Acta Cryst. (1992). C**48**, 195–197

1,8,9,10,11,18,19,20,21,21,23,23-Dodecachloroheptacyclo-[16.2.1.$1^{3,16}$.$1^{8,11}$.$0^{2,17}$.$0^{4,15}$.$0^{7,12}$]tricosa-9,19-diene

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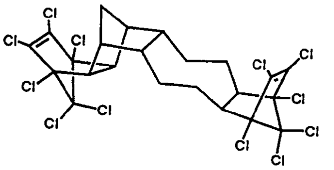
Abstract. $C_{23}H_{18}Cl_{12}$, $M_r = 719.8$, orthorhombic, $P2_12_12_1$, $a = 8.7156\,(3)$, $b = 12.2513\,(7)$, $c = 26.5392\,(12)$ Å, $V = 2833.8\,(4)$ Å^3, $Z = 4$, $D_x = 1.687$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 12.0$ cm^{-1}, $F(000) = 1440$, $T = 297$ K, $R = 0.040$ for 5627 observations with $I > 3\sigma(I)$ (of 6748 unique data). The *endo-endo* isomer of the four possible Diels–Alder diadducts is preferred. The cyclooctane ring adopts the chair conformation. The near-zero torsion angles of the chair occur at the ring-fusion bonds, and have magnitudes of 6.7 (4) and 3.9 (4)°. The C═C bonds have lengths of 1.318 (5) and 1.312 (5) Å.

Experimental. The title compound (1) was prepared by allowing 1 equivalent of 1,1-hexachlorocyclopentadiene to react with 1 equivalent of tricyclo[8.2.1.$0^{2,9}$]trideca-5,11-diene (Garcia, 1990) neat at 406–413 K (Akhtar, Fray & Yarrow, 1968).



(1)

Crystals that deposited in the reaction flask, m.p. > 523 K (dec.), were suitable; a clear colorless crystal with dimensions 0.38 × 0.40 × 0.48 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 $12 > \theta > 10°$. The ω–2θ scans were designed for $I = 25\sigma(I)$, subject to maximum scan time = 120 s, scan rates varied from 0.61 to 3.30° min^{-1}. An octant of data having $1 < \theta < 30°$, $0 \le h \le 12$, $0 \le k \le 17$, $0 \le l \le 37$ and a second octant having $1 < \theta < 25°$, $-10 \le h \le -1$, $0 \le k \le 14$, $0 \le l \le 31$ were measured and corrected for background, Lorentz, polarization and decay. ψ scans of four reflections exhibited no decrease in intensity with rotation about the diffraction vector, thus no absorption correction was applied. Three standard reflections (200, 040, 006) decreased in intensity by 6.4%, and a linear correction was applied. A total of 7134 data was measured. Equivalent zonal reflections were averaged, $R_{\rm int} = 0.019$, yielding 6748 unique data, of which 5627 had $I > 3\sigma(I)$ and were used in the refinement. Systematic absences $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd indicated space group $P2_12_12_1$. The structure was solved by direct methods using *MULTAN*80 (Main *et al.*, 1980), refined by full-matrix least squares based on F, with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$, 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 ΔF synthesis and were refined with isotropic thermal parameters. Final $R = 0.0403$ for 5627 observed data (0.056 for all 6748 data), $wR = 0.0468$ and $S = 2.237$ for 388 variables. Maximum shift 0.06σ in the final cycle, maximum residual density 0.65, minimum -0.65 e Å^{-3}. The inversion-related structure was refined in identical fashion, to yield $R = 0.0409$, $wR = 0.0478$ and $S = 2.283$. The fractional coordinates for the former refinement are given in Table 1. Fig. 1 is a perspective drawing showing the atom numbering, and Fig. 2 illustrates the unit cell. Bond distances, angles and selected torsion angles are presented in Table 2.†

Related literature. Ring-fusion bond lengths C(1)—C(2) 1.569 (5) Å and C(5)—C(6) 1.585 (4) Å of the title molecule are similar to those of *endo-endo-anti-*

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† Lists of H-atom coordinates and thermal parameters, bond distances and angles involving H atoms, anisotropic thermal parameters, torsion angles, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54455 (43 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*

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

	x	y	z	B_{eq}(Å^2)
Cl(1)	−0.1371 (1)	0.0925 (1)	0.55201 (4)	4.78 (2)
Cl(2)	−0.0500 (2)	−0.16757 (9)	0.55939 (4)	6.04 (2)
Cl(3)	0.3411 (2)	−0.19298 (9)	0.55618 (4)	6.74 (3)
Cl(4)	0.4926 (1)	0.0529 (1)	0.54888 (4)	6.05 (3)
Cl(5)	0.1948 (1)	0.24564 (7)	0.54209 (3)	4.52 (2)
Cl(6)	0.1832 (1)	0.09945 (8)	0.62537 (3)	4.03 (2)
Cl(7)	0.5508 (1)	0.3371 (1)	0.24451 (4)	5.16 (2)
Cl(8)	0.3390 (1)	0.1598 (1)	0.17997 (4)	5.64 (2)
Cl(9)	−0.0369 (1)	0.23493 (8)	0.19158 (4)	4.51 (2)
Cl(10)	−0.0591 (1)	0.44647 (7)	0.26764 (4)	3.86 (2)
Cl(11)	0.3080 (1)	0.51922 (8)	0.30632 (5)	5.05 (2)
Cl(12)	0.2653 (1)	0.50167 (8)	0.19967 (4)	5.01 (2)
C(1)	0.0853 (4)	0.0428 (3)	0.3836 (1)	3.13 (6)
C(2)	0.2628 (4)	0.0216 (3)	0.3834 (1)	3.28 (6)
C(3)	0.3664 (4)	0.1166 (3)	0.3710 (1)	3.35 (7)
C(4)	0.3626 (4)	0.1536 (3)	0.3152 (1)	3.28 (6)
C(5)	0.3169 (4)	0.2730 (3)	0.3096 (1)	2.82 (6)
C(6)	0.1406 (4)	0.3017 (2)	0.3156 (1)	2.59 (5)
C(7)	0.0304 (4)	0.2070 (3)	0.3231 (1)	2.93 (6)
C(8)	0.0290 (4)	0.1597 (3)	0.3773 (1)	3.03 (6)
C(9)	0.0342 (4)	−0.0125 (3)	0.4348 (1)	3.46 (6)
C(10)	0.0842 (4)	0.0652 (3)	0.4768 (1)	2.75 (6)
C(11)	0.0444 (4)	0.0461 (3)	0.5336 (1)	2.90 (6)
C(12)	0.0844 (4)	−0.0690 (3)	0.5495 (1)	3.36 (7)
C(13)	0.2349 (4)	−0.0786 (3)	0.5486 (1)	3.62 (7)
C(14)	0.2999 (4)	0.0300 (3)	0.5323 (1)	3.32 (7)
C(15)	0.2632 (4)	0.0528 (3)	0.4761 (1)	2.87 (6)
C(16)	0.2900 (4)	−0.0348 (3)	0.4352 (1)	3.63 (7)
C(17)	0.1465 (5)	−0.1074 (3)	0.4374 (1)	4.03 (8)
C(18)	0.1826 (4)	0.1054 (3)	0.5589 (1)	2.90 (6)
C(19)	0.3542 (3)	0.3214 (3)	0.2565 (1)	3.16 (6)
C(20)	0.2628 (4)	0.2574 (3)	0.2176 (1)	3.21 (6)
C(21)	0.1184 (4)	0.2856 (3)	0.2226 (1)	2.97 (6)
C(22)	0.1074 (3)	0.3664 (2)	0.2656 (1)	2.69 (6)
C(23)	0.2590 (4)	0.4285 (3)	0.2574 (1)	3.22 (6)

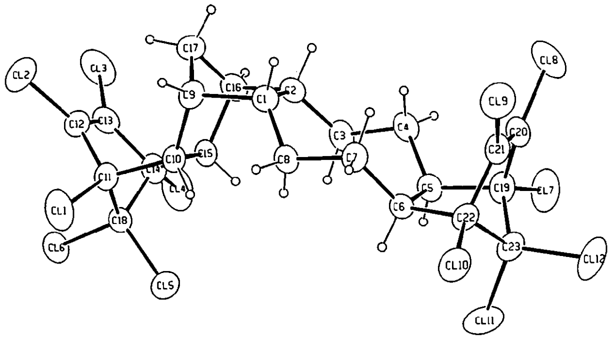

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecule, representing C atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radius.

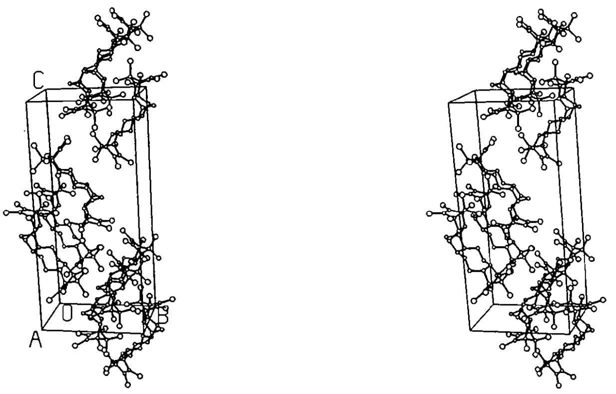

Fig. 2. Stereoview of the unit cell.

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

Cl(1)—C(11)	1.751 (3)	C(6)—C(7)	1.519 (4)
Cl(2)—C(12)	1.703 (4)	C(6)—C(22)	1.573 (4)
Cl(3)—C(13)	1.691 (4)	C(7)—C(8)	1.550 (5)
Cl(4)—C(14)	1.760 (3)	C(9)—C(10)	1.531 (5)
Cl(5)—C(18)	1.778 (3)	C(9)—C(17)	1.520 (5)
Cl(6)—C(18)	1.766 (3)	C(10)—C(11)	1.563 (4)
Cl(7)—C(19)	1.753 (3)	C(10)—C(15)	1.568 (4)
Cl(8)—C(20)	1.693 (4)	C(11)—C(12)	1.512 (5)
Cl(9)—C(21)	1.701 (3)	C(11)—C(18)	1.559 (4)
Cl(10)—C(22)	1.753 (3)	C(12)—C(13)	1.318 (5)
Cl(11)—C(23)	1.763 (4)	C(13)—C(14)	1.509 (5)
Cl(12)—C(23)	1.775 (4)	C(14)—C(15)	1.550 (4)
C(1)—C(2)	1.569 (5)	C(14)—C(18)	1.549 (5)
C(1)—C(8)	1.522 (5)	C(15)—C(16)	1.544 (5)
C(1)—C(9)	1.582 (5)	C(16)—C(17)	1.536 (5)
C(2)—C(3)	1.509 (5)	C(19)—C(20)	1.522 (5)
C(2)—C(16)	1.559 (5)	C(19)—C(23)	1.552 (5)
C(3)—C(4)	1.549 (5)	C(20)—C(21)	1.312 (5)
C(4)—C(5)	1.524 (5)	C(21)—C(22)	1.513 (4)
C(5)—C(6)	1.585 (4)	C(22)—C(23)	1.540 (4)
C(5)—C(19)	1.562 (4)		

C(2)—C(1)—C(8)	118.2 (3)	C(10)—C(11)—C(12)	110.9 (3)
C(2)—C(1)—C(9)	102.1 (3)	C(10)—C(11)—C(18)	100.0 (2)
C(8)—C(1)—C(9)	114.1 (3)	C(12)—C(11)—C(18)	97.8 (2)
C(1)—C(2)—C(3)	117.5 (3)	Cl(2)—C(12)—C(11)	123.1 (3)
C(1)—C(2)—C(16)	102.7 (3)	Cl(2)—C(12)—C(13)	128.6 (3)
C(3)—C(2)—C(16)	116.3 (3)	C(11)—C(12)—C(13)	108.0 (3)
C(2)—C(3)—C(4)	114.8 (3)	Cl(3)—C(13)—C(12)	128.1 (3)
C(3)—C(4)—C(5)	112.4 (3)	Cl(3)—C(13)—C(14)	124.0 (3)
C(4)—C(5)—C(6)	117.2 (3)	C(12)—C(13)—C(14)	107.4 (3)
C(4)—C(5)—C(19)	113.5 (3)	Cl(4)—C(14)—C(13)	115.3 (3)
C(6)—C(5)—C(19)	102.0 (2)	Cl(4)—C(14)—C(15)	114.2 (2)
C(5)—C(6)—C(7)	117.2 (2)	Cl(4)—C(14)—C(18)	114.8 (2)
C(5)—C(6)—C(22)	101.8 (2)	C(13)—C(14)—C(15)	110.9 (3)
C(7)—C(6)—C(22)	112.3 (2)	C(13)—C(14)—C(18)	98.5 (3)
C(6)—C(7)—C(8)	114.4 (3)	C(15)—C(14)—C(18)	101.3 (3)
C(1)—C(8)—C(7)	116.9 (3)	C(10)—C(15)—C(14)	102.2 (2)
C(1)—C(9)—C(10)	106.2 (3)	C(10)—C(15)—C(16)	103.2 (3)
C(1)—C(9)—C(17)	100.7 (3)	C(14)—C(15)—C(16)	121.2 (3)
C(10)—C(9)—C(17)	105.1 (3)	C(2)—C(16)—C(15)	106.8 (3)
C(9)—C(10)—C(11)	123.1 (3)	C(2)—C(16)—C(17)	99.5 (3)
C(9)—C(10)—C(15)	102.3 (2)	C(15)—C(16)—C(17)	104.7 (3)
C(11)—C(10)—C(15)	102.6 (2)	C(9)—C(17)—C(16)	94.6 (3)
Cl(1)—C(11)—C(10)	114.9 (2)	Cl(5)—C(18)—Cl(6)	106.9 (2)
Cl(1)—C(11)—C(12)	115.7 (2)	Cl(5)—C(18)—C(11)	112.9 (2)
Cl(1)—C(11)—C(18)	115.3 (2)	Cl(5)—C(18)—C(14)	115.0 (2)
Cl(6)—C(18)—C(11)	114.4 (2)	C(20)—C(21)—C(22)	108.0 (3)
Cl(6)—C(18)—C(14)	115.4 (2)	Cl(10)—C(22)—C(6)	114.1 (2)
C(11)—C(18)—C(14)	92.0 (2)	Cl(10)—C(22)—C(21)	116.3 (2)
Cl(7)—C(19)—C(5)	114.1 (2)	Cl(10)—C(22)—C(23)	116.0 (2)
Cl(7)—C(19)—C(20)	116.4 (2)	C(6)—C(22)—C(21)	107.2 (2)
Cl(7)—C(19)—C(23)	115.6 (2)	C(6)—C(22)—C(23)	102.2 (2)
C(5)—C(19)—C(20)	107.9 (3)	C(21)—C(22)—C(23)	99.3 (2)
C(5)—C(19)—C(23)	101.3 (2)	Cl(11)—C(23)—Cl(12)	108.0 (2)
C(20)—C(19)—C(23)	99.5 (3)	Cl(11)—C(23)—C(19)	114.5 (2)
Cl(8)—C(20)—C(19)	124.0 (2)	Cl(11)—C(23)—C(22)	114.5 (2)
Cl(8)—C(20)—C(21)	128.5 (3)	Cl(12)—C(23)—C(19)	113.5 (2)
C(19)—C(20)—C(21)	107.3 (3)	Cl(12)—C(23)—C(22)	113.5 (2)
Cl(9)—C(21)—C(20)	128.2 (3)	C(19)—C(23)—C(22)	92.5 (2)
Cl(9)—C(21)—C(22)	123.6 (2)		

C(8)—C(1)—C(2)—C(3)	−6.7 (4)	C(4)—C(5)—C(6)—C(7)	−3.9 (4)
C(2)—C(3)—C(4)—C(5)	122.1 (3)	C(9)—C(10)—C(11)—C(12)	49.7 (4)
C(13)—C(14)—C(15)—C(16)	−47.4 (4)	C(7)—C(6)—C(22)—C(21)	−57.7 (3)
C(4)—C(5)—C(19)—C(20)	61.7 (3)	C(6)—C(7)—C(8)—C(1)	−114.9 (3)
C(8)—C(1)—C(9)—C(10)	−53.1 (4)	C(3)—C(2)—C(16)—C(15)	60.6 (4)

1,6,7,8,9,14,15,16,17,17,18,18-dodecachloropentacyclo[$12.2.1.1^{6,9}.0^{2,13}.0^{5,10}$]octadeca-7,15-diene (2) (Garcia, Fronczek & McLaughlin, 1991*a*) [C(1*a*)—C(2*a*) 1.573 (4), C(5*a*)—C(6*a*) 1.573 (4) and C(1*b*)—C(2*b*) 1.579 (5), C(5*b*)—C(6*b*) 1.579 (5) Å respectively for the two independent molecules in the asymmetric unit], *endo-endo-syn*-1,6,7,8,9,14,15,16,17,17,-18,18-dodecachloropentacyclo[$12.2.1.1^{6,9}.0^{2,13}.0^{5,10}$]-octadeca-7,15-diene (3) (Garcia *et al.*, 1991*a*) [C(1)—C(2) 1.572 (3), C(5)—C(6) 1.574 (3) Å], *endo-endo-*

anti-1,6,7,8,9,14,15,16-octachloropentacyclo[12.2.1.-$1^{6,9}.0^{2,13}.0^{5,1}$]octadeca-7,15-diene (4) (Garcia, Fronczek & McLauglin, 1991*b*) [C(5)—C(6) 1.587 (3), C(5′)—C(6′) 1.587 (3) Å], *endo-endo-anti*-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 (5) (Garcia, Fronczek & McLauglin, 1991*c*) [C(5)—C(6) 1.579 (3), C(5′)—C(6′) 1.579 (3) Å], *endo-endo-anti*-17,17,18,18-tetramethoxypentacyclo-[12.2.1.$1^{6,9}.0^{2,13}.0^{5,10}$]octadeca-7,15-diene (6) (Garcia *et al.*, 1991*c*) [C(5)—C(6) 1.575 (1), C(5′)—C(6′) 1.575 (1) Å] and *endo-endo-anti*-pentacyclo[12.2.1.-$1^{6,9}.0^{2,13}.0^{5,10}$]octadeca-7,15-diene-17,18-dione (7) (Garcia, Fronczek & McLauglin, 1991*d*) [C(5)—C(6) 1.576 (1), C(5′)—C(6′) 1.576 (1) Å]. Bond lengths C(12)—C(13) 1.318 (5), C(20)—C(21) 1.312 (5) Å of the title compound are similar to those of (2) [C(12*a*)—C(13*a*) 1.317 (5) and C(12*a*′)—C(13*a*′) 1.317 (5), C(12*b*)—C(13*b*) 1.314 (5) Å respectively for the two independent molecules], (3) [C(12)—C(13) 1.317 (4), C(12′)—C(13′) 1.314 (4) Å], (4) [C(12)—C(13) 1.327 (3) and C(12′)—C(13′) 1.327 (3) Å], (5) [C(12)—C(13) 1.324 (3) and C(12′)—C(13′) 1.324 (3) Å], (6) [C(12)—C(13) 1.329 (1) and C(12′)—C(13′) 1.329 (1) Å] and (7) [C(12)—C(13) 1.325 (2) and C(12′)—C(13′) 1.325 (2) Å]. Bond angles at the geminal chlorine bridge of the title compound [C(11)—C(18)—C(14) 92.0 (2) and C(19)—C(23)—C(22) 92.5 (2)°] are similar to those of (2) [92.3 (2), 92.5 (2) and 92.3 (2), 92.5 (2)° respectively from the two independent molecules] and (3) [92.3 (2) and 92.4 (2)°]. The bond angle at the geminal methylene bridge C(9)—C(17)—C(16) 94.6 (3)° is similar to that of (4) [92.2 (2)°].

Torsion angles C(8)—C(1)—C(2)—C(3) and C(4)—C(5)—C(6)—C(7) at the ring fusion of the title compound are −6.7 (4) and −3.9 (4)° in accordance with those of (2) [±0.5 (4) and ±0.7 (4)° respectively for the two independent molecules], (3) [−0.8 (3) and 0.7 (2)°], (4) [±0.3 (3)°], (5) [±1.8 (3)°], (6) [±0.9 (1)°] and (7) [±0.8 (1)°].

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The Major Diels–Alder Adduct of 1,2,3,4-Tetrachloro-1,3-cyclopentadiene with 1,9,10,11-Tetrachloro-12,12-dimethoxytricyclo[8.2.1.$0^{2,8}$]dodeca-5,10-diene

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Abstract. *endo-endo-anti*-1,6,7,8,9,14,15,16-Octachloro-17,17-dimethoxypentacyclo[12.2.1.$1^{6,9}.0^{2,13}.0^{5,10}$]-octadeca-7,15-diene, $C_{20}H_{20}Cl_8O_2$, $M_r = 576.0$, monoclinic, $P2_1/c$, $a = 20.078$ (2), $b = 11.4098$ (7), $c = 10.7579$ (6) Å, $\beta = 103.629$ (7)°, $V = 2395.0$ (3) Å^3, $Z = 4$, $D_x = 1.604$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 90.11$ cm^{-1}, $F(000) = 1168$, $T = 296$ K, $R = 0.051$ for 3061 observations with $I > 3\sigma(I)$ (of 4911 unique

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