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Structure of a Diels–Alder Adduct of Cyclopentadiene and Tetrachloro-1,4-benzoquinone

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Abstract. 4a,6,7,8a-Tetrachloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione, $C_{11}H_6Cl_4O_2$, $M_r = 311{\cdot}98$, monoclinic, $P2_1/n$, $a = 8{\cdot}004\,(1)$, $b = 13{\cdot}815\,(3)$, $c = 10{\cdot}879\,(1)$ Å, $\beta = 101{\cdot}12\,(1)°$, $V = 1180{\cdot}3\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}756$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 9{\cdot}91$ cm^{-1}, $F(000) = 624$, $T = 295$ K, $R = 0{\cdot}0306$ for 1221 reflections. The $C(sp^2)$—Cl distances of 1·702 (3) Å are significantly shorter than the $C(sp^3)$—Cl distances of 1·791 (3) Å. There is a lengthening of the C—C bonds about the sp^3 C atoms that are bonded to Cl, which presumably is related to the electron-withdrawing power of Cl.

Experimental. The title compound was prepared by the dropwise addition of freshly prepared cyclopentadiene in toluene to a slurry of a slight molar excess of tetrachloro-1,4-benzoquinone in toluene. The resulting mixture was chromatographed over Al_2O_3 and recrystallized from chloroform to give colorless transparent crystals. A prismatic crystal of dimensions $0{\cdot}125 \times 0{\cdot}175 \times 0{\cdot}375$ mm was mounted on a Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer. Data collected in the Wyckoff mode ($3 \leq 2\theta \leq 45°$; 2θ fixed, ω varied) using a variable scan rate, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($39{\cdot}94 \leq 2\theta \leq 43{\cdot}24°$), angles measured by a centering routine; systematic absences ($hk0$, $h+k = 2n+1$, $00l$, $l = 2n+1$) and Laue symmetry $2/m$ consistent with space group $P2_1/n$, monitored reflections ($2\bar{4}1$ and 045) showed only statistical variations in intensities; 1543 reflections measured ($-8 \leq h \leq 8$, $0 \leq k \leq 14$, $0 \leq l \leq 11$); $1221 \geq 3\sigma(I)$; Lorentz–polarization corrections, ψ-scan empirical absorption correction (transmission factors 0·642–0·688); structure solved by direct methods, block-cascade anisotropic least-squares refinement, H atoms found in a difference map and refined isotropically; $R = 0{\cdot}0306$, $wR = 0{\cdot}0285$ for 178 parameters, $R = 0{\cdot}0477$ for all reflections, $S = 1{\cdot}257$, $(\Delta/\sigma)_{\max} = 0{\cdot}088$, largest peaks in the final difference map of $-0{\cdot}20$ and $0{\cdot}022$ e Å^{-3}; function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + 0{\cdot}00014F_o^2]^{-1}$. Computer programs for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986). Structure factors and anomalous-dispersion corrections from *International Tables for X-ray*

Table 1. *Atomic coordinates* (× 10^4) *and isotropic thermal parameters* (Å^2 × 10^3)

	x	y	z	U*
C(1)	4438 (4)	8028 (2)	912 (3)	42 (1)
C(2)	4809 (5)	8185 (3)	2296 (3)	48 (1)
C(3)	3606 (5)	7771 (3)	2766 (4)	51 (1)
C(4)	2402 (4)	7296 (2)	1700 (3)	43 (1)
C(4a)	3424 (3)	6423 (2)	1323 (3)	33 (1)
Cl(4a)	2065 (1)	5638 (1)	264 (1)	52 (1)
C(5)	4061 (4)	5774 (2)	2447 (3)	37 (1)
O(5)	3104 (3)	5509 (2)	3102 (2)	65 (1)
C(6)	5867 (4)	5472 (2)	2726 (3)	33 (1)
Cl(6)	6345 (1)	4571 (1)	3797 (1)	53 (1)
C(7)	7064 (3)	5924 (2)	2234 (3)	32 (1)
Cl(7)	9172 (1)	5645 (1)	2678 (1)	49 (1)
C(8)	6679 (4)	6725 (2)	1323 (3)	37 (1)
O(8)	7816 (3)	7206 (2)	1046 (2)	58 (1)
C(8a)	4842 (4)	6943 (2)	734 (3)	35 (1)
Cl(8a)	4717 (1)	6681 (1)	−895 (1)	53 (1)
C(9)	2501 (4)	8005 (3)	647 (4)	50 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and valence angles* (°)

C(1)—C(2)	1·493 (5)	C(1)—C(8a)	1·554 (4)
C(1)—C(9)	1·522 (5)	C(2)—C(3)	1·306 (6)
C(3)—C(4)	1·507 (5)	C(4)—C(4a)	1·556 (4)
C(4)—C(9)	1·520 (5)	C(4a)—Cl(4a)	1·790 (3)
C(4a)—C(5)	1·523 (4)	C(4a)—C(8a)	1·580 (4)
C(5)—O(5)	1·200 (4)	C(5)—C(6)	1·479 (4)
C(6)—Cl(6)	1·698 (3)	C(6)—C(7)	1·338 (4)
C(7)—Cl(7)	1·707 (3)	C(7)—C(8)	1·478 (4)
C(8)—O(8)	1·210 (4)	C(8)—C(8a)	1·516 (4)
C(8a)—Cl(8a)	1·793 (3)		
C(2)—C(1)—C(8a)	105·0 (2)	C(2)—C(1)—C(9)	101·0 (3)
C(8a)—C(1)—C(9)	100·6 (2)	C(1)—C(2)—C(3)	108·3 (3)
C(2)—C(3)—C(4)	107·4 (3)	C(3)—C(4)—C(4a)	104·5 (2)
C(3)—C(4)—C(9)	100·4 (3)	C(4a)—C(4)—C(9)	101·2 (3)
C(4)—C(4a)—Cl(4a)	110·8 (2)	C(4)—C(4a)—C(5)	110·9 (2)
Cl(4a)—C(4a)—C(5)	103·1 (2)	C(4)—C(4a)—C(8a)	102·1 (2)
Cl(4a)—C(4a)—C(8a)	114·2 (2)	C(5)—C(4a)—C(8a)	116·0 (2)
C(4a)—C(5)—O(5)	120·2 (3)	C(4a)—C(5)—C(6)	119·6 (3)
O(5)—C(5)—C(6)	120·2 (3)	C(5)—C(6)—Cl(6)	115·4 (2)
C(5)—C(6)—C(7)	122·2 (3)	Cl(6)—C(6)—C(7)	122·2 (2)
C(6)—C(7)—Cl(7)	121·8 (2)	C(6)—C(7)—C(8)	123·0 (2)
Cl(7)—C(7)—C(8)	115·2 (2)	C(7)—C(8)—O(8)	120·5 (3)
C(7)—C(8)—C(8a)	119·4 (3)	O(8)—C(8)—C(8a)	120·0 (3)
C(1)—C(8a)—C(4a)	101·8 (2)	C(1)—C(8a)—C(8)	110·3 (2)
C(4a)—C(8a)—C(8)	116·9 (2)	C(1)—C(8a)—Cl(8a)	110·2 (2)
C(4a)—C(8a)—Cl(8a)	113·7 (2)	C(8)—C(8a)—Cl(8a)	104·0 (2)
C(1)—C(9)—C(4)	94·0 (3)		

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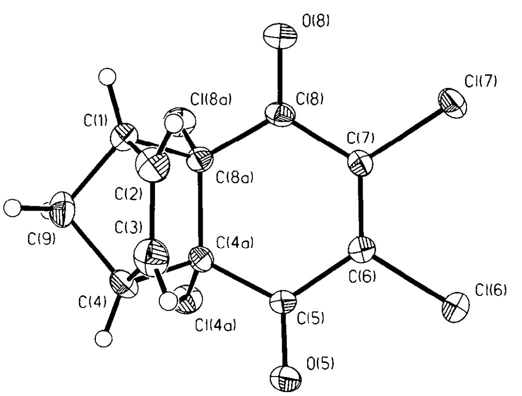

Fig. 1. Drawing of the title compound. Thermal ellipsoids are drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.

Crystallography (1974). Table 1 lists atomic positional parameters and U_{eq} values, while Table 2 gives bond lengths and bond angles. Fig. 1 is a drawing of the title compound.*

Related literature. The reaction between cyclopentadienes and 1,4-benzoquinones has been used extensively to prepare methanonaphthalenes (Cookson, Crundwell, Hill & Hudec, 1964), which are photochemically converted into precursors for the preparation of cage compounds and related species (Marchand, LaRoe, Sharma, Suri & Reddy, 1986; Goverdhan, Srikrishna, Reddy & Nair, 1981). The crystal structure of 4a,7-dibromo-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione has been reported (Syed, Umrigar, Griffin & Stevens, 1984).

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51049 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6,7-Dimethoxy-2,2-dimethyl-4-chromanone

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Abstract. $C_{13}H_{16}O_4$, $M_r = 236{\cdot}27$, orthorhombic, *Pccn*, $a = 18{\cdot}230$ (4), $b = 15{\cdot}950$ (3), $c = 8{\cdot}410$ (2) Å, $V = 2445{\cdot}3$ (3) Å^3, $Z = 8$, $D_x = 1{\cdot}28$ g cm^{-3}, Cu *Kα* radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 7{\cdot}9$ cm^{-1}, $F(000) = 1008$, $T = 293$ K, final $R = 0{\cdot}046$ for 997 observed reflections. The methoxy groups are coplanar with the aromatic ring. The dihydropyronic ring shows a distorted sofa conformation.

Experimental. The title compound (Fig. 1) was purchased from the Aldrich Chemical Company. Crystals grown from acetone. Data collected on an Enraf–Nonius CAD-4 diffractometer, graphite monochromator. The crystal had dimensions 0·1 × 0·2 × 0·2 mm. Cell parameters measured on the diffractometer using 25 reflections in the 2θ range 20–40°. Range of indices $0 \leq h \leq 20$, $0 \leq k \leq 17$, $0 \leq l \leq 9$ ($\theta < 60°$). Three standards 151, 333, 325, measured after every 200 reflections, showed a variation of 0·9%. No absorption corrections. Lorentz and polarization corrections. 1405 unique reflections measured. 997 observed reflections with $I > 3{\cdot}0\sigma(I)$. Direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) used for structure determination. H atoms located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement (on *F*) for non-H atoms, isotropic for H atoms. $\sum w(F_o - F_c)^2$ minimized. $wR = 0{\cdot}046$, max. $\Delta/\sigma = 0{\cdot}92$. Max. peak height in the final difference Fourier map $0{\cdot}49$ e Å^{-3}, $S = 1{\cdot}5$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius *SDP* (Frenz, 1984).

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