Acta Cryst. (1981). B**37**, 2237–2239

1,2,3,5,7,8-Hexachloro-1,3a,4,5,6,6a-hexahydro-1,4-ethenopentalene (α-Chlordene)*

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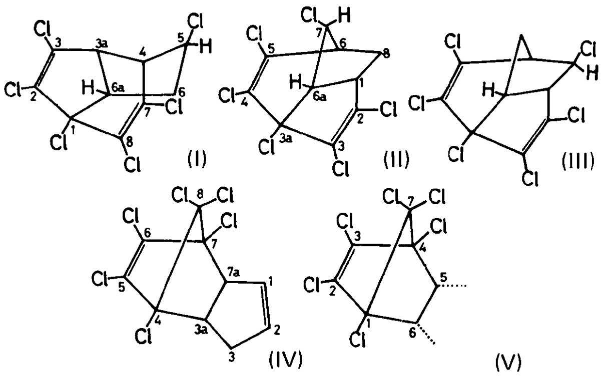
(*Received* 11 *December* 1980; *accepted* 19 *May* 1981)

Abstract. $C_{10}H_6Cl_6$, $M_r = 338\cdot9$, monoclinic, $P2_1/n$, $a = 7\cdot574\,(1)$, $b = 12\cdot178\,(2)$, $c = 13\cdot259\,(5)$ Å, $\beta = 94\cdot24\,(2)°$, $V = 1219\cdot6\,(8)$ Å^3, $D_x = 1\cdot84$ Mg m^{-3}, $Z = 4$, $F(000) = 672$, $\mu(\text{Mo } K\alpha) = 1\cdot36$ mm^{-1}, $R = 0\cdot035$ for 1757 observed reflections. The structure, proposed on the basis of spectroscopic evidence, has now been confirmed. The substituted methano-bridged ring system bears considerable structural similarity to the equivalent part of the hexachloronorbornene nucleus.

Introduction. The title compound is one of three bridged structural isomers of formula $C_{10}H_6Cl_6$ isolated from the 45 or more compounds in technical chlordane insecticide (Sovocool, Lewis, Harless, Wilson & Zehr, 1977). The structures of these isomers, α-chlordene (1,2,3,5,7,8-hexachloro-1,3a,4,5,6,6a-hexahydro-1,4-ethenopentalene) (I); β-chlordene (2,3,3a,4,5,7-hexachloro-3a,6,7,7a-tetrahydro-1,6-methano-1*H*-indene) (II); and γ-chlordene (2,3,3a,4,5,8-hexachloro-3a,6,7,7a-tetrahydro-1,6-methano-1*H*-indene) (III) were proposed on the basis of ^{1}H NMR and gas chromatography–mass spectroscopy evidence (Cochrane, Parlar, Gäb & Korte, 1975). They are formed by the rearrangement of the parent compound chlordene (IV) by the action of chlorine or free-radical initiating agents (Cochrane *et al.*, 1975) and no longer possess the basic hexachloronorbornene nucleus (V) common to chlordane and the other 'cyclodiene' insecticides.



(I) (II) (III)

(IV) (V)

The X-ray structure of α-chlordene was determined as part of an investigation of the structural systematics of halogenated hydrocarbons.

Colourless crystals, m.p. 466–468 K, were obtained from isopropyl alcohol. 6912 reflections ($2\theta_{\max} = 70°$)

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 ×10^4) [*defined as* $U_{eq} = (U_{11}\,U_{22}\,U_{33})^{1/3}$]

	x	y	z	U_{eq}
Cl(1)	−3759 (1)	−1054 (1)	3738 (1)	372 (5)
Cl(2)	−4834 (1)	886 (1)	1996 (1)	429 (6)
Cl(3)	−7670 (1)	−246 (1)	199 (1)	460 (6)
Cl(5)	−6913 (1)	−4763 (1)	1008 (1)	425 (6)
Cl(7)	−1677 (1)	−2729 (1)	243 (1)	410 (3)
Cl(8)	−829 (1)	−1242 (1)	2185 (1)	385 (5)
C(1)	−4454 (4)	−1389 (3)	2466 (2)	268 (16)
C(2)	−5400 (4)	−471 (3)	1865 (3)	304 (19)
C(3)	−6490 (4)	−921 (2)	1160 (2)	296 (17)
C(4)	−5101 (4)	−2829 (2)	791 (2)	265 (16)
C(3a)	−6548 (4)	−2148 (2)	1272 (2)	265 (16)
C(5)	−5073 (4)	−3889 (2)	1425 (2)	290 (16)
C(6)	−5248 (4)	−3474 (2)	2509 (2)	309 (17)
C(7)	−3276 (4)	−2349 (2)	1036 (2)	263 (16)
C(6a)	−5900 (4)	−2287 (2)	2402 (2)	266 (16)
C(8)	−2912 (3)	−1743 (2)	1855 (2)	241 (16)
H(3a)	−7856	−2399	1144	
H(4)	−5407	−2920	35	
H(5)	−3937	−4413	1397	
H(61)	−6026	−3806	2844	
H(62)	−4136	−3634	2914	
H(6a)	−6979	−2132	2865	

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* Cyclodienes. VIII. Part VII: Kennard, Smith & Palm (1981).

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Table 2. *Bond distances* (Å) *and angles* (°)

C(1)–Cl(1)	1·777 (3)	C(3a)–C(4)	1·549 (4)
C(2)–Cl(2)	1·713 (3)	C(4)–C(5)	1·540 (4)
C(3)–Cl(3)	1·712 (3)	C(5)–C(6)	1·538 (4)
C(5)–Cl(5)	1·807 (3)	C(6)–C(6a)	1·531 (4)
C(7)–Cl(7)	1·725 (3)	C(6a)–C(3a)	1·551 (4)
C(8)–Cl(8)	1·718 (3)	C(6a)–C(1)	1·546 (4)
C(1)–C(2)	1·521 (5)	C(4)–C(7)	1·514 (4)
C(2)–C(3)	1·320 (4)	C(7)–C(8)	1·325 (4)
C(3)–C(3a)	1·503 (4)	C(8)–C(1)	1·532 (5)
C(1)–C(2)–C(3)	108·2 (3)	C(5)–C(6)–C(6a)	105·9 (2)
C(1)–C(2)–Cl(2)	123·5 (2)	C(6)–C(6a)–C(3a)	105·6 (2)
C(3)–C(2)–Cl(2)	127·7 (2)	C(6)–C(6a)–C(1)	116·1 (2)
C(2)–C(3)–C(3a)	111·4 (3)	C(3a)–C(6a)–C(1)	98·5 (2)
C(2)–C(3)–Cl(3)	126·3 (3)	C(4)–C(7)–C(8)	121·5 (3)
C(3a)–C(3)–Cl(3)	122·3 (2)	C(4)–C(7)–Cl(7)	115·9 (2)
C(3)–C(3a)–C(4)	117·7 (2)	C(8)–C(7)–Cl(7)	122·4 (2)
C(3)–C(3a)–C(6a)	101·2 (2)	C(7)–C(8)–C(1)	118·0 (3)
C(6a)–C(3a)–C(4)	99·0 (2)	C(7)–C(8)–Cl(8)	122·6 (2)
C(3a)–C(4)–C(5)	101·9 (2)	C(1)–C(8)–Cl(8)	119·2 (2)
C(3a)–C(4)–C(7)	111·6 (2)	C(8)–C(1)–C(2)	106·1 (2)
C(5)–C(4)–C(7)	103·4 (2)	C(8)–C(1)–Cl(1)	112·5 (2)
C(4)–C(5)–C(6)	103·7 (2)	C(8)–C(1)–C(6a)	109·7 (2)
C(4)–C(5)–Cl(5)	110·3 (2)	Cl(1)–C(1)–C(6a)	111·9 (2)
C(6)–C(5)–Cl(5)	111·2 (2)	C(2)–C(1)–Cl(1)	115·1 (2)
		C(2)–C(1)–C(6a)	100·8 (2)

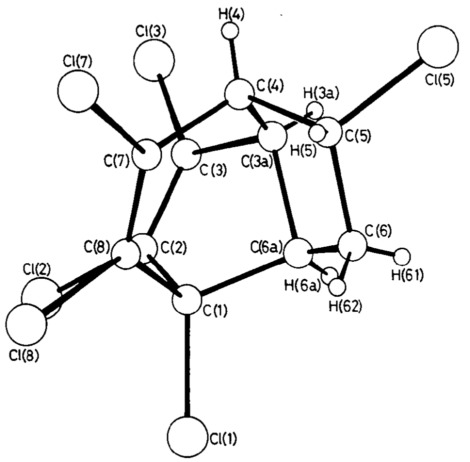

Fig. 1. Molecular configuration and atom numbering scheme for α-chlordene.

were collected from one crystal mounted on a Philips PW1100 automatic four-circle diffractometer (graphite-crystal-monochromated Mo $K\alpha$ radiation). A reduced data set was obtained ($2\theta_{\max} = 50°$, 2394 unique reflections), of which 1757 with $I > 2\cdot5\sigma(I)$ were considered observed and were used in structure solution and refinement. The structure was solved by the multisolution Σ_2 sign-expansion direct-methods approach of *SHELX* (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms reduced R $[= \sum ||F_o| - |F_c||/\sum F_o]$ from an initial value of 0·44 to 0·033 and $R_w[= (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$ to 0·028. $w = 1\cdot43/[(\sigma F_o)^2 + 4\cdot6 \times 10^{-5}(F_o)^2]$ was found to be suitable. Hydrogen atoms were located in a difference-Fourier synthesis and included in the refinement at fixed positions with their isotropic U's set invariant at 0·05 Å^2. A final difference map revealed no features higher than 0·092 e Å^{-3}. No corrections were made for extinction. Scattering factors used were those of Cromer & Mann (1968) for non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for hydrogen atoms.

Atomic positional parameters are given in Table 1.[*] Interatomic distances and angles are listed in Table 2. The molecular configuration and atom numbering scheme are shown in Fig. 1.

Discussion. This determination confirms the structure previously proposed for the α-isomer (Cochrane *et al.*, 1975). Bond distances and angles about the seven-membered bridged diene ring are relatively normal with the exception of those associated with the C(2)—C(3) double bond where the *exo*-C(2)—C(3) angles are enlarged [123·5 (2), 127·7 (2)°; 122·3 (2), 126·3 (3)°] while the *endo*-C—C—C angles are contracted [108·2, 111·4 (3)°]. These distortions, along with those of the *endo* angles about C(3a) [117·7, 99·0 (2)°] compared with the 'normal' tetrahedral angles about C(4), reflect the constraints imposed on the ring system by the bridging system at C(6a). This bridged section of the molecule may be matched directly with the hexachloronorbornene nucleus, the basic structural group of the cyclodiene compounds. The bridgehead angle is 98·5 (2)° and compares with a mean of 92·6° for a series of 13 'cyclodienes' (Kennard & Smith, 1981) which in contrast have an unconstrained geminal dichloro group at the bridgehead. Of interest also is the relatively long C(5)—Cl(5) bond distance [1·807 (3) Å] which is comparable to the values for isolated C—Cl bonds to saturated rings in similar compounds, *e.g.* 1·812 Å in compound K (2,4,4,5,6,6,7,8-octachloro-octahydro-1,5-ethenopentalene) from technical chlordane insecticide (Gäb, Born, Parlar & Korte, 1977); 1·806 Å in 2,2,5-*endo*,6-*exo*,8,9,10-heptachlorobornane from toxaphene insecticide (Palmer, Wong, Lundin, Khalifa & Casida, 1975); 1·79 Å in both *cis*- and *trans*-chlordane and their bridged photoisomers (Knox, Raston & White, 1979) and the mean of 1·794 Å for 22 values for the series of five isomeric 1,2,3,4,5,6-hexachlorocyclohexanes (Smith, 1978). Those distances are shorter than the 'large' values found in other 'cyclodiene' compounds (Kennard, Smith & Palm, 1981) (1·83–1·85 Å) or in compounds

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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 36191 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

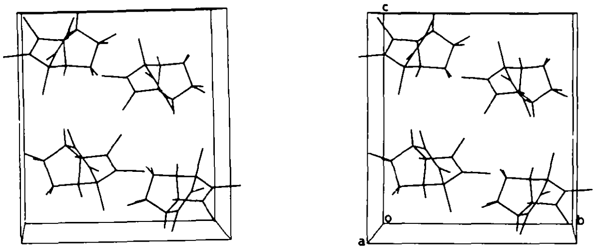

Fig. 2. Stereoview perpendicular to the *bc* plane.

such as *trans*-2,5-dichloro-1,4-dioxane (Altona, Knobler & Romers, 1963) (1·85, 1·86 Å).

Packing in the cell (Fig. 2) is similar to that for the chlordanes and those cyclodienes with no functional-group interaction. The cell contains discrete structural units with a total of five intermolecular Cl—Cl contacts ranging from 3·174 (2) to 3·423 (2) Å.

The authors wish to thank the US Environmental Protection Agency for a sample of α-chlordene, the Universities of Stockholm and Queensland for use of facilities and for financial support and the Queensland Institute of Technology for provision of data preparation services. GS also thanks the Queensland Institute of Technology for leave to work on this project.

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Acta Cryst. (1981). B**37**, 2239–2242

α-Acetonitrile at 215 K

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(*Received* 24 *March* 1981; *accepted* 22 *May* 1981)

Abstract. CH_3CN, $M_r = 41·1$, m.p. 227 K. At 215 K: monoclinic, $P2_1/c$, $a = 4·11$ (1), $b = 8·27$ (1), $c = 7·98$ (1) Å, $\beta = 100·4$ (2)°, $Z = 4$, $D_c = 1·02$ Mg m^{-3}, $F(000) = 88$, μ(Cu $K\alpha$) = 0·504 mm^{-1}. $R = 5·66\%$ (303 reflexions). Acetonitrile undergoes a solid–solid phase transition at approximately 211 K. The structure of the high-temperature form has been determined from single-crystal Weissenberg film data (microdensitometer measurements). The C—C—N angle is 179·6 (2)°, C—C = 1·443 (3) and C—N = 1·132 (3) Å. The two shortest intermolecular contacts are between N and H but the distances are only slightly less than the sum of the van der Waals radii. One of the contacts generates an almost linear $C{\equiv}N\cdots H{-}C$ system.

Introduction. Table 1 lists melting points for trihydrido-cyanides and trimethyl-cyanides of Group IV elements. In both series the melting points show a general increase down the group.

For the trimethyl-cyanides there is a large increase in melting point between Ge and Sn. The Si, Ge, and Sn species all have crystal structures which involve molecules aligned in a head-to-tail fashion:

Table 1. *Melting points* (K)

CH_3CN	227	$(CH_3)_3CCN$	289
SiH_3CN	305	$(CH_3)_3SiCN$	285
GeH_3CN	310	$(CH_3)_3GeCN$	311
		$(CH_3)_3SnCN$	462

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