Crystal Structure of 6,6,12,12-Tetrachloro-3,3,9,9-tetramethoxytricyclo-[9,1,0,0^{5,7}]dodecane: $C_{16}H_{24}Cl_4O_4$

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The structure of the title compound has been determined by single-crystal *X*-ray diffraction. Crystals are triclinic with $Z = 1$ in a unit cell of dimensions: $a = 998{\cdot}8(3)$, $b = 819{\cdot}5(3)$, $c = 637{\cdot}7(2)$ pm, $\alpha = 93{\cdot}07(1)$, $\beta = 91{\cdot}40(1)$, $\gamma = 110{\cdot}70(1)°$, space group $P\bar{1}$. The structure was solved by Patterson and Fourier methods and refined by least-squares using 1504 observed three-dimensional diffractometer to R 0·043. The molecule has a centre of symmetry coincident with a crystallographic centre of symmetry. It possesses approximate $2/m$ symmetry and its conformation is in agreement with that predicted by Dunitz.

INTEREST in the stereochemistry of 6,6,12,12-tetrachloro-3,3,9,9-tetramethoxytricyclo[9,1,0,0^{5,7}]dodecane and the related tetrabromo-analogue[1] prompted us to carry out an *X*-ray structural investigation.

EXPERIMENTAL

Crystals of the tetrachloro-compound are colourless triclinic blocks showing the following pinacoids {100}, {010}, and {001} and in some cases also {$\bar{1}$10}.

Crystal Data.—$C_{16}H_{24}Cl_4O_4$, $M = 422{\cdot}18$. Triclinic, $a = 998{\cdot}8(3)$, $b = 819{\cdot}5(3)$, $c = 637{\cdot}7(2)$ pm, $\alpha = 93{\cdot}07(1)$, $\beta = 91{\cdot}40(1)$, $\gamma = 110{\cdot}70(1)°$, $U = 487 \times 10^6$ pm^3, $Z = 1$, $D_m = 1{\cdot}43(1)$ (by flotation), $Z = 1$, $D_c = 1{\cdot}44$. Possible space groups $P1$ and $P\bar{1}$, shown to be the latter by the distribution of Cl ⋯ Cl vectors in the Patterson synthesis and also by the subsequent successful refinement. Mo-K_α radiation, $\lambda = 71{\cdot}07$ pm; μ(Mo-K_α) = 6·2 cm^{-1}.

Intensity Measurements.—Three-dimensional *X*-ray diffraction data from a small single crystal (*ca.* 0·3 × 0·3 × 0·3 mm) were collected on a computer-controlled[2] Stoe four-circle diffractometer by use of Mo-K_α radiation with graphite monochromator (002). A coupled θ—2θ step scan with $\Delta 2\theta$ 0·04°, a counting time of 4 s per step and a peak width of 1·6° were used. In the range 2θ =

TABLE 1

Fractional co-ordinates and thermal motion parameters * derived from the least-squares refinement, with estimated standard deviations in parentheses

(i) Non-hydrogen atoms: parameters × 10^4

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	12 517(1)	2214(1)	236(2)	547(4)	525(6)	580(6)	336(5)	48(5)	110(5)
Cl(2)	13 760(1)	4217(2)	−3303(2)	574(4)	907(9)	664(6)	421(5)	296(6)	176(6)
O(1)	11 699(3)	7358(3)	4629(4)	627(18)	522(15)	377(12)	262(13)	−9(12)	−1(11)
O(2)	12 822(3)	8741(3)	1688(4)	424(13)	459(15)	533(14)	137(11)	8(12)	57(12)
C(1)	8997(4)	6111(5)	2063(5)	419(18)	456(21)	369(18)	237(16)	50(15)	42(15)
C(2)	10 345(4)	7475(5)	1405(5)	419(18)	451(21)	400(18)	201(16)	12(15)	68(16)
C(3)	11 692(4)	7290(5)	2384(5)	472(22)	427(21)	363(18)	199(16)	6(15)	16(15)
C(4)	11 863(4)	5549(5)	1785(5)	463(22)	430(21)	408(18)	224(16)	6(15)	42(16)
C(5)	12 061(4)	5326(5)	−544(5)	402(18)	433(21)	420(18)	208(16)	68(15)	67(15)
C(6)	12 432(4)	3819(5)	−1423(5)	437(22)	504(21)	455(21)	257(18)	120(15)	87(16)
C(7)	11 600(5)	8917(6)	5638(7)	953(35)	622(27)	512(25)	389(25)	29(23)	−116(21)
C(8)	14 250(4)	8892(7)	2366(7)	432(22)	812(33)	746(31)	156(22)	−60(21)	59(25)

(ii) Hydrogen atoms: parameters × 10^3

Atom	x	y	z	U/Å^2	Atom	x	y	z	U/Å^2
H(1,1)	905(3)	568(4)	346(5)	12(9)	H(7,1)	1052(5)	886(6)	556(7)	51(14)
H(2,1)	1038(4)	878(5)	182(6)	21(10)	H(7,2)	1192(5)	893(6)	715(7)	64(15)
H(2,2)	1044(4)	753(5)	2(6)	21(10)	H(7,3)	1212(5)	1014(6)	496(7)	49(13)
H(4,1)	1267(4)	545(5)	257(5)	19(10)	H(8,1)	1455(5)	800(7)	139(8)	75(17)
H(4,2)	1104(4)	461(4)	236(5)	11(9)	H(8,2)	1436(5)	837(6)	391(7)	57(14)
H(5,1)	1258(4)	645(5)	−120(5)	17(9)	H(8,3)	1493(5)	1040(6)	232(7)	67(16)

* The Debye–Waller factor is defined as $T = \exp[-2\pi^2\Sigma\Sigma a_i^* a_j^* h_i h_j U_{ij}]$ for non-hydrogen atoms and $T = \exp[-8\pi^2 U \sin^2 \theta/\lambda^2]$ for hydrogen atoms.

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[1] P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *Chem. Comm.*, 1970, 1219.

[2] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, 'The Oak Ridge Computer-Controlled *X*-ray Diffractometer,' U.S. Atomic Energy Commission, Report ORNL 143, 1968.

5—55°, 2505 observations covering four octants of reciprocal space ($\pm h$, $+k$, $\pm l$) were collected. A standard reflection was measured every 25 observations and was used during processing to put all data on a common scale. 1504 symmetry-independent observed intensities had $I \geqslant 3\,\sigma\,(I)$, and of these 112 had been observed more than once. The data were corrected for Lorentz and polarisation effects but not for absorption or extinction.

TABLE 2

Interatomic distances (pm) and angles (°) [7] with estimated standard deviations in parentheses

(i) Distances

Cl(1)–C(6)	175·5(4)	C(1)–H(1,1)	98(3)
Cl(2)–C(6)	176·5(4)	C(2)–H(2,1)	108(4)
O(1)–C(3)	143·0(4)	C(2)–H(2,2)	89(4)
O(1)–C(7)	143·6(5)	C(4)–H(4,1)	96(4)
O(2)–C(3)	142·0(4)	C(4)–H(4,2)	100(4)
O(2)–C(8)	144·1(6)	C(5)–H(5,1)	100(4)
C(1)–C(2)	150·1(5)	C(7)–H(7,1)	107(5)
C(2)–C(3)	152·9(6)	C(7)–H(7,2)	108(4)
C(3)–C(4)	152·5(5)	C(7)–H(7,3)	101(5)
C(4)–C(5)	151·2(5)	C(8)–H(8,1)	106(5)
C(5)–C(6)	149·6(5)	C(8)–H(8,2)	111(5)
C(5)–C(1*)	154·6(5)	C(8)–H(8,3)	119(5)
C(6)–C(1*)	149·7(6)		

(ii) Angles

C(3)–O(1)–C(7)	115·8(3)	H(4,1)–C(4)–H(4,2)	101(3)
C(3)–O(2)–C(8)	116·0(3)	C(4)–C(5)–C(6)	120·7(3)
C(6*)–C(1)–C(2)	120·1(3)	C(4)–C(5)–C(1*)	124·4(3)
C(6*)–C(1)–H(1,1)	115(2)	C(4)–C(5)–H(5,1)	114(2)
C(6*)–C(1)–C(5*)	58·9(2)	C(1*)–C(5)–C(6)	58·9(3)
C(5*)–C(1)–C(2)	124·2(3)	C(1*)–C(5)–H(5,1)	114(2)
C(5*)–C(1)–H(1,1)	111(2)	C(6)–C(5)–H(5,1)	113(2)
C(2)–C(1)–H(1,1)	116(2)	Cl(1)–C(6)–C(5)	119·5(3)
C(1)–C(2)–C(3)	112·4(3)	Cl(1)–C(6)–C(1*)	119·4(3)
C(1)–C(2)–H(2,1)	112(2)	Cl(1)–C(6)–Cl(2)	111·1(2)
C(1)–C(2)–H(2,2)	115(2)	Cl(2)–C(6)–C(5)	118·4(3)
C(3)–C(2)–H(2,1)	108(2)	Cl(2)–C(6)–C(1*)	118·6(3)
C(3)–C(2)–H(2,2)	108(2)	C(5)–C(6)–C(1*)	62·2(2)
H(2,1)–C(2)–H(2,2)	100(3)	O(1)–O(7)–H(7,1)	110(2)
C(2)–C(3)–O(1)	112·3(3)	O(1)–C(7)–H(7,2)	106(3)
C(2)–C(3)–O(2)	103·6(3)	O(1)–C(7)–H(7,3)	118(3)
C(2)–C(3)–C(4)	114·0(3)	H(7,1)–C(7)–H(7,2)	110(4)
O(1)–C(3)–O(2)	110·6(3)	H(7,1)–C(7)–H(7,3)	100(3)
O(1)–C(3)–O(4)	103·8(3)	H(7,2)–C(7)–H(7,3)	113(4)
O(2)–C(3)–C(4)	112·7(3)	O(2)–C(8)–H(8,1)	108(3)
C(3)–C(4)–C(5)	112·0(3)	O(2)–C(8)–H(8,2)	116(3)
C(3)–C(4)–H(4,1)	111(2)	O(2)–C(8)–H(8,3)	104(2)
C(3)–C(4)–H(4,2)	107(2)	H(8,1)–C(8)–H(8,2)	99(4)
C(5)–C(4)–H(4,1)	109(2)	H(8,1)–C(8)–H(8,3)	118(4)
C(5)–C(4)–H(4,2)	116(2)	H(8,2)–C(8)–H(8,3)	113(4)

* Atom related by centre of symmetry of molecule. Hydrogen atoms are numbered according to the carbon atom to which they are bonded.

Structure Solution and Refinement.—The positions of the two chlorine atoms in the asymmetric unit were found from an unsharpened Patterson synthesis.[3] A Fourier synthesis[3] using observed data phased with the two chlorine atoms produced a satisfactory trial structure. After successive cycles of full-matrix least-squares[4] refinement a difference-electron density synthesis revealed all the hydrogen atom positions. Final refinement was by full-matrix least-squares using two blocks of parameters, the first consisting of all non-hydrogen-atom parameters and the second of hydrogen-atom parameters. Alternative refinement of these blocks was carried out until all parameter shifts were $<0{\cdot}1\,\sigma$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$ for all reflection data. Atomic scattering factors for neutral carbon, chlorine, and oxygen were taken from ref. 5 and for hydrogen from ref. 6. The final R was 0·043. Positional and thermal parameters are listed in Table 1 and bond distances and angles[7] in Table 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20397 (6 pp., 1 microfiche).† All computational work was carried out on the University of London ATLAS computer and University College IBM 360 computer.

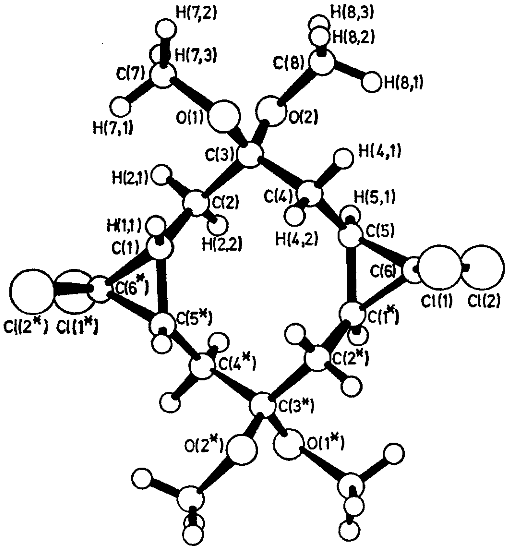

FIGURE 1 Perspective drawing of the molecule

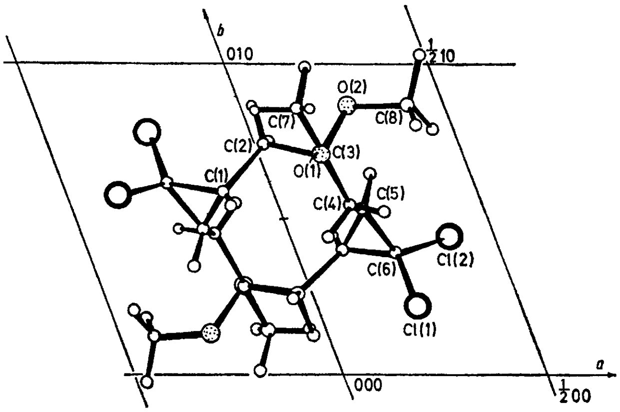

FIGURE 2 The crystal structure projected onto (001)

DISCUSSION

Description of the Molecular Structure.—The molecular structure of this substituted tricyclododecane (Figures 1 and 2) can best be described with reference to cyclo-

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[3] J. Dollimore, A Fourier Program for LUNA, University of London Institute of Computer Science, Circular No. 1.2.

[4] G. Shearing, A Crystallographic SFLS Program in AA, University of Manchester, 1965.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[7] J. Dollimore, A Distance Angle Program for LUNA, University of London Computer Science, Circular No. 4.

decane. In Dunitz's[8] detailed review of the conformations of medium rings, the carbon atoms forming the normal cyclodecane ring are classified as types (I), (II), and (III). Deductions are made to establish the favoured positions for substitution and the likely position for a *cis*-double bond assuming the stable conformation of cyclodecane to be preserved as far as possible. The conclusions reached are that geminal substituents must be placed on type (II) carbon atoms and the *cis*-double bond is most likely to be formed between carbon atoms types (II) and (III). Similar arguments may be used to deduce the structure of the substituted tricyclododecane. The cyclopropyl groups are most likely to be formed using a type (II) and a type (III) atom. The $\widehat{\mathrm{C{-}C}}\mathrm{{-}C{-}C}$ torsion angle would then be equivalent to the C=C–C–C torsion angle and should be *ca.* 120°. Hence the expected conformation appears to resemble closely that suggested for tetraethyl-*cis,cis*-cyclodeca-3,8-diene-1,1,6,6-tetracarboxylate.[8]

TABLE 3

Selected torsion angles (°)

Cl(1*)–C(6*)–C(1)–C(2)	4
Cl(1*)–C(6*)–C(1)–C(5*)	−110
Cl(1*)–C(6*)–C(1)–H(1,1)	149
Cl(2*)–C(6*)–C(1)–C(2)	−137
Cl(2*)–C(6*)–C(1)–C(5*)	109
Cl(2*)–C(6*)–C(1)–H(1,1)	8
O(1)–C(3)–O(2)–C(8)	60
O(1)–C(3)–C(2)–C(1)	−57
O(1)–C(3)–C(4)–C(5)	−173
C(1)–C(2)–C(3)–C(4)	61
C(1)–C(6*)–C(5*)–C(4*)	−114
C(1)–C(6*)–C(5*)–H(5,1*)	105
C(2)–C(3)–O(2)–C(8)	−179
C(2)–C(3)–O(1)–C(7)	−58
C(3)–C(2)–C(1)–C(5*)	−115
C(3)–C(2)–C(1)–C(6*)	174
C(3)–C(2)–C(1)–H(1,1)	29
C(2)–C(1)–C(5*)–C(6*)	−107
C(2)–C(1)–C(5*)–H(5,1*)	149
C(2)–C(1)–C(5*)–C(4*)	1
Cl(1*)–C(6*)–C(5*)–C(4*)	−4
Cl(1*)–C(6*)–C(5*)–C(1)	110
Cl(1*)–C(6*)–C(5*)–H(5,1*)	−145
Cl(2*)–C(6*)–C(5*)–C(4*)	137
Cl(2*)–C(6*)–C(5*)–C(1)	−109
Cl(2*)–C(6*)–C(5*)–H(5,1*)	−4
O(2)–C(3)–O(1)–C(7)	57
O(2)–C(3)–C(4)–C(5)	−53
O(2)–C(3)–C(2)–C(1)	−176
C(2)–C(3)–C(4)–C(5)	64
C(2)–C(1)–C(6*)–C(5*)	114
C(5*)–C(6*)–C(1)–H(1,1)	−101
C(4)–C(3)–O(1)–C(7)	178
C(4)–C(3)–O(2)–C(8)	−56
C(3)–C(4)–C(5)–C(1*)	−117
C(3)–C(4)–C(5)–C(6)	172
C(3)–C(4)–C(5)–H(5,1)	32
C(4*)–C(5*)–C(1)–C(6*)	108
C(4*)–C(5*)–C(1)–H(1,1)	−145

* Atom related by centre of symmetry of molecule.

The structure found experimentally possesses approximate $2/m$ symmetry and agrees well with the predicted conformation.

The mirror plane passes through the four chlorine atoms. The $\widehat{\mathrm{C{-}C}}\mathrm{{-}C{-}C}$ torsion angles are 115 and 117° (Table 3) and the methoxy-groups are extra-annular. The unfavourable interactions between hydrogen atoms on type (I) and (III) carbon atoms in cyclodecane appear to have been reduced by the introduction of the cyclopropyl groups. The distances H(2,2) · · · H(5,1), H(4,2) · · · H(1,1) are 270(5) and 254(5) pm and H(4,2) · · · H(2,2*) is 231(5) pm. These distances are all acceptable as normal van der Waal separations. The atoms C(6), C(5), C(4), C(3), O(1), C(7) and C(6*), C(1), C(2), C(3), O(2), C(8) form *trans*-extended chains.

The molecular structure of the tetrabromo-derivative is, we believe, the same as that of the tetrachloro-compound. Preliminary work has shown that the molecule also lies on a crystallographic centre of symmetry.

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[8] J. D. Dunitz, *Perspectives in Structural Chem.*, 1968, **2**, 1.