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1,2,3,4-Tetrachloro-11,11-dimethoxy-1,4,5,6,9,10-hexahydro-*endo*-1,4-*exo*-6,9-dimethanonaphthalene

Alexander J. Blake,* Anja Dietel, Wan-Sheung Li and Neil R. Thomas

School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England

Correspondence e-mail:
a.j.blake@nottingham.ac.uk

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Key indicators

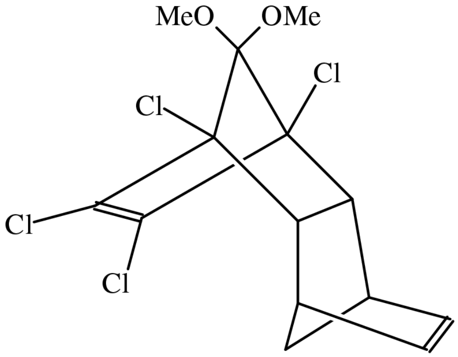
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.082
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{14}H_{14}Cl_4O_2$, is the *endo* product of a Diels–Alder reaction between 1,2,3,4-tetrachloro-5,5-dimethoxycyclopenta-1,3-diene and bicyclo[2.2.1]hepta-2,5-diene. The molecule possesses non-crystallographic C_s symmetry.

Comment

The title compound, (I), was produced as a key intermediate in the preparation of a hapten suitable for generating antibodies specific either for the organochlorine pesticide aldrin which has been shown to accumulate in fatty tissue or for dieldrin, the compound to which aldrin is metabolized by epoxidation in mammals. Both aldrin and dieldrin are known to persist in the environment and have been reported to possess carcinogenic properties by the Environmental Protection Agency in the USA (Stevenson *et al.*, 1999).



(I)

The structure of the title compound was determined primarily to discover whether the product of the Diels–Alder reaction between 1,2,3,4-tetrachloro-5,5-dimethoxycyclopenta-1,3-diene and bicyclo[2.2.1]hepta-2,5-diene had an *endo* or an *exo* configuration at C5—C10. The molecule possesses non-crystallographic C_s symmetry, the mirror plane passing through C11 and C12, and bisecting the C2—C3, C5—C10 and C7—C8 bonds. The *endo,exo*-adduct is that required to match the stereochemistry of aldrin and dieldrin.

A number of related structures have been determined, for example, aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene; DeLacy & Kennard, 1972), isodrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-*endo*-1,4-*endo*-5,8-dimethanonaphthalene; Kennard *et al.*, 1979) and dechloroethoxyisodrin (*endo,endo*-3,5,6,11,-11-pentachloro-4-ethoxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene; Mackenzie *et al.*, 1993).

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Experimental

The title compound was prepared by a Diels–Alder reaction between 1,2,3,4-tetrachloro-5,5-dimethoxycyclopenta-1,3-diene (2.0 ml, 3.00 g, 0.011 mol) and bicyclo[2.2.1]hepta-2,5-diene (3.5 ml, 3.00 g, 0.033 mol) following the method described by McCulloch *et al.* (1969). The two oils were mixed together and heated under reflux (358 K) overnight. The crude product was then purified by distillation, first at atmospheric pressure to remove the unreacted bicyclo[2.2.1]hepta-2,5-diene and then under high vacuum with the required product distilling over at 409–413 K at 1 mm Hg. The product solidified in the receiver and was purified by recrystallization from acetone/petroleum ether to afford 0.76 g of white needle-like crystals (19% yield), m.p. 389–391 K; δH ($CDCl_3$): 6.28 (2H, *s*, 7,8-CH), 3.59 (3H, *s*, 11-OCH_3), 3.55 (3H, *s*, 11-OCH_3), 2.82 (2H, *br s*, 6,9-CH), 2.55 (2H, *s*, 5,10-CH), 1.38 (2H, *dd*, *J* = 10 and 18 Hz, 12-CH_2). Crystal suitable for diffraction studies were grown from acetone/petroleum ether.

Crystal data

$C_{14}H_{14}Cl_4O_2$
$M_r = 356.05$
Orthorhombic, *Pbca*
$a = 13.259$ (5) Å
$b = 14.383$ (4) Å
$c = 15.635$ (4) Å
$V = 2981.7$ (16) Å^3
$Z = 8$
$D_x = 1.586$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 44 reflections
$\theta = 13$–15°
$\mu = 0.79$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.77 × 0.50 × 0.48 mm

Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scan (*X-RED*; Stoe & Cie, 1995)
$T_{min} = 0.681$, $T_{max} = 0.713$
2614 measured reflections
2614 independent reflections

2298 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
random variation: ±2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.082$
$S = 1.19$
2614 reflections
181 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 4.29P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

The crystal was transferred into the nitrogen stream of an Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986) operating at 150 (2) K. H atoms were located from difference Fourier syntheses and their geometries were idealized. Methyl H atoms were refined as part of a rigid group with $U_{iso}(H) = 1.5U_{eq}(C)$; other H atoms were refined using a riding model and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2001).

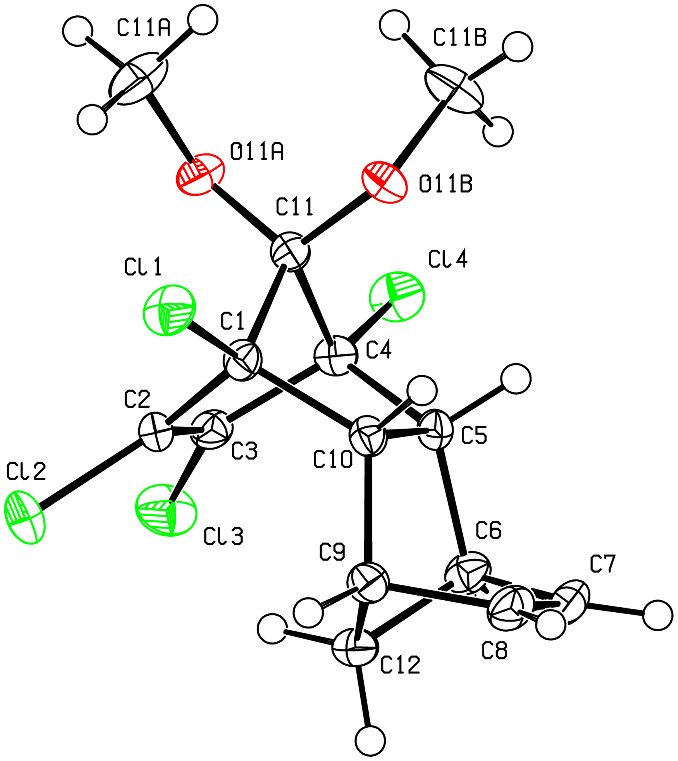

Figure 1
A general view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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