

sur ce cycle, occupent des positions axiales, ce qui amène, autour de C(1)–C(2) ou de C(4)–C(5), les liaisons C–Br à être en situation antipériplanaire avec les liaisons C(1)–C(7) ou C(5)–C(6) dirigées vers les carbonés du pont éthano (Fig. 2).

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Références

- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1976). *MULTAN 76. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et Louvain-la-Neuve, Belgique.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-endo-1,4-endo-5,8-dimethanonaphthalene (Isodrin)

BY COLIN H. L. KENNARD

Department of Chemistry, University of Queensland, Brisbane 4067, Australia

GRAHAM SMITH

Department of Chemistry, Queensland Institute of Technology, Brisbane 4000, Australia

AND SVEN HOVMÖLLER

Arrhenius Laboratory, University of Stockholm, Fack, Stockholm, Sweden

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Abstract. C₁₂H₈Cl₆, orthorhombic, *Pbca*, *a* = 14.909 (6), *b* = 14.781 (12), *c* = 12.880 (18) Å, *M_r* = 364.9, *Z* = 8, *D_x* = 1.71 Mg m⁻³, *μ*(Mo *K_α*) = 1.18 mm⁻¹, *R* = 0.088, 996 observed reflexions. The *endo-endo* configuration of isodrin has been confirmed. The molecules have approximate *m* point symmetry and form semi-cylinders with the peripheral double-bond pair lying parallel, separated by a perpendicular distance of 2.86 Å. No intermolecular associations were found.

Introduction. The title compound is a member of the important series of commercial cyclodiene insecticides which includes dieldrin, aldrin, endrin, heptachlor and endosulfan. Isodrin is the stereoisomer of aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-endo-1,4-exo-5,8-dimethanonaphthalene), the crystal structure of which is known (DeLacy & Kennard, 1972) and which has a toxicity towards insects which is comparable to that of dieldrin (Brooks, 1974).

Crystals (m.p. 513–515 K) were grown from a mixture of isopropyl alcohol and water. The structure was determined by X-ray diffraction. 996 reflections with *I* > 2.5σ(*I*) were considered observed out of 2382 in a unique set collected from one crystal (0.25 × 0.30

Table 1. Atomic positional parameters (×10⁴) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	2656 (3)	2161 (4)	9701 (4)
Cl(2)	3118 (3)	2446 (3)	7527 (3)
Cl(3)	969 (3)	1584 (3)	8046 (5)
Cl(4)	-2 (3)	2901 (3)	9764 (4)
Cl(5)	1423 (3)	4567 (4)	10403 (4)
Cl(6)	3295 (3)	4315 (3)	9084 (4)
C(1)	2003 (11)	4031 (11)	7592 (12)
C(2)	1333 (10)	3290 (10)	7311 (12)
C(3)	1380 (10)	2666 (10)	8295 (12)
C(4)	987 (10)	3134 (10)	9156 (12)
C(5)	1537 (11)	3811 (11)	9426 (12)
C(6)	2307 (11)	3771 (11)	8730 (12)
C(7)	1431 (13)	4928 (14)	7241 (15)
C(8)	670 (12)	5005 (12)	8003 (15)
C(9)	94 (12)	4377 (12)	7771 (13)
C(10)	461 (13)	3818 (13)	6947 (15)
C(11)	2354 (11)	2771 (11)	8489 (12)
C(12)	924 (15)	4531 (17)	6409 (18)
H(1)	2533	4189	7085
H(2)	1578	2869	6673
H(7)	1830	5360	7430
H(8)	730	5372	8501
H(9)	-434	4091	8121
H(10)	-48	3400	6719
H(121)	1429	4207	6008
H(122)	337	4759	6112

Table 2. *Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses (applicable to the last figure)*

Cl(1)—C(11)	1.86 (1.5)	C(1)—C(7)	1.64 (2.0)	C(4)—C(5)	1.34 (2.0)	C(8)—H(8)	0.84
Cl(2)—C(11)	1.75 (1.6)	C(1)—H(1)	1.05	C(5)—C(6)	1.46 (2.1)	C(9)—C(10)	1.45 (2.1)
Cl(3)—C(3)	1.74 (1.5)	C(2)—C(3)	1.57 (2.0)	C(6)—C(11)	1.51 (1.9)	C(9)—H(9)	1.00
Cl(4)—C(4)	1.70 (1.5)	C(2)—C(10)	1.59 (2.1)	C(7)—C(8)	1.50 (2.2)	C(10)—C(12)	1.44 (2.3)
Cl(5)—C(5)	1.69 (1.5)	C(2)—H(2)	1.09	C(7)—C(12)	1.44 (2.2)	C(10)—H(10)	1.02
Cl(6)—C(6)	1.74 (1.6)	C(3)—C(4)	1.43 (2.0)	C(7)—H(7)	0.91	C(12)—H(121)	1.03
C(1)—C(2)	1.53 (1.9)	C(3)—C(11)	1.48 (2.0)	C(8)—C(9)	1.30 (2.0)	C(12)—H(122)	1.01
C(1)—C(6)	1.58 (1.9)						
C(2)—C(1)—C(6)	103.5 (1.8)	Cl(4)—C(4)—C(5)	124.2 (1.2)	C(8)—C(7)—C(12)	96.9 (1.6)		
C(2)—C(1)—C(7)	100.1 (1.8)	C(3)—C(4)—C(5)	108.1 (1.7)	C(7)—C(8)—C(9)	107.1 (1.7)		
C(6)—C(1)—C(7)	127.0 (1.9)	Cl(5)—C(5)—C(4)	128.6 (1.1)	C(8)—C(9)—C(10)	109.0 (1.7)		
C(1)—C(2)—C(3)	101.6 (1.8)	Cl(5)—C(5)—C(6)	124.4 (1.2)	C(2)—C(10)—C(9)	111.9 (1.5)		
C(1)—C(2)—C(10)	104.7 (1.8)	C(4)—C(5)—C(6)	107.0 (1.9)	C(2)—C(10)—C(12)	96.3 (1.5)		
C(3)—C(2)—C(10)	124.3 (1.9)	Cl(6)—C(6)—C(1)	111.9 (1.1)	C(9)—C(10)—C(12)	96.7 (1.7)		
Cl(3)—C(3)—C(2)	112.0 (1.1)	Cl(6)—C(6)—C(5)	119.1 (1.2)	Cl(1)—C(11)—Cl(2)	107.6 (0.8)		
Cl(3)—C(3)—C(4)	116.2 (1.1)	Cl(6)—C(6)—C(11)	117.9 (1.2)	Cl(1)—C(11)—C(3)	109.2 (1.2)		
Cl(3)—C(3)—C(11)	118.2 (1.2)	C(1)—C(6)—C(5)	109.5 (1.9)	Cl(1)—C(11)—C(6)	108.2 (1.2)		
C(2)—C(3)—C(4)	108.9 (1.8)	C(1)—C(6)—C(11)	93.4 (1.7)	Cl(2)—C(11)—C(3)	119.3 (1.2)		
C(2)—C(3)—C(11)	96.8 (1.8)	C(5)—C(6)—C(11)	101.7 (1.6)	Cl(2)—C(11)—C(6)	116.4 (1.2)		
C(4)—C(3)—C(11)	103.7 (1.7)	C(1)—C(7)—C(8)	105.8 (1.4)	C(3)—C(11)—C(6)	95.3 (1.8)		
Cl(4)—C(4)—C(3)	127.7 (1.1)	C(1)—C(7)—C(12)	98.6 (1.6)	C(7)—C(12)—C(10)	101.1 (1.8)		

× 0.30 mm) mounted on a Philips PW 1100 four-circle diffractometer ($2\theta_{\max} < 50^\circ$, graphite-monochromated Mo $K\alpha$ radiation), with a scan width of 0.8° and a scan speed of $0.08^\circ \text{ s}^{-1}$. Accurate cell parameters were determined by least-squares refinement from 10 reflections collected in the 2θ range $12\text{--}26^\circ$. No correction was made for absorption [$\mu(\text{Mo } K\alpha) = 1.18 \text{ mm}^{-1}$].

The structure was solved by multiresolution Σ_2 sign expansion (Sheldrick, 1976). Full-matrix least-squares refinement, with only the temperature factors of the Cl atoms anisotropic, reduced R [$= \sum |F_o| - |F_c| / \sum F_o$] from an initial value of 0.39 to 0.088 and R_w [$= (\sum w|F_o| - |F_c|^2 / \sum w|F_o|^2)^{1/2}$] to 0.089. The H positions were included in the refinement at their calculated positions and were allowed to refine with their isotropic thermal parameters fixed at $U = 0.05 \text{ \AA}^2$. Three low-angle intense reflections (004, 020, 102) were considered to be affected by extinction and were removed before the last cycle of refinement. A final difference electron density synthesis revealed no features greater than 0.29 e \AA^{-3} . The high residual R is considered to be the result of the large number of unobserved reflections, a consequence of the high thermal motion of the Cl atoms.

Positional parameters are given in Table 1.* Interatomic distances and angles are in Table 2.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34011 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The *endo-endo* configuration for isodrin has been confirmed in this structural study. In the analogous stereoisomeric compounds, endrin (*endo-endo*) and dieldrin (*endo-exo*), the double bond C(8)=C(9) in isodrin or aldrin is replaced by an 8,9-epoxy group. Fig. 1 illustrates the configuration of the two six-membered rings by viewing the molecule parallel to the plane through the bridgehead atoms C(11) and C(12) and the methano-bridged chlorides Cl(1) and Cl(2), which is also the approximate molecular mirror plane. In only one cyclodiene studied so far, β -endosulfan (Smith, Kennard & Shields, 1977), does the molecular mirror plane lie on a crystallographic mirror plane.

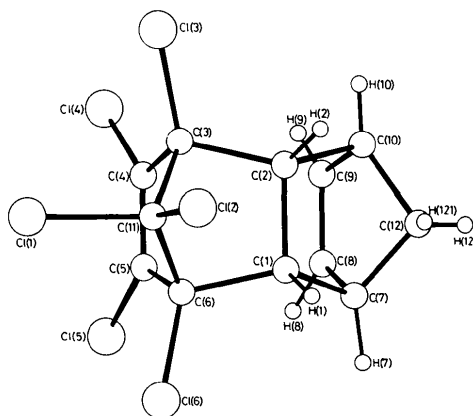


Fig. 1. Molecular configuration and numbering scheme used for isodrin in a perspective view of the molecule viewed perpendicular to the plane of C(1), C(2), C(3).

The interatomic distances and angles in the hexachloronorborene moiety for the four related compounds are similar except that the bonds from C(3) and C(6) to C(11) are somewhat shorter, the angle C(3)–C(11)–C(6) is greater and the C(11)–Cl(1) bond is significantly longer in isodrin (1.86 Å compared with the mean of 1.77 Å). Long C–Cl bonds are, however, not uncommon among the members of the cyclodiene series, but only where Cl is substituted at C(7) or C(10), for example isobenzan (1.84 Å), heptachlor (1.85 Å) and heptachlor epoxide (1.817 Å) (Hovmöller, Smith & Kennard, 1978). In the non-chlorinated residue, the angle C(7)–C(12)–C(10) [101.1 (2)°] is significantly larger than that found in aldrin [93.7 (5)°]. This is probably due to the shortness of C(7)–C(12) (1.44 compared with 1.54 Å) as a result of the interaction between the two sets of double bonds within the molecule. The mid-point double bond to double bond distances for isodrin and aldrin are 2.86 and 4.50 Å respectively.

The overall shape of isodrin is more equidimensional than that of aldrin, with the mid-point of C(8)=C(9) to Cl(1) and Cl(2) being 5.23 and 4.93 Å respectively. The longest distances across the approximate mirror plane [Cl(3)–Cl(6)] are similar (5.49, 5.53 Å), but this is expected because of the relatively constant size and shape found for all members of the cyclodiene series. There were no close intermolecular constants; consequently, only van der Waals forces hold the solid together (Fig. 2).

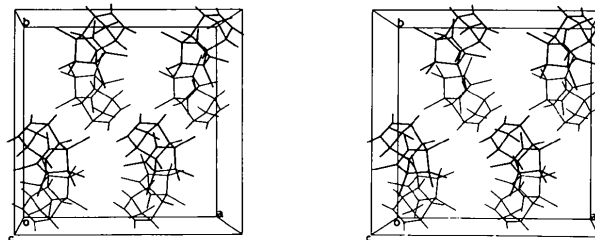


Fig. 2. Stereoview of the packing of isodrin viewed down the *c* axis.

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References

- BROOKS, G. T. (1974). *Chlorinated Insecticides*, Vol. 11, pp. 118–119. Cleveland, Ohio: CRC Press.
- DE LACY, T. P. & KENNARD, C. H. L. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 2153–2158.
- HOVMÖLLER, S., SMITH, G. & KENNARD, C. H. L. (1978). *Cryst. Struct. Commun.* **7**, 467–471.
- SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SMITH, G., KENNARD, C. H. L. & SHIELDS, K. G. (1977). *Aust. J. Chem.* **30**, 911–916.

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Thiochroman-4-one 1,1-Dioxide

BY S. E. EALICK, DICK VAN DER HELM AND J. R. BAKER

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, USA

AND K. D. BERLIN

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074, USA

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Abstract. C₉H₈O₃S, *M_r* = 196.21, orthorhombic, *Pca*2₁, *Z* = 4. At *T* = 298 K: *a* = 14.901 (1), *b* = 7.7875 (3), *c* = 7.4373 (3) Å, *V* = 863.0 Å³, *D_c* = 1.510, *D_m* = 1.508 Mg m⁻³. At *T* = 113 K: *a* = 15.014 (9), *b* = 7.678 (5), *c* = 7.281 (5) Å, *V* = 839.3 Å³. Final *R* value for all 935 intensity data is 0.026. The structure solution shows a small difference between the S–O distances: 1.440 (2) and 1.450 (2) Å while the

two S–C distances are the same: 1.763 (2) and 1.766 (2) Å.

Introduction. Thiochroman-4-one 1,1-dioxide is a keto sulfone which serves as precursor for a number of polycyclic pyrazoles, isoxazoles and imines which show a variety of bactericidal and drug potentiation effects. Thiochroman-4-one 1,1-dioxide itself shows 100%