

cis,syn,cis-2,3,4,8,9-Pentachloro-1,5,7,7-tetramethoxy-tricyclo[4.3.0.0^{2,5}]nona-3,8-dieneRichard Gilardi,^{a*} Datong Tang^b
and Philip E. Eaton^b^aLaboratory for the Structure of Matter,
Naval Research Laboratory, Washington,
DC 20375-5341, USA, and ^bDepartment of
Chemistry, The University of Chicago,
5735 S. Ellis Avenue, Chicago, IL 60637, USA

Correspondence e-mail: gilardi@nrl.navy.mil

Key indicators

Single-crystal X-ray study

T = 294 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.037

wR factor = 0.092

Data-to-parameter ratio = 16.6

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

The title compound, $\text{C}_{13}\text{H}_{13}\text{Cl}_5\text{O}_4$, is a highly substituted tricyclic fused-ring diene formed when a nonachloro-homocubane slowly reacts with anhydrous sodium methoxide in tetrahydrofuran at room temperature. Four chloro substituents on the starting material are replaced by methoxy groups. In addition to this replacement, which was detected by NMR techniques, an unexpected opening of the homocubane cage was discovered by the single-crystal X-ray analysis reported herein.

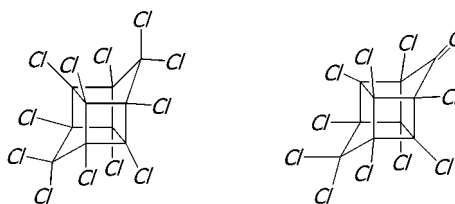
Received 15 April 2002

Accepted 29 April 2002

Online 11 May 2002

Comment

The determination of the three-dimensional structure of polycyclic organic compounds is sometimes a question of distinguishing between isomers that differ only in long-range stereochemical features, such as *syn* or *anti* ring fusions, and this is difficult to do with only NMR evidence. If the compounds are perhalo derivatives, or nearly so, the task is made even more difficult by the lack of ^1H NMR signals. Several misassignments of this type of structure were recently corrected by crystallographic analyses (Eaton *et al.*, 2001, 2002). The title compound is one of several new compounds of this type discovered in a study (Tang, 2002) of the reactions of the perhalo compounds known as mirex and kepone



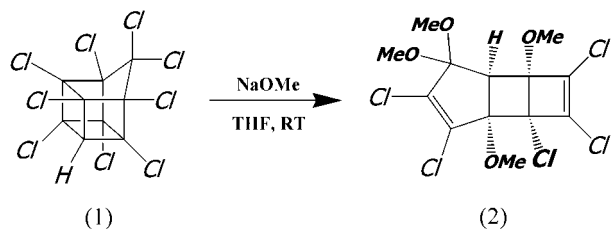
Mirex

Kepone

These pentacyclic cage compounds are called bis-homocubanes and are of interest as possible intermediates leading to a more economical route to cubanes. Cubanes are also pentacyclic cage compounds, although they are subject to more strain, due to their greater number of four-membered rings. They are rather difficult to make in large quantities. This is primarily because one stage occurring in all known syntheses is a photochemical closure step, which is expensive and hard to scale up. In contrast, mirex and kepone are usually formed by non-photochemical dimerizations of hexachlorocyclopentadiene (Prins, 1946). These syntheses have long ago been scaled up economically. Kepone was produced in quantities up to 200 tonnes per year as an agricultural insecticide in the early 1970's (Kepone, 2000), but production was halted in

1975 when several workers developed serious neurological disorders.

The keto-bridge in kepone has been removed (Scherer *et al.*, 1966) to form a homocubane (1), but nobody has yet found a way to remove the remaining dichloromethylene bridge to form a cubane.



We found that molecule (1) reacts slowly with anhydrous sodium methoxide in tetrahydrofuran at room temperature to form a single product, which appeared to be a tetramethoxy derivative from NMR evidence. However, in the reaction an opening of the homocubane cage system also occurs, which was detected by the X-ray analysis reported herein. The mechanism for this reaction is still unclear.

The molecular structure of (2) is presented in Fig. 1. Although the homocubane 'cage' is opened in the course of the reaction, the *cis-syn-cis* ring junction topology preserves an overall cup-like shape, containing several close intramolecular distances (see Fig. 1). This ring system is uncommon. Surprisingly, a search of the Cambridge Structural Database (CSD; Version 5.22 of October 2001, using Conquest

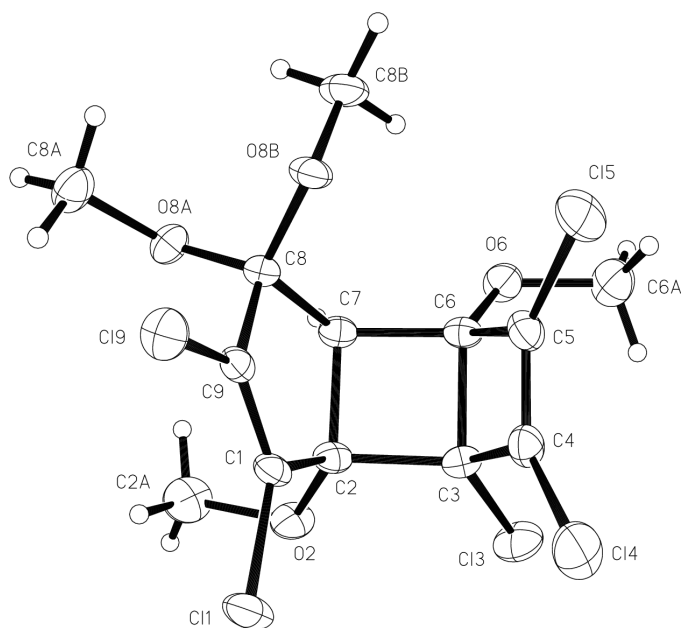


Figure 1
View of the title compound, with 50% probability ellipsoids. Internal steric strain is indicated by the occurrence of several short C...C distances (C1...C4, C5...C7, and C5...C6A) in the 2.9–3.0 Å range, compared to the C...C van der Waals distance of 3.4 Å (Rowland & Taylor, 1996).

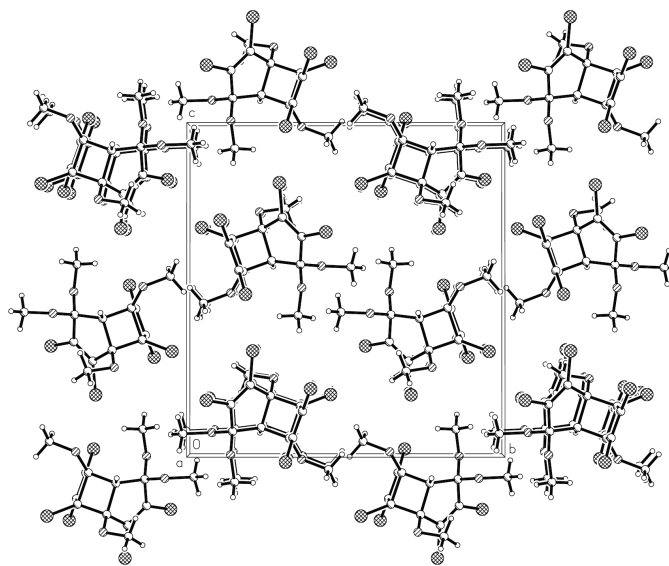


Figure 2
A view of the packing of the title molecule down the *a* axis. No intermolecular contacts are more than 0.1 Å below normal van der Waals contacts.

1.3; Allen & Kennard, 1993) for the all-carbon 4/4/5 three-ring system seen in (2) revealed no hits. This search allowed for any type of bond order, but disallowed any further ring closures or fusions. However, when atoms other than carbon were allowed, three examples of the 4/4/5 system were found (Cadogan *et al.*, 1986; Paquette *et al.*, 1972; Maier *et al.*, 1994), with heteroatoms N, O and S occurring in the five-membered ring. Each contained one cyclobutene ring situated exactly as in (2). This ring is extremely strained and quite asymmetric because of the introduction of a double bond. In (2), the double-bond distance C4=C5 is 1.317 (4) Å, with average adjacent bond angles of 95.1°, while the opposite bond in the same ring is very long, 1.586 (3) Å, with average adjacent bond angles of only 84.9°. A close similarity to this pattern is displayed in each of the three 4/4/5 ring systems cited above.

Fig. 2 illustrates the packing of (2), which appears to be an example of simple close packing, marked by no particularly close interactions.

Experimental

1,2,3,4,6,7,8,9,9-Nonachloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane, (1) (45 mg, 0.11 mmol), was dissolved in anhydrous tetrahydrofuran (1 ml). Anhydrous sodium methoxide (70 mg, 1.3 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 2 d. The mixture was diluted with diethyl ether (1 ml), cautiously quenched with ice/water, and extracted with diethyl ether (3 × 2 ml). The extract was washed with brine (2 ml) and dried over anhydrous MgSO₄. Removal of solvent and column chromatography (pentane:ether, 10:1) afforded the title compound (27 mg, 63%) as a white solid. Slow evaporation of a pentane solution gave crystals suitable for X-ray analysis. ¹H NMR (CDCl₃): δ 3.55 (s, 3H), 3.41 (s, 3H), 3.39 (s, 3H), 3.32 (s, 3H), 3.03 p.p.m. (s, 1H); ¹³C NMR (acetone-*d*₆): δ 138.4, 133.3, 131.4, 131.1, 104.9, 87.5, 86.5, 78.9, 54.7 (OCH₃), 54.5 (OCH₃), 53.4, 51.5 (OCH₃), 51.4 (OCH₃) p.p.m.

Crystal data

$C_{13}H_{13}Cl_5O_4$
 $M_r = 410.48$
 Monoclinic, $P2_1/n$
 $a = 7.390$ (2) Å
 $b = 14.878$ (4) Å
 $c = 15.635$ (5) Å
 $\beta = 91.91$ (2)°
 $V = 1718.1$ (15) Å³
 $Z = 4$

Data collection

Bruker P4 diffractometer
 $2\theta/\omega$ scans
 Absorption correction: by
 integration (Wuensch & Prewitt,
 1965)
 $T_{\min} = 0.807$, $T_{\max} = 0.826$
 3371 measured reflections
 3371 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.092$
 $S = 1.02$
 3371 reflections
 203 parameters
 H-atom parameters constrained

$D_x = 1.587$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 36
 reflections
 $\theta = 5.5$ – 17.8°
 $\mu = 0.86$ mm⁻¹
 $T = 294$ (2) K
 Truncated octahedron, colorless
 $0.50 \times 0.44 \times 0.16$ mm

2609 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 26.0^\circ$
 $h = -9 \rightarrow 9$
 $k = 0 \rightarrow 18$
 $l = 0 \rightarrow 19$
 3 standard reflections
 every 97 reflections
 intensity decay: 4.0%

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.9092P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997) in SHELXTL;

molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

RG acknowledges financial support from the Office of Naval Research, Mechanics Division.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
 Bruker (2001). SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Cadogan, J. I. G., Cameron, D. K., Gosney, I., Highcock, R. M. & Newlands, S. F. (1986). *Chem. Commun.* pp. 766–767.
 Eaton, P. E., Tang, D. & Gilardi, R. (2001). *J. Org. Chem.* **66**, 1492–1493.
 Eaton, P. E., Tang, D. & Gilardi, R. (2002). *Tetrahedron Lett.* **43**, 3–5.
 Kepone (2000). A fact sheet in 'Ninth Annual Report on Carcinogens', published by National Toxicology Program, Research Triangle Park, NC 27709–2233, USA; available on the Web at <http://ehis.niehs.nih.gov/rocl/ninth/rahc/kepone.pdf>.
 Maier, G., Born, D., Bauer, I., Wolf, R., Boese, R. & Cremer, D. (1994). *Chem. Ber.* **127**, 173–189.
 Paquette, L. A., Haluska, R. J., Short, M. R., Read, L. K. & Clardy, J. (1972). *J. Am. Chem. Soc.* **94**, 529.
 Prins, H. J. (1946). *Recl Trav. Chim.* **65**, 455–467.
 Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
 Scherer, K. V., Ungefug, G. A. & Lunt, R. S. (1966). *J. Am. Chem. Soc.* **88**, 2859–2860.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
 Siemens (1994). XSCANS. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA. (Current suppliers: Bruker AXS Inc., Madison, Wisconsin, USA.)
 Tang, D. (2002). PhD thesis, University of Chicago Chemistry Department, USA.
 Wuensch, B. & Prewitt, C. (1965). *Z. Kristallogr.* **122**, 24–59.