Acta Cryst. (1992). C**48**, 200–201

The 1:1 Diels–Alder Adduct of 1,5-Cyclooctadiene and 1,2,3,4-Tetrachloro-5,5-dimethoxy-1,3-cyclopentadiene

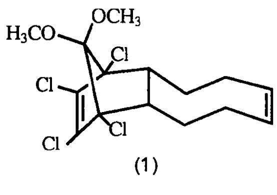
By Jingyi Li, Frank R. Fronczek and Mark L. McLaughlin[*]

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, *USA*

(*Received* 3 *June* 1991; *accepted* 8 *July* 1991)

Abstract. *endo*-1,10,11,12-Tetrachloro-13,13-dimethoxytricyclo[8.2.1.$0^{2,9}$]trideca-5,11-diene, $C_{15}H_{18}Cl_4O_2$, $M_r = 372.1$, orthorhombic, $P2_12_12_1$, $a = 8.9729\,(5)$, $b = 13.0584\,(6)$, $c = 14.1178\,(5)$ Å, $V = 1654.2\,(2)$ Å^3, $Z = 4$, $D_x = 1.494$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 7.19$ cm^{-1}, $F(000) = 768$, $T = 299$ K, $R = 0.033$ for 2373 observations with $I > 3\sigma(I)$ (of 3483 unique data). The cyclooctene ring adopts the chair conformation. Near-zero torsion angles of the chair occur at the ring-fusion bond, −1.3 (3)°, and at the double bond, −0.6 (5)°. The torsion angles about the bonds comprising the sides of the chair are 111.2 (3) and −109.5 (3)°. The norbornenyl C=C bond length is 1.316 (3) Å and the cyclooctenyl C=C bond length is 1.309 (4) Å.

Experimental. The title compound (1) was prepared by slowly heating a 1:10 mixture of 1,2,3,4-tetrachloro-5,5-dimethoxy-1,3-cyclopentadiene and 1,5-cyclooctadiene to 432 K under argon. The excess 1,5-cyclooctadiene was removed under reduced pressure and the residue was diluted with ether. A white solid was filtered. The filtrate was concentrated to afford a thick yellowish clear liquid, which after standing became solid (Eaton, Sidhu, Langford, Cullison & Cornel, 1980).



(1)

Crystals of (1) were grown in methanol, m.p. 344–345 K. A clear colorless crystal with dimensions 0.28 × 0.38 × 0.40 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Cell dimensions were determined from setting angles of 25 reflections having $13 > \theta > 10°$. Intensities were collected by ω–2θ scans designed for $I = 25\sigma(I)$, subject to maximum scan time = 90 s, scan rates varied from 0.72 to 3.30° min^{-1}. One octant of data having $1 < \theta < 33°$, $0 \le h \le 13$, $0 \le k \le 20$, $0 \le l \le 21$ was measured and corrected for background, Lorentz, polarization, decay and absorption. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 93.1%. Three standard reflections (400, 060, 006) were measured every 10000 s, exhibiting 4.1% intensity decline. A linear decay correction was applied. The space group was determined from systematic absences $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd. The structure was solved by direct methods using *MULTAN*11/82 (Main *et al.*, 1982), refined by full-matrix least squares based on F, using data for which $I > 3\sigma(I)$, with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o)^2]^{-1}$, using the Enraf–Nonius *Structure Determination Package* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974) and anomalous coefficients of Cromer (1974). H-atom coordinates were located by ΔF synthesis and were refined with isotropic thermal parameters; heavy-atom coordinates were refined with anisotropic thermal parameters. Final $R = 0.033$ for 2373 observed data (0.069 for all 3483 data), $wR = 0.035$ and $S = 1.568$ for 262 variables. Maximum shift 0.03σ in the final cycle, maximum residual density 0.21, minimum −0.23 e Å^{-3}. Refinement of the inversion-related structure under identical conditions yielded $R = 0.035$, $wR = 0.037$ and $S = 1.642$.

Refined fractional coordinates and equivalent isotropic displacement parameters for the former refinement are listed in Table 1.[†] Bond distances, angles and selected torsion angles are presented in Table 2. Fig. 1 is an *ORTEP* (Johnson, 1965) drawing of the title compound showing the atom numbering and Fig. 2 illustrates the unit cell.

---

[*] Author to whom correspondence should be addressed.

[†] Lists of bond distances and angles involving H atoms, structure factors, anisotropic thermal parameters, torsion angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54456 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/92/010200-02$03.00

Table 1. *Coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Cl(1)	0.03955 (7)	0.86374 (5)	0.31655 (5)	3.94 (1)
Cl(2)	0.29581 (9)	0.86461 (6)	0.14858 (5)	4.76 (1)
Cl(3)	0.46067 (9)	1.09719 (7)	0.14013 (5)	5.43 (2)
Cl(4)	0.30478 (8)	1.24881 (5)	0.29839 (6)	4.93 (1)
O(1)	0.0547 (2)	1.0869 (1)	0.4065 (1)	3.27 (3)
O(2)	0.0368 (2)	1.1108 (1)	0.2441 (1)	3.52 (3)
C(1)	0.2885 (2)	0.9551 (2)	0.3989 (2)	2.54 (4)
C(2)	0.3624 (2)	1.0654 (2)	0.3950 (2)	2.76 (4)
C(3)	0.5328 (3)	1.0727 (2)	0.3895 (2)	3.68 (5)
C(4)	0.6139 (3)	1.0463 (2)	0.4826 (2)	4.46 (6)
C(5)	0.7006 (3)	0.9480 (2)	0.4774 (2)	4.43 (6)
C(6)	0.6396 (3)	0.8570 (2)	0.4790 (2)	4.41 (6)
C(7)	0.4745 (3)	0.8381 (2)	0.4871 (2)	3.99 (5)
C(8)	0.3875 (3)	0.8610 (2)	0.3950 (2)	3.17 (4)
C(9)	0.1775 (2)	0.9601 (2)	0.3139 (2)	2.54 (4)
C(10)	0.2680 (3)	0.9651 (2)	0.2239 (2)	2.89 (4)
C(11)	0.3316 (2)	1.0558 (2)	0.2202 (2)	3.14 (4)
C(12)	0.2842 (3)	1.1142 (2)	0.3079 (2)	2.90 (4)
C(13)	0.1213 (2)	1.0737 (2)	0.3191 (2)	2.71 (4)
C(14)	0.0108 (4)	1.1889 (2)	0.4302 (2)	5.02 (7)
C(15)	−0.1163 (3)	1.0808 (2)	0.2398 (2)	4.57 (6)

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

Cl(1)—C(9)	1.766 (2)	C(2)—C(12)	1.553 (3)
Cl(2)—C(10)	1.707 (2)	C(3)—C(4)	1.540 (4)
Cl(3)—C(11)	1.707 (2)	C(4)—C(5)	1.503 (4)
Cl(4)—C(12)	1.773 (2)	C(5)—C(6)	1.309 (4)
O(1)—C(13)	1.383 (3)	C(6)—C(7)	1.507 (4)
O(1)—C(14)	1.428 (3)	C(7)—C(8)	1.546 (4)
O(2)—C(13)	1.389 (3)	C(9)—C(10)	1.510 (3)
O(2)—C(15)	1.430 (3)	C(9)—C(13)	1.569 (3)
C(1)—C(2)	1.586 (3)	C(10)—C(11)	1.316 (3)
C(1)—C(8)	1.518 (3)	C(11)—C(12)	1.515 (3)
C(1)—C(9)	1.561 (3)	C(12)—C(13)	1.562 (3)
C(2)—C(3)	1.534 (3)		

C(13)—O(1)—C(14)	116.4 (2)	C(10)—C(9)—C(13)	99.9 (2)
C(13) - O(2) C(15)	117.5 (2)	Cl(2)···C(10)···C(9)	124.7 (2)
C(2)—C(1)—C(8)	119.3 (2)	Cl(2)—C(10)—C(11)	127.2 (2)
C(2)—C(1)—C(9)	101.7 (2)	C(9)—C(10)—C(11)	107.7 (2)
C(8)—C(1)—C(9)	112.2 (2)	Cl(3)—C(11)—C(10)	127.2 (2)
C(1)—C(2)—C(3)	118.3 (2)	Cl(3)—C(11)—C(12)	124.9 (2)
C(1)—C(2)—C(12)	102.2 (2)	C(10)—C(11)—C(12)	107.5 (2)
C(3)—C(2)—C(12)	112.6 (2)	Cl(4)—C(12)—C(2)	114.8 (2)
C(2)—C(3)—C(4)	114.4 (2)	Cl(4)—C(12)—C(11)	114.1 (2)
C(3)—C(4)—C(5)	113.2 (2)	Cl(4)—C(12)—C(13)	116.1 (2)
C(4)—C(5)—C(6)	123.9 (2)	C(2)—C(12)—C(11)	108.3 (2)
C(5)—C(6)—C(7)	124.1 (3)	C(2)—C(12)—C(13)	101.8 (2)
C(6)—C(7)—C(8)	113.6 (2)	C(11)—C(12)—C(13)	100.1 (2)
C(1)—C(8)—C(7)	114.9 (2)	O(1)—C(13)—O(2)	113.6 (2)
Cl(1)—C(9)—C(1)	113.7 (1)	O(1)—C(13)—C(9)	107.4 (2)
Cl(1)—C(9)—C(10)	115.2 (2)	O(1)—C(13)—C(12)	116.9 (2)
Cl(1)—C(9)—C(13)	116.6 (1)	O(2)—C(13)—C(9)	118.0 (2)
C(1)—C(9)—C(10)	107.8 (2)	O(2)—C(13)—C(12)	108.4 (2)
C(1)—C(9)—C(13)	102.0 (2)	C(9)—C(13)—C(12)	90.8 (2)

C(14)—O(1)—C(13)—O(2)	−54.6 (3)	C(1)—C(2)—C(3)—C(4)	−73.2 (3)
C(15)—O(2)—C(13)—O(1)	−49.5 (3)	C(1)—C(2)—C(12)—C(13)	38.9 (2)
C(8)—C(1)—C(2)—C(3)	−1.3 (3)	C(2)—C(3)—C(4)—C(5)	111.2 (3)
C(9)—C(1)—C(2)—C(3)	−125.3 (2)	C(4)—C(5)—C(6)—C(7)	−0.6 (5)
C(9)—C(1)—C(2)—C(12)	−1.0 (2)	C(6)—C(7)—C(8)—C(1)	−109.5 (3)
C(2)—C(1)—C(8)—C(7)	74.4 (3)	C(9)—C(10)—C(11)—C(12)	−0.3 (2)
C(2)—C(1)—C(9)—C(13)	−37.0 (2)	C(10)—C(11)—C(12)—C(13)	−35.3 (2)

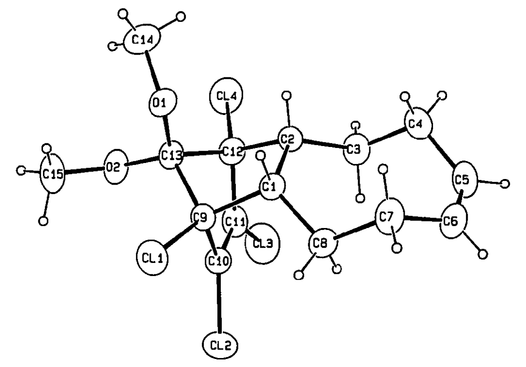


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecule, representing C atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radius.

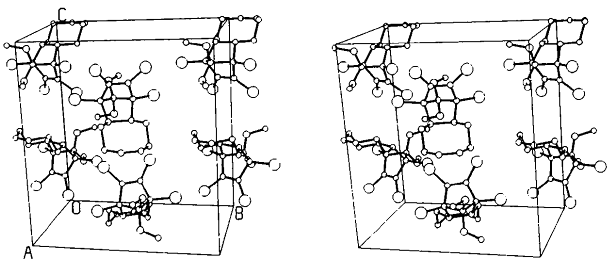


Fig. 2. Stereoview of the unit cell.

Related literature. Torsion angles about the bonds of the eight-membered ring comprising the sides of the chair differ slightly from one another, C(2)—C(3)—C(4)—C(5) = 111.2 (3) and C(1)—C(6)—C(7)—C(8) = 109.5 (3)°, but are comparable to those of the corresponding Diels–Alder diadduct 1,6,7,8,9,14,15,16-octachloro-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}0^{2,13}.0^{5,10}]octadeca-7,15-diene and the dechlorinated Diels–Alder diadduct 17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (Garcia, Fronczek & McLaughlin, 1991). The intramolecular C(14)···C(15) distance [3.243 (3) Å] is shorter than the corresponding distances of the diadduct [3.332 (5) Å] and of the dechlorinated diadduct [3.510 (2) Å].

We thank the Louisiana Educational Quality Support Fund Grant No. LEQSF(1987–90)-RD-A-5 for support of this research.

References

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Eaton, P. E., Sidhu, S. R., Langford, E. G., Cullison, D. A. & Cornel, L. (1980). *Tetrahedron*, **37**, 4479–4494.

Frenz, B. A. & Okaya, Y. (1980). *Enraf–Nonius Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

Garcia, J. G., Fronczek, F. R. & McLaughlin, M. L. (1991). *Acta Cryst.* **C47**, 206–209.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.