

The Major Diels–Alder Diadduct of 1,2,3,4-Tetrachloro-1,3-cyclopentadiene with 1,5-Cyclooctadiene

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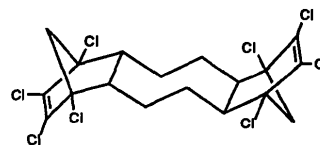
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Abstract. *endo-endo-anti*-1,6,7,8,9,14,15,16-Octachloropentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene, C₁₈H₁₆Cl₈, *M_r* = 515.9, monoclinic, *P*2₁/*n*, *a* = 8.7121 (12), *b* = 11.349 (3), *c* = 11.141 (2) Å, β = 112.34 (2)°, *V* = 1018.9 (4) Å³, *Z* = 2, *D_x* = 1.682 g cm⁻³; λ(Mo *K*α) = 0.71073 Å, μ = 11.16 cm⁻¹, *F*(000) = 520, *T* = 296 K, *R* = 0.031 for 1403 observations with *I* > 3σ(*I*) (of 2216 unique data). The molecule is centrosymmetric; the cyclooctane ring adopts the chair conformation. The zero torsion angle of the chair occurs at the ring-fusion bonds, with a magnitude of ±0.3 (3)°. The endocyclic torsion angles about the bonds adjacent to the eclipsed bond are ±75.6 (2)° and the torsion angles about the bonds comprising the sides of the chair are ±117.8 (3)°. The C=C bond has a length of 1.327 (3) Å.

Experimental. The title compound (1) was prepared by slowly heating a 4:1 mixture of 1,2,3,4-tetrachloro-1,3-cyclopentadiene (Roedig & Hörnig, 1955) with 1,5-cyclooctadiene to 453 K and filtering the white solid (Akhtar, Fray & Yarrow, 1968). Crystals grown by slow cooling of toluene, m.p. 397–400 K (dec.), were suitable; a clear colorless crystal of dimensions 0.07 × 0.25 × 0.42 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Mo *K*α radiation and a graphite monochromator. Cell dimensions were determined from setting angles of 25 reflections having 11 > θ > 9°. The ω–2θ scans were designed for *I* = 50σ(*I*), subject to maximum scan time = 120 s, scan rates varied from 0.53–4.00° min⁻¹, sinθ/λ < 0.639 Å⁻¹. One quadrant of data having 1 < θ < 27°, 0 ≤ *h* ≤ 10, 0 ≤ *k* ≤ 13, -13 ≤ *l* ≤ 13 was measured and corrected for background, Lorentz, polarization, and absorption. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 0.873. Three standard reflections (200, 020, 002) measured every 10 000 s exhibited only random fluctuations, so no correction for decay was needed. The space group was determined by systematic absences

*h*0*l* with *h* + *l* odd and 0*k*0 with *k* odd. Redundant 0*kl* and 0*k* \bar{l} data were averaged; *R*_{int} = 0.017 (2216 unique reflections). The structure was solved by direct methods, refined by full-matrix least squares based upon *F*, using data for which *I* > 3σ(*I*), weights *w* = 4*F*_o²[σ²(*I*) + (0.02*F*_o²)²]⁻¹ using the *Enraf–Nonius Structure Determination Package* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). Heavy-atom coordinates were refined with anisotropic thermal parameters; H-atom coordinates were located by Δ*F* and were refined with isotropic thermal parameters. Final *R* = 0.031 for 1403 observed data (0.083 for all 2216 data), *wR* = 0.031, and *S* = 1.471 for 150 variables. Maximum shift was 0.01σ in the final cycle, max. residual density 0.24 and min. -0.26 e Å⁻³.



(1)

The fractional coordinates of the title compound are given in Table 1. Fig. 1 is a perspective drawing showing the atom numbering for the title molecule and Fig. 2 shows the unit cell. Bond distances, angles and selected torsion angles are presented in Table 2.†

Related literature. Single-bond distances which are analogous to C(1)–C(6) and C(4)–C(5) are found in 1,2,4,5,6,7,8,9-octachloro-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one, 1.572 (3) and 1.573 (3) Å (Galesic, Matijasic & Bruvo, 1985); 3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-pentacyclo[6.2.1.1^{3,6}.0^{2,7}]do-

† Lists of 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 53388 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Coordinates and equivalent isotropic thermal parameters for (1)*

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B _{eq} (Å ²)
Cl(1)	1.34819 (7)	0.45827 (7)	0.77053 (7)	4.07 (2)
Cl(2)	1.04042 (8)	0.26149 (6)	0.67812 (7)	3.88 (2)
Cl(3)	0.67313 (8)	0.40808 (7)	0.57332 (7)	4.14 (2)
Cl(4)	0.74960 (9)	0.69585 (7)	0.60402 (7)	4.19 (2)
C(1)	1.1438 (3)	0.4981 (2)	0.7554 (2)	2.80 (6)
C(2)	1.0111 (3)	0.4091 (2)	0.6840 (2)	2.65 (5)
C(3)	0.8671 (3)	0.4659 (2)	0.6440 (2)	2.72 (6)
C(4)	0.9059 (3)	0.5922 (2)	0.6889 (2)	2.71 (5)
C(5)	0.9566 (3)	0.5950 (2)	0.8391 (2)	2.67 (5)
C(6)	1.1289 (3)	0.5273 (2)	0.8867 (2)	2.61 (6)
C(7)	1.0715 (3)	0.6083 (2)	0.6752 (2)	3.17 (6)
C(8)	1.1495 (3)	0.4214 (2)	0.9748 (2)	2.84 (6)
C(9)	0.8230 (3)	0.5497 (2)	0.8836 (2)	2.97 (6)

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

Cl(1)	C(1)	1.782 (2)	C(3)	C(4)	1.514 (4)				
Cl(2)	C(2)	1.700 (3)	C(4)	C(5)	1.560 (3)				
Cl(3)	C(3)	1.702 (2)	C(4)	C(7)	1.518 (4)				
Cl(4)	C(4)	1.776 (2)	C(5)	C(6)	1.587 (3)				
C(1)	C(2)	1.514 (3)	C(5)	C(9)	1.518 (4)				
C(1)	C(6)	1.553 (4)	C(6)	C(8)	1.519 (4)				
C(1)	C(7)	1.527 (4)	C(8)	C(9)	1.539 (4)				
C(2)	C(3)	1.327 (3)							
Cl(1)	C(1)	C(2)	114.6 (2)	Cl(4)	C(4)	C(7)	115.6 (2)		
Cl(1)	C(1)	C(6)	113.8 (1)	C(3)	C(4)	C(5)	108.1 (2)		
Cl(1)	C(1)	C(7)	116.0 (2)	C(3)	C(4)	C(7)	100.5 (2)		
C(2)	C(1)	C(6)	108.5 (2)	C(5)	C(4)	C(7)	102.3 (2)		
C(2)	C(1)	C(7)	100.1 (2)	C(4)	C(5)	C(6)	101.3 (2)		
C(6)	C(1)	C(7)	102.3 (2)	C(4)	C(5)	C(9)	113.8 (2)		
Cl(2)	C(2)	C(1)	125.6 (2)	C(6)	C(5)	C(9)	118.2 (2)		
Cl(2)	C(2)	C(3)	127.0 (2)	C(1)	C(6)	C(5)	101.3 (2)		
C(1)	C(2)	C(3)	106.7 (2)	C(1)	C(6)	C(8)	114.1 (2)		
Cl(3)	C(3)	C(2)	127.9 (2)	C(5)	C(6)	C(8)	117.6 (2)		
Cl(3)	C(3)	C(4)	125.1 (2)	C(1)	C(7)	C(4)	92.2 (2)		
C(2)	C(3)	C(4)	106.6 (2)	C(6)	C(8)	C(9)	115.3 (2)		
Cl(4)	C(4)	C(3)	114.9 (1)	C(5)	C(9)	C(8)	115.0 (2)		
Cl(4)	C(4)	C(5)	113.9 (2)						
Cl(1)	C(1)	C(2)	Cl(2)	28.7 (3)	C(7)	C(1)	C(2)	C(3)	-35.1 (2)
C(7)	C(1)	C(6)	C(5)	37.4 (2)	C(1)	C(2)	C(3)	C(4)	0.2 (3)
C(3)	C(4)	C(7)	C(1)	-52.5 (2)	C(4)	C(5)	C(6)	C(1)	-0.3 (2)
C(9)	C(5)	C(6)	C(8)	-0.3 (3)	C(6)	C(5)	C(9)	C(8)	75.7 (3)
C(5)	C(6)	C(8)	C(9)	-75.6 (3)	C(6)	C(8)	C(9)	C(5)	117.8 (3)

deca-4,9-diene, 1.550 (4) and 1.556 (3) Å (Battiste, Griggs, Sackett, Coxon & Steel, 1987); [(9,10- η :11 σ)-3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-11-yl](η^5 -cyclopentadienyl)nickel(II), 1.546 (3) and 1.550 (3) Å (Battiste *et al.*, 1987); 1,2,3,4,7,7-hexachloro-5,6-bis(chloromethyl)bicyclo-[2.2.1]hept-2-ene [Alodan (Hoechst)[®]], 1.568 (7) and 1.549 (7) Å (Kennard, Smith & Palm, 1981); 1,6,7,8,9,14,15,16-octachloro-17,17,18,18-tetramethoxy-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene, 1.561 (3) and 1.555 (4) Å and 17,17,18,18-tetramethoxy-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene, 1.566 (1) and 1.564 (1) Å (Garcia, Fronczek & McLaughlin, 1991) are similar to those

in the title compound, 1.533 (4) and 1.560 (3) Å, respectively. The bond angle C1—C7—C4 [92.2 (2)°] of the title compound is similar to the analogous bond angles of 1,2,4,5,6,7,8,9-octachloro-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one [91.6 (1)°] (Galesic, Matijasic & Bruvo, 1985); 3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-pentacyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (Battiste *et al.*, 1987) and [(9,10- η :11 σ)-3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-11-yl](η^5 -cyclopentadienyl)nickel(II) (Battiste *et al.*, 1987) [90.9 (2)° and 90.7 (2)° respectively]; 1,2,3,4,7,7-hexachloro-5,6-bis(chloromethyl)bicyclo-[2.2.1]hept-2-ene [Alodan (Hoechst)[®]] (Kennard, Smith & Palm, 1981) [92.9 (4)°]; 1,6,7,8,9,14,15,16-octachloro-17,17,18,18-tetramethoxy-pentacyclo-[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene [90.9 (2)°] and 17,17,18,18-tetramethoxy-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene [93.9 (8)°] (Garcia, Fronczek & McLaughlin 1991). The near-zero torsion angle C(9)—C(5)—C(6)—C(8) [-0.3 (3)°] as well as torsion angle C(5)—C(9)—C(8)—C(6') [117.8 (2)°] in the title compound are in accordance with 1,6,7,8,9,14,15,16-octachloro-17,17,18,18-tetramethoxy-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene [1.8 (3)°, -119.0 (2)°] and 17,17,18,18-tetramethoxy-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene [0.9 (1)°, 117.8 (1)°], respectively (Garcia, Fronczek & McLaughlin, 1991).

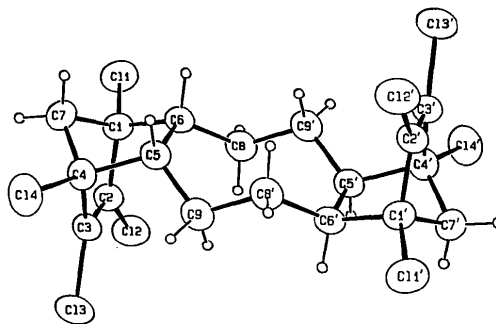


Fig. 1. ORTEP drawing (Johnson, 1965) of the title molecule, representing heavy atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radius.

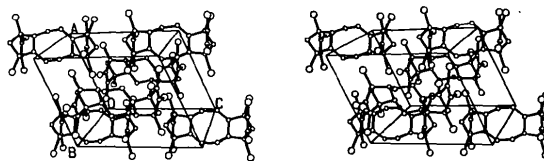


Fig. 2. Stereoview of the unit cell.

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Structure of 3-Benzylidene-2-chloro-1-cyclohexenecarbaldehyde

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Abstract. $C_{14}H_{13}ClO$, $M_r = 232.7$, orthorhombic, *Pbca*, $a = 11.733$ (3), $b = 7.470$ (2), $c = 26.922$ (3) Å, $V = 2359.6$ Å³, $Z = 8$, $D_x = 1.31$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 26.8$ cm⁻¹, $F(000) = 976$, $T = 296$ K, $R = 0.05$ for 1304 observed reflections with $I > 4\sigma(I)$. The cyclohexane ring adopts a sofa conformation. The interplanar angles between the two rings is 36 (1)°. The benzylidene ring is planar. The Cl—C distance is 1.736 (4) Å.

Experimental. 3-Benzylidene-2-chloro-1-cyclohexenecarbaldehyde was prepared by the following procedure: a benzylidenecyclohexane was produced from a condensation reaction (Claisen-Schmidt) of cyclohexanone and benzaldehyde. The benzylidenecyclohexanone was then allowed to undergo a Vilsmeier-Hacck (Lotzbeyer & Bodendorf, 1967) reaction which gave the title compound and the product was purified through column chromatography.

A crystal of dimensions 0.32 × 0.38 × 0.48 mm was grown from alcohol solution, and mounted on an Enraf-Nonius CAD-4 diffractometer. The cell parameters and their e.s.d.'s were derived from a least-squares treatment of 25 reflections ($25 < \theta < 35^\circ$). Intensities of reflections (h 0 → 13, k 0 → 8, l 0 → 32) collected with ω -2 θ scan: $\theta_{\text{max}} = 75^\circ$. Two reference reflections measured every 100 reflections

showed no significant variation. 1983 unique reflections were collected, from which 1304 were considered observed, having $I > 4\sigma(I)$, $R_{\text{int}} = 0.01$. Intensity data were corrected for Lp effects. No absorption correction. Structure solved by Patterson synthesis using *SHELXS86* (Sheldrick, 1986) and refinement was carried out by full-matrix least-squares method using *SHELX76* (Sheldrick, 1976). All H atoms located from difference Fourier map and were refined isotropically. In the final stage of refinement weights were introduced resulting in $R = 0.05$, $wR = 0.06$, $S = 1.69$, $w = 1/[\sigma^2|F| + 0.031021|F|^2]$, $(\Delta/\sigma)_{\text{av}} = 0.005$, $(\Delta/\sigma)_{\text{max}} = 0.08$ for 1304 reflections.

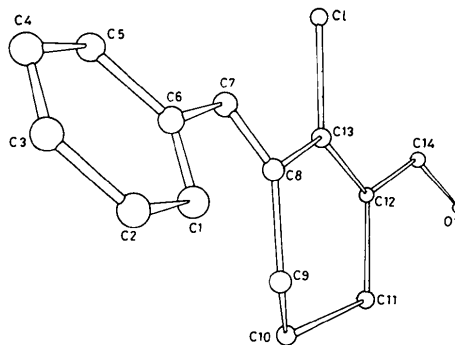


Fig. 1. A view of the molecule with the atom numbering.