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Structure 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

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Abstract. $C_{12}H_6Cl_8O_3$, M_r=481·80, monoclinic, $P2_1/c$, a = 11·028 (9), b = 11·871 (3), c = 13·231 (9) Å, β = 93·14 (3)°, V = 1730 (2) Å^3, Z = 4, D_x = 1·850 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·32 mm^{-1}, F(000) = 952, T = 293 K, final R = 0·035 for 3518 observed reflections. The C(sp^3)—Cl and C(sp^2)—Cl bond-length ranges are 1·744 (2)–1·767 (2) and 1·688 (2)–1·696 (2) Å, respectively. The C(sp^3)—C(sp^3) bond lengths are somewhat extended and range from 1·572 (3) to 1·585 (3) Å. The bridgehead C—C—C and O—C—O angles are 91·6 (1) and 114·6 (2)°, respectively, while the O—C—O—C torsion angles are −53·5 (2) and −47·6 (3)°. The five-membered ring adjacent to the norbornene ring system is in the *endo* configuration with respect to it.

Introduction. In the cycloaddition reaction between 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene with dimethyl dibromomaleic ester the product was not dimethyl 5,6-dibromo-1,2,3,4-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (Vančik, Sunko & Lovrić, 1985) as expected. The X-ray structure determination showed that the result of the reaction was a partially hydrolyzed dimer of the cyclopentadiene derivative. The structure determination was undertaken to give additional information on this interesting strained molecule.

Experimental. Intensity data collected from a crystal 0·25 × 0·34 × 0·42 mm with crystal faces ±(1$\bar{1}$0), ±(001), ±($\bar{1}$11), ±(1$\bar{1}$1). Philips PW 1100 four-circle diffractometer, θ–2θ scanning technique, scan width 1·80°, scan rate 0·06 s^{-1}. Unit-cell parameters obtained from least-squares analysis of 16 reflections with 2θ values ranging from 12 to 20°. Absent reflections $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ confirmed space group $P2_1/c$. Out of 4362 reflections scanned within a quadrant ±h,k,l (h ±15, k 16, l 18), up to sinθ/λ ≤ 0·70 Å^{-1}, 4166 unique reflections classified as observed. Three standard reflections ($\bar{3}1\bar{2}$, $10\bar{6}$, $0\bar{6}0$) measured every 2 h showed an averaged variation of 1·0 (1)%. Corrections applied for Lorentz and polarization effects. No correction for absorption or extinction. Structure solved by direct methods

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(*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Of 23 non-H atoms only six C atoms were not obtained from E map calculated with 300 largest E values ($E \geq 1{\cdot}73$). In the subsequent calculations performed mainly with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) 9 strong low-order reflections strongly affected by extinction and 3 weak reflections near the background were rejected, so 3518 reflections with $I > 3\sigma(I)$ were used. Remaining non-H atoms located from a Fourier map and all H atoms from a difference map. Parameters of non-H and H atoms were varied separately. Block-diagonal least-squares refinement on F with anisotropic thermal parameters for non-H and isotropic for H atoms (which were assigned as 10% greater than those of the bonded C atoms and kept fixed during the refinement) gave $R = 0{\cdot}035$ and $wR = 0{\cdot}043$; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 0{\cdot}5/\sigma^2(F_o)$, giving $S = 1{\cdot}00$. Max. and mean parameter shifts of the non-H atoms were $< 0{\cdot}2$ and $0{\cdot}1$, respectively (the analogous shifts for the H atoms were 0·7 and 0·2). Final difference map revealed no residuals greater than 0·48 e Å^{-3}. Scattering factors of Cromer & Mann (1968) for non-H and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from Cromer & Liberman (1970). All calculations performed on a Univac 1110 computer at the University Computing Centre in Zagreb.

Discussion. The final atomic parameters are listed in Table 1* and intramolecular bond lengths and angles in Table 2. Fig. 1 is a perspective view of the molecule.

The C(sp^3)—Cl and C(sp^2)—Cl bond lengths in the ranges 1·744 (2)–1·767 (2) and 1·688 (2)–1·696 (2) Å, respectively, do not differ significantly from the values determined in the crystal structures of similar compounds containing these bonds (Smith, Kennard & Shields, 1977; Smith & Kennard, 1977; Van Hemelrijk & Lenstra, 1981; Van Hemelrijk, Lenstra & Geise, 1981).

All the C(sp^3)—C(sp^3) bond lengths, ranging from 1·572 (3) to 1·585 (3) Å, are obviously remarkably lengthened. The C(1),C(2),C(6),C(7) and C(1),C(7),C(8),C(9) atoms from the six-membered ring are planar within ±0·008 (2) and ±0·002 (2) Å, respectively. The angle between their mean planes is 111·4 (1)° and the angles with the plane through C(1),C(7),C(10) are 123·0 (1) and 125·6 (1)°, respectively. The atoms of the C(2),C(3),C(4),C(5),C(6) five-membered ring deviate from their mean plane within ±0·023 (3) Å. This

Table 1. *Fractional positional parameters* (×10^4; ×10^5 *for* Cl) *and equivalent isotropic temperature factors* (×10^2) *for non-*H *atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Cl(1)	25528 (6)	−22732 (5)	38896 (4)	4·36 (2)
Cl(2)	4083 (6)	−4573 (6)	37649 (5)	4·72 (2)
Cl(4)	34948 (8)	28128 (6)	38034 (6)	6·63 (3)
Cl(5)	22710 (7)	25919 (5)	14429 (5)	5·29 (2)
Cl(6)	1545 (5)	6781 (6)	16446 (5)	4·47 (2)
Cl(7)	22248 (6)	−974 (5)	1598 (4)	3·91 (2)
Cl(8)	48088 (6)	5224 (6)	13248 (5)	4·94 (2)
Cl(9)	50311 (6)	−8282 (7)	36037 (5)	5·34 (2)
O(1)	2742 (2)	560 (2)	4789 (1)	5·76 (7)
O(2)	2783 (2)	−2273 (1)	1335 (1)	3·88 (6)
O(3)	894 (1)	−1809 (1)	1891 (1)	3·57 (4)
C(1)	2568 (2)	−1217 (2)	2974 (1)	2·85 (6)
C(2)	1782 (2)	−153 (2)	3206 (2)	2·97 (6)
C(3)	2474 (2)	699 (2)	3906 (2)	3·70 (7)
C(4)	2717 (2)	1701 (2)	3307 (2)	3·79 (7)
C(5)	2233 (2)	1602 (2)	2359 (2)	3·51 (7)
C(6)	1655 (2)	470 (2)	2147 (2)	2·83 (6)
C(7)	2416 (2)	−320 (2)	1467 (1)	2·66 (6)
C(8)	3728 (2)	−239 (2)	1882 (2)	3·07 (6)
C(9)	3816 (2)	−761 (2)	2766 (2)	3·23 (6)
C(10)	2100 (2)	−1530 (2)	1865 (1)	2·84 (5)
C(11)	2734 (3)	−3445 (2)	1615 (2)	6·18 (11)
C(12)	265 (2)	−2115 (2)	952 (2)	4·91 (9)

Table 2. *Intramolecular bond lengths* (Å) *and angles* (°) *involving non-*H *atoms*

C(1)—Cl(1)	1·744 (2)	C(6)—Cl(6)	1·767 (2)
C(1)—C(2)	1·572 (3)	C(6)—C(7)	1·573 (3)
C(1)—C(9)	1·517 (3)	C(7)—Cl(7)	1·751 (2)
C(1)—C(10)	1·573 (3)	C(7)—C(8)	1·522 (3)
C(2)—Cl(2)	1·759 (3)	C(7)—C(10)	1·576 (3)
C(2)—C(3)	1·545 (3)	C(8)—Cl(8)	1·696 (2)
C(2)—C(6)	1·585 (3)	C(8)—C(9)	1·322 (3)
C(3)—O(1)	1·201 (3)	C(9)—Cl(9)	1·694 (2)
C(3)—C(4)	1·463 (3)	C(10)—O(2)	1·376 (3)
C(4)—Cl(4)	1·688 (2)	C(10)—O(3)	1·373 (3)
C(4)—C(5)	1·341 (3)	C(11)—O(2)	1·442 (3)
C(5)—Cl(5)	1·690 (2)	C(12)—O(3)	1·436 (3)
C(5)—C(6)	1·506 (3)		
Cl(1)—C(1)—C(2)	114·6 (1)	C(2)—C(6)—C(5)	103·6 (2)
Cl(1)—C(1)—C(9)	115·2 (1)	C(2)—C(6)—C(7)	101·7 (2)
Cl(1)—C(1)—C(10)	117·5 (1)	C(5)—C(6)—C(7)	113·9 (2)
C(2)—C(1)—C(9)	105·3 (2)	Cl(7)—C(7)—C(6)	115·8 (1)
C(2)—C(1)—C(10)	102·5 (2)	Cl(7)—C(7)—C(8)	114·0 (1)
C(9)—C(1)—C(10)	99·8 (2)	Cl(7)—C(7)—C(10)	116·8 (1)
Cl(2)—C(2)—C(1)	114·5 (1)	C(6)—C(7)—C(8)	106·4 (2)
Cl(2)—C(2)—C(3)	106·9 (2)	C(6)—C(7)—C(10)	102·6 (2)
Cl(2)—C(2)—C(6)	115·6 (1)	C(8)—C(7)—C(10)	99·2 (2)
C(1)—C(2)—C(3)	112·6 (2)	Cl(8)—C(8)—C(7)	123·6 (2)
C(1)—C(2)—C(6)	103·0 (2)	Cl(8)—C(8)—C(9)	127·9 (2)
C(3)—C(2)—C(6)	104·0 (2)	C(7)—C(8)—C(9)	108·1 (2)
O(1)—C(3)—C(2)	125·5 (2)	Cl(9)—C(9)—C(1)	123·9 (2)
O(1)—C(3)—C(4)	126·7 (2)	Cl(9)—C(9)—C(8)	128·2 (2)
C(2)—C(3)—C(4)	107·8 (2)	C(1)—C(9)—C(8)	107·7 (2)
Cl(4)—C(4)—C(3)	121·9 (2)	O(2)—C(10)—O(3)	114·6 (2)
Cl(4)—C(4)—C(5)	126·9 (2)	O(2)—C(10)—C(1)	117·8 (2)
C(3)—C(4)—C(5)	111·2 (2)	O(2)—C(10)—C(7)	106·1 (2)
Cl(5)—C(5)—C(4)	125·8 (2)	O(3)—C(10)—C(1)	107·6 (2)
Cl(5)—C(5)—C(6)	120·9 (2)	O(3)—C(10)—C(7)	117·4 (2)
C(4)—C(5)—C(6)	113·3 (2)	C(1)—C(10)—C(7)	91·6 (1)
Cl(6)—C(6)—C(2)	115·7 (1)	C(10)—O(2)—C(11)	117·3 (2)
Cl(6)—C(6)—C(5)	108·9 (1)	C(10)—O(3)—C(12)	117·5 (2)
Cl(6)—C(6)—C(7)	112·7 (1)		

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42302 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

mean plane shows angles of 117·2 (1) and 131·3 (1)° with the mean planes through C(1),C(2),C(6),C(7) and C(1),C(7),C(8),C(9), respectively, while the angle with the plane through C(1),C(7),C(10) is 5·9 (1)°. The quoted mean-plane angles are comparable with those found in the related but essentially unsubstituted norbornene derivatives with *endo* five-membered rings (Bellobono, Destro, Gramaccioli & Simonetta, 1969; Destro, Filippini, Gramaccioli & Simonetta, 1969). The *endo* configuration of the C(2),C(3),C(4),C(5),C(6) five-membered ring with regard to the norbornene ring has resulted in rather close intramolecular $C(sp^2)\cdots C(sp^2)$ distances: C(3)···C(9) 2·777 (3), C(4)···C(9) 3·258 (3) and C(5)···C(8) 2·830 (3) Å. Similar values for the corresponding distances have been found by Bellobono, Destro, Gramaccioli & Simonetta (1969) in the cyclopentadiene dimer derivative.

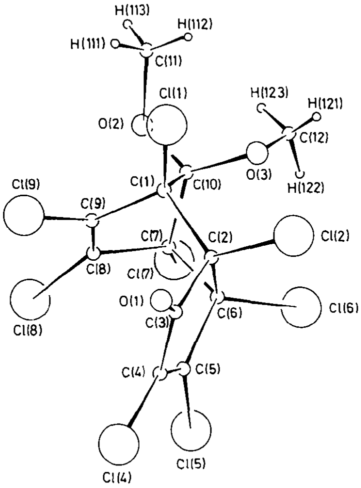

Fig. 1. A perspective view of the molecule along **c** showing the atomic numbering.

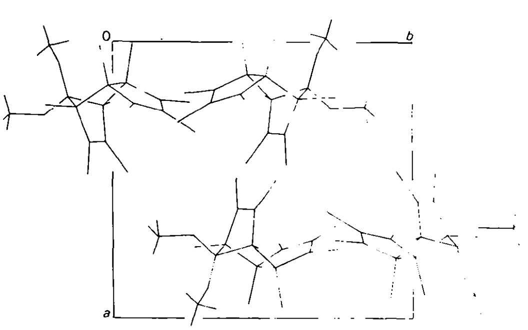

Fig. 2. A projection of the structure viewed along **c**.

The six-membered ring shows a boat conformation ($^{1,7}B$, according to the numbering given in this work) with puckering parameters (Cremer & Pople, 1975) Q, θ and φ of 0·969 (2) Å, 90·4 (1)° and −0·3 (1)°, respectively. The five-membered rings show envelope conformations. The puckering parameters Q and φ for the C(10),C(7),C(8),C(9),C(1) ring are 0·587 (2) Å and −0·3 (2)°, for the C(10),C(1),C(2),C(6),C(7) ring 0·622 (2) Å and 1·3 (2)°, and for the C(2),C(3),-C(4),C(5),C(6) ring 0·035 (3) Å and 108 (4)°, respectively.

The C—C—C and O—C—O bridgehead angles of 91·6 (1) and 114·6 (2)°, as well as the O(3)—C(10)—O(2)—C(11) and O(2)—C(10)—O(3)—C(12) torsion angles of −53·5 (2) and −47·6 (3)° are in accord with corresponding literature data (Van Hemelrijk & Lenstra, 1981; Van Hemelrijk, Lenstra & Geise, 1981, 1982).

The packing of the molecules is illustrated in Fig. 2. There are no intermolecular distances significantly shorter than the sum of the van der Waals radii.

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