

References

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1,2,3,4,7,7-Hexachloro-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene [Alodan (Hoechst)[®]]*

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Abstract. C₉H₆Cl₈, *M_r* = 397.8, orthorhombic, *Pbca*, *a* = 16.596 (3), *b* = 11.893 (4), *c* = 14.379 (5) Å, *Z* = 8, *D_x* = 1.86 Mg m⁻³, *μ*(Mo *Kα*) = 1.55 mm⁻¹, *R* = 0.047, 1858 observed reflections. The configuration of the hexachloro-8,9,10-trinorbornene moiety is similar to that found in other cyclodiene insecticides. The Cl atoms of the *endo*-chloromethyl groups in the cyclopentene ring adopt different relative conformations, thus destroying the mirror symmetry of the molecule. One C–Cl bond adopts a parallel, the other a perpendicular orientation with respect to the plane containing the bridgehead chlorines.

Introduction. Alodan[†] is the trademark (Hoechst–Roussel) given to the simplest ‘cyclodiene’ compound having insecticidal properties. Activity appears in Alodan and compounds with a single halomethyl group at the unsubstituted positions of the hexachloro-8,9,10-trinorbornene moiety, the activity increasing I > Br (Bromodan) > Cl (Alodan) (Soloway, 1965). Alodan has low mammalian toxicity and some acaricidal activity and was introduced as a dusting powder or a

solution concentrate for control of animal ectoparasites (Brooks, 1974). The X-ray structure was determined as part of a continuing investigation of the systematics of structural features of agriculturally important chemicals.

Colourless prismatic crystals (m.p. 376 K) were grown from aqueous isopropyl alcohol. 1858 unique reflections with *I* > 2.5σ(*I*) were considered observed out of a reduced data set of 2471 (2θ_{max} = 54°) from a total of 6912 reflections (2θ_{max} = 70°) collected from one crystal on a Philips PW1100 four-circle diffractometer. Monochromatized Mo *Kα* (λ = 0.7107 Å) radiation was used. The data were corrected for Lorentz and monochromator polarization effects and for absorption.

The structure was solved by the multiresolution Σ₂ 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* (= Σ ||*F_o*| – |*F_c*|| / Σ *F_o*) from an initial value of 0.30 to 0.047 and *R_w* [= (Σ *w*||*F_o*| – |*F_c*||² / Σ *w*|*F_o*|²)^{1/2}] to 0.051. *w* = 1.77[(σ*F_o*)² + 0.00127(*F_o*)²] was found to be suitable. H atoms were located in a difference-Fourier synthesis and their parameters were allowed to refine. A final difference-Fourier map revealed no features higher than 0.19 e Å⁻³. No corrections were made for extinction.

* Cyclodienes. VIII. Part VII: Isodrin (Kennard, Smith & Hovmöller, 1979).

† Common name: 5,6-bis(chloromethyl)-1,2,3,4,7,7-hexachloro-norborn-2-ene.

Table 1. Atomic positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters (Cl , $\times 10^4$; C , $\times 10^3$) defined as $U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$

	x	y	z	U_{eq} (\AA^2)
Cl(1)	3579 (1)	-24 (1)	5580 (1)	436 (9)
Cl(2)	3489 (1)	277 (1)	7545 (1)	404 (8)
Cl(3)	5377 (1)	-249 (1)	6768 (1)	421 (8)
Cl(4)	5194 (1)	-2130 (1)	8457 (1)	412 (8)
Cl(5)	3246 (1)	-3116 (1)	8434 (1)	386 (8)
Cl(6)	2254 (1)	-1798 (1)	6771 (1)	426 (8)
Cl(12)	3661 (1)	-4502 (1)	4984 (1)	576 (11)
Cl(21)	6201 (1)	-2561 (1)	5787 (1)	515 (10)
C(1)	3684 (3)	-2524 (4)	5955 (3)	29 (3)
C(2)	4585 (3)	-2098 (4)	5948 (4)	25 (3)
C(3)	4580 (3)	-1221 (4)	6762 (3)	27 (3)
C(4)	4457 (3)	-1873 (4)	7660 (3)	27 (3)
C(5)	3700 (3)	-2243 (4)	7662 (3)	27 (3)
C(6)	3310 (3)	-1842 (4)	6765 (4)	27 (3)
C(11)	3736 (3)	-696 (4)	6662 (3)	28 (3)
C(12)	3521 (5)	-3778 (5)	6065 (4)	38 (3)
C(21)	5198 (3)	-3044 (5)	6026 (4)	34 (3)
H(1)	3450	-2218	5346	
H(2)	4593	-1667	5341	
H(121)	3944	-4129	6474	
H(122)	3062	-3904	6310	
H(211)	5072	-3599	5495	
H(212)	5213	-3394	6574	

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Cl(1)-C(11)	1.768 (4)	C(1)-C(6)	1.549 (7)
Cl(2)-C(11)	1.766 (4)	C(2)-C(3)	1.568 (7)
Cl(3)-C(3)	1.757 (4)	C(3)-C(4)	1.520 (7)
Cl(4)-C(4)	1.704 (4)	C(4)-C(5)	1.331 (7)
Cl(5)-C(5)	1.696 (4)	C(5)-C(6)	1.520 (7)
Cl(6)-C(6)	1.753 (4)	C(6)-C(11)	1.543 (7)
Cl(12)-C(12)	1.792 (4)	C(3)-C(11)	1.540 (7)
Cl(21)-C(21)	1.794 (4)	C(1)-C(12)	1.524 (8)
		C(2)-C(21)	1.521 (7)
C(6)-C(1)-C(2)	102.5 (4)	C(5)-C(4)-Cl(4)	128.1 (3)
C(6)-C(1)-C(12)	111.3 (4)	C(4)-C(5)-C(6)	107.2 (4)
C(2)-C(1)-C(12)	118.9 (4)	C(4)-C(5)-Cl(5)	128.5 (3)
C(1)-C(12)-Cl(12)	110.9 (3)	C(6)-C(5)-Cl(5)	123.9 (3)
C(3)-C(2)-C(21)	116.1 (4)	C(5)-C(6)-C(1)	107.6 (4)
C(3)-C(2)-C(1)	101.8 (4)	C(5)-C(6)-Cl(6)	99.4 (4)
C(1)-C(2)-C(21)	113.3 (4)	C(5)-C(6)-Cl(6)	115.5 (3)
C(2)-C(21)-Cl(21)	111.7 (3)	C(1)-C(6)-Cl(6)	101.9 (4)
C(2)-C(3)-C(4)	107.2 (4)	C(1)-C(6)-Cl(6)	114.8 (3)
C(2)-C(3)-C(11)	101.8 (4)	C(11)-C(6)-Cl(6)	115.6 (3)
C(2)-C(3)-Cl(3)	115.9 (3)	C(6)-C(11)-C(3)	92.9 (4)
C(4)-C(3)-Cl(3)	115.6 (3)	C(6)-C(11)-Cl(1)	114.6 (3)
C(4)-C(3)-C(11)	99.4 (4)	C(6)-C(11)-Cl(2)	113.8 (3)
Cl(3)-C(3)-C(11)	114.7 (3)	C(3)-C(11)-Cl(1)	113.5 (3)
C(3)-C(4)-C(5)	107.3 (4)	C(3)-C(11)-Cl(2)	114.2 (3)
C(3)-C(4)-Cl(4)	124.5 (3)	Cl(1)-C(11)-Cl(2)	107.6 (2)

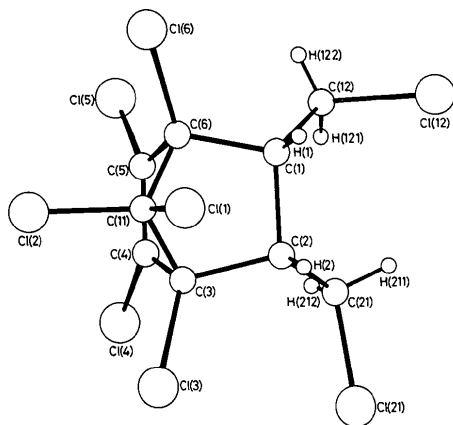


Fig. 1. Molecular configuration and atom-naming scheme for Alodan. The numbering scheme follows the convention used for other members of this series.

Scattering factors used were those of Cromer & Mann (1968) for non-hydrogen atoms and Stewart, Davidson & Simpson (1965) for H atoms.

Atomic positional parameters are given in Table 1.* Interatomic distances and angles are in Table 2. The molecular conformation is shown in Fig. 1. For ease of comparison, the atom numbering follows the convention employed for all other members of the 'cyclodiene' series.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36123 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Alodan has a relatively inflexible hexachloro-8,9,10-trinorbornene nucleus common to the 'cyclodiene' series of insecticides. Alodan's bond distances and angles compare closely with those of other members of the series. However, the C-Cl distances in the chloromethyl substituent groups at C(12) and C(21) [1.792 (4), 1.794 (4) \AA] are closer to other C-Cl distances in this compound and to those of the hexachloro-8,9,10-trinorbornene group of the other 'cyclodienes', but they are considerably shorter than the abnormally long C-Cl bonds found in similar isolated environments in other comparable 'cyclodienes' [isobenzan, 1.84 \AA (Smith & Kennard, 1977); heptachlor, 1.85 \AA (Shields & Kennard, 1973); heptachlor epoxide, 1.82 \AA (Hovmöller, Smith & Kennard, 1978)]. The *exo*-C(1) and C(2) angles are less regular and are somewhat larger [111.3 (4)–118.9 (4) $^\circ$] than expected for a similar strain-free environment. The major structural difference between Alodan and the other 'cyclodienes' is the presence of chloromethyl groups in place of the closed-ring systems between C(1) and C(2) [*i.e.* -CHCl-O-CHCl- (isobenzan); -CHCl-CH=CH- (heptachlor); -CHClCH-CH- (heptachlor epoxide)]. Both

groups have the *endo* configuration which is the only one known for substituent groups at these positions in the 'cyclodienes'. However, in Alodan the relative disposition of the Cl atoms in these groups is different, one C-Cl bond being approximately perpendicular, the other parallel to the pseudo-mirror plane of the hexachloro-8,9,10-trinorbornene moiety with a Cl-Cl

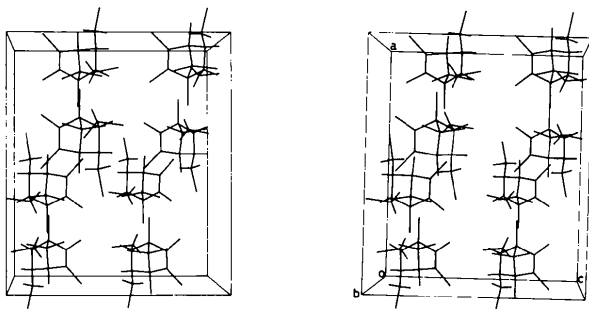


Fig. 2. Stereoscopic view of the packing in the cell perpendicular to the *ac* plane.

separation of 4.94 Å. The torsion angles C(3)–C(2)–C(21)–Cl(21) and C(6)–C(1)–C(12)–Cl(12) are -74.1 (5) and $+161.6$ (6) $^\circ$ respectively. On the other hand, the Cl atoms in heptachlor, heptachlor epoxide, and isobenzan are fixed in semi-parallel orientations, with comparative Cl–Cl distances of 3.57 and 3.60 Å for the two independent molecules of isobenzan. Interatomic repulsion between these two Cl atoms would favour the conformation found in Alodan, giving also a favourable interactive Cl(12)–H(211) distance of 2.68 Å. Packing of the molecules in the unit cell (Fig. 2) results in a range of intermolecular Cl–Cl distances of 3.32–3.89 Å which is similar to that found for other members of this series of compounds and for the 1,2,3,4,5,6-hexachlorocyclohexane isomers (Smith, 1978) where van der Waals intermolecular forces operate.

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Refinement of 2-Nitroguanidine by Neutron Powder Diffraction

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Abstract. $C(NH_2)_2NNO_2$, $CH_4N_4O_2$, orthorhombic, *Fdd2*, $a = 17.6152$ (5), $b = 24.8502$ (7), $c = 3.5880$ (1) Å, $Z = 16$. The structure has been refined by profile analysis of powder neutron diffraction data at room temperature: $R_i = 0.057$ (for 324 integrated intensities) and $R_w = 0.020$. The molecules are linked together by a three-dimensional network of hydrogen bonds.

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Introduction. The crystal structure of 2-nitroguanidine was studied earlier by Bryden, Burkardt, Hughes & Donohue (1956) (referred to as BBHD hereafter), using visually estimated intensity data from rotation photographs. They reported the existence of hydrogen bonds, but did not report the H positions. This study was undertaken to determine the H positions by using the neutron powder diffraction method.

The sample powder was packed loosely in a cylindrical vanadium container, 20 mm in diameter and