(1)	3 856(3)	2 232(3)	819(3)	3 900	2 200	850
C(1)	4 172(11)	3 973(11)	646(11)	4 210	3 970	680
H(1)	3 684(17)	4 730(17)	1 473(17)			

(*b*) γ-Isomer

	This work			From ref. 6		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Cl(1)	39(2)	3 591(2)	3 194(1)	20	3 530	3 200
Cl(2)	2 114(2)	1 202(2)	1 553(1)	2 100	1 220	1 560
Cl(3)	3 372(2)	5 022(2)	3 005(2)	3 390	5 030	3 010
Cl(4)	7 114(2)	3 504(2)	4 648(2)	7 160	3 500	4 670
Cl(5)	5 757(2)	3 295(2)	937(1)	5 760	3 310	940
Cl(6)	1 477(3)	972(2)	4 737(2)	1 470	1 000	4 740
C(1)	992(8)	2 213(6)	2 877(5)	1 000	2 170	2 900
C(2)	1 801(8)	2 644(6)	2 171(5)	1 860	2 580	2 210
C(3)	3 670(8)	3 343(6)	2 810(5)	3 680	3 390	2 710
C(4)	4 976(8)	2 649(7)	3 913(5)	4 980	2 810	3 890
C(5)	4 117(8)	2 457(6)	4 622(5)	4 080	2 390	4 580
C(6)	2 475(9)	1 545(6)	3 958(5)	2 580	1 449	3 990
H(1)	−203(10)	1 486(7)	2 363(6)			
H(2)	868(9)	3 322(7)	1 553(6)			
H(3)	4 174(10)	3 306(7)	2 311(6)			
H(4)	5 369(10)	1 731(7)	3 774(6)			
H(5)	3 797(9)	3 367(7)	4 811(6)			
H(6)	3 000(10)	594(8)	3 803(6)			

Photographic intensity data ($h0$—$6l$) were collected by use of a Stoe equi-inclinational Weissenberg goniometer. Intensities were estimated visually up to 2θ 123°. After data reduction and averaging of equivalents (hkl, klh, lhk), a final set of 285 unique reflections were obtained and used in the refinement. The reported [3] chlorine and carbon co-ordinates gave an initial R of 0.265 and their positions were verified in an initial electron-density synthesis. Full-matrix anisotropic least-squares refinement reduced R to 0.108 and the weighted factor $R'\{= [\Sigma w|F_o| - |F_c|^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$ to 0.114. Hydrogen atom positions were located in a difference Fourier synthesis at R 0.112. A final difference-Fourier showed no significant features.

γ-(aaaeee)-1,2,3,4,5,6-*Hexachlorocyclohexane*.— *Crystal data*. $C_6H_6Cl_6$, $M = 290.8$. Monoclinic, $a = 850.2(1)$, $b = 1\,025.1(1)$, $c = 1\,391.4(2)$ pm, $\beta = 121.26(1)°$, $U = 1.037$ nm^3, $D_m = 1.85$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.86$ g cm^{-3}. $F(000) = 576$. Mo-K_α radiation (graphite monochromator), $\lambda = 71.07$ pm; μ(Mo-K_α) = 15.83 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5, No. 14).

Intensity data were collected by use of a Syntex $P\bar{1}$ four-circle computer-controlled diffractometer. Of a possible 1 303 reflections 995 were considered observed up to 2θ 50°. The published co-ordinates [6] gave an R 0.290 for all carbon and chlorine atoms. The structure was verified by an electron-density synthesis. Full-matrix least-squares anisotropic refinement reduced R to 0.045 and R' to 0.053. All hydrogen-atom positions were located in a difference-Fourier synthesis at R 0.12 and these were given isotropic temperature factors equal to those of the adjacent bonded atom. Adjustment of the weighting scheme was applied after analysis of the results. A final difference-Fourier revealed no unexplained electron density.

All atomic parameters are listed in the Table. Thermal parameters, interatomic distances and angles, and observed and calculated structure factor amplitudes for both compounds are listed in Supplementary Publication No. SUP 21583 (7 pp., 1 microfiche).* Scattering factors used for chlorine and carbon were taken from ref. 11, and for hydrogen from ref. 12. All calculations were carried out with local versions of standard programmes on a CYBER 76 computer. No corrections were applied for absorption, extinction, or anomalous dispersion.

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

‡ Previous results: $a = 852$, $b = 1\,027$, $c = 1\,394$ pm, $\beta = 121.27°$ (ref. 6); and $a = 848.8$, $b = 1\,023.4$, $c = 1\,391.2$ pm, $\beta = 121.24°$ (ref. 7).

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