Lists of structure factors and anisotropic thermal parameters, together with a thermal ellipsoid plot for (2*b*) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55352 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1008]

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Bis(5-chloro-2-hydroxy-1,3-xylyl)-18-crown-4

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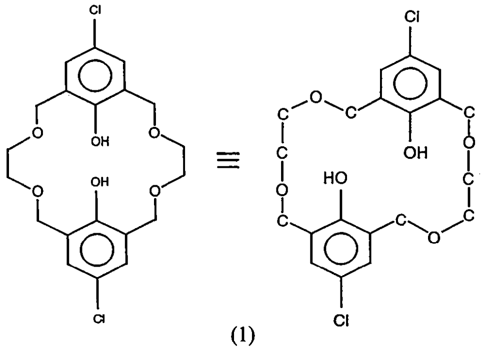
Abstract

The molecule lies about an inversion centre and the 18-membered macrocycle has a rectangular conformation dictated by a pair of O—H···O intramolecular hydrogen bonds between phenolic OH groups and proximal ether O atoms [O···O 2.735(3) Å].

Comment

Metacyclophanes with pendant functional groups have become important structures for studying aspects of host-guest chemistry such as the role of host preorganization and of synergism in ion binding between macrocyclic arrays and potential ligating groups. Substituted phenolic groups have been particularly useful in this regard either as single subunits in crown ether arrays or in multifunctional systems, the most important of the latter being the calixarenes. The phenolic groups provide convenient points of attachment for other functional groups. We have studied crown ethers with a single pendant phenolic group and have demonstrated synergism in binding of ammonia and primary amines (Browne, Ferguson, McKervey, Mulholland, O'Connor & Parvez, 1985; Ferguson, Kaitner, Browne & McKervey, 1988). We have now extended our study of functional macrocycles to include crown ether systems with more than one phenolic unit and report here on the crystal and molecular structure of the 18-membered macrocycle (1) with two phenolic units.



(1)

Macrocycle (1) was synthesized from 2,6-bis(bromomethyl)-4-chlorophenol, which was first protected as its *o*-allyl ether. Cyclization with ethylene glycol and sodium hydride yielded a macrocycle which on deprotection using palladium on carbon in the presence of hydrochloric acid furnished crystals of (1).

The conformation of this centrosymmetric molecule (1) (Fig. 1) is determined by an intramolecular O—H···O hydrogen bond (and its inversion-centre-related one) between phenolic hydroxyl O(1) and proximal ether oxygen O(2) [O(1)···O(2) 2.735(3), O(1)—H 1.09, H···O(2) 1.82 Å, O(1)—H···O(2) 139°]. Similar hydrogen bonding was also found in 2-hydroxy-1,3-xylyl-18-crown-5 (2) and in 5-nitro-2-hydroxy-1,3-xylyl-18-crown-5 (3) (Browne, Ferguson, McKervey, Mulholland, O'Connor & Parvez, 1985). As a result of the intramolecular O—H···O hydrogen bonding, the 18-membered macrocycle adopts an approximately rectangular conformation, with the aromatic ring plane inclined at 128.31(4)° to the best plane through the C and O atoms of the 18-membered ring, and with the hydroxyl oxygen O(1) lying in the plane of the aromatic ring. The macrocycle ring torsion angles are either near to *gauche*, or fully extended *trans* values.

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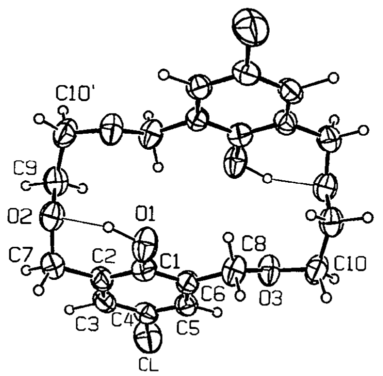
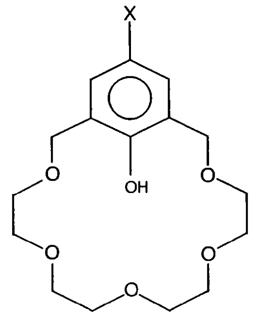


Fig. 1. A view of molecule (1) showing the general conformation and the intramolecular hydrogen bonding with the crystallographic numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of arbitrary size.

Molecular dimensions (Table 2) are normal. A search of the 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for any fragment with the same C- and O-atom skeleton as molecule (1) yielded no hits.



(2) $X = H$

(3) $X = NO_2$

Experimental

Crystal data

$C_{20}H_{22}Cl_2O_6$
$M_r = 429.29$
Orthorhombic
Pcab
$a = 6.5779$ (15) Å
$b = 15.5650$ (13) Å
$c = 19.2172$ (22) Å
$V = 1967.6$ (5) Å^3
$Z = 4$
$D_x = 1.449$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.70930$ Å
Cell parameters from 25 reflections
$\theta = 20.00$–$25.00°$
$\mu = 0.36$ mm^{-1}
$T = 293$ K
Plate
0.15 × 0.30 × 0.33 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: none
2149 measured reflections
2149 independent reflections
1171 observed reflections [$I_{net} > 3.0\sigma(I_{net})$]

$\theta_{max} = 26.94°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity variation: ±1.0%

Refinement

Refinement on F
Final $R = 0.0427$
$wR = 0.0373$
$S = 1.09$
1171 reflections
127 parameters
$w = 1/[\sigma^2(F)+0.0008F^2]$
$(\Delta/\sigma)_{max} = 0.03$

$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl	0.13443 (15)	0.32911 (6)	0.73618 (5)	0.08153
O(1)	0.5434 (3)	0.59813 (12)	0.57668 (11)	0.05939
O(2)	0.1820 (3)	0.68462 (11)	0.58317 (10)	0.05267
O(3)	0.7299 (3)	0.34843 (12)	0.56061 (10)	0.05411
C(1)	0.4422 (4)	0.53708 (18)	0.61435 (14)	0.04351
C(2)	0.2652 (5)	0.55617 (18)	0.65125 (14)	0.04499
C(3)	0.1703 (4)	0.49178 (19)	0.68887 (14)	0.04665
C(4)	0.2549 (5)	0.41090 (17)	0.68970 (14)	0.04668
C(5)	0.4297 (5)	0.39144 (17)	0.65346 (14)	0.04491
C(6)	0.5262 (4)	0.45472 (17)	0.61502 (14)	0.04125
C(7)	0.1804 (5)	0.64641 (19)	0.65119 (15)	0.05630
C(8)	0.7160 (5)	0.43719 (17)	0.57396 (16)	0.05037
C(9)	0.0337 (5)	0.64844 (19)	0.53708 (16)	0.05237
C(10)	0.9233 (5)	0.32167 (19)	0.53472 (16)	0.05715

Table 2. *Geometric parameters* (Å, °)

Cl—C(4)	1.745 (3)	C(2)—C(3)	1.385 (4)
O(1)—C(1)	1.368 (3)	C(2)—C(7)	1.511 (4)
O(2)—C(7)	1.436 (3)	C(3)—C(4)	1.377 (4)
O(2)—C(9)	1.433 (4)	C(4)—C(5)	1.378 (4)
O(3)—C(8)	1.408 (3)	C(5)—C(6)	1.385 (4)
O(3)—C(10)	1.428 (4)	C(6)—C(8)	1.502 (4)
C(1)—C(2)	1.395 (4)	C(9)—C(10)^i	1.483 (4)
C(1)—C(6)	1.396 (4)		
C(7)—O(2)—C(9)	113.26 (21)	Cl—C(4)—C(5)	118.50 (21)
C(8)—O(3)—C(10)	114.06 (22)	C(3)—C(4)—C(5)	122.2 (3)
O(1)—C(1)—C(2)	121.82 (25)	C(4)—C(5)—C(6)	119.7 (3)
O(1)—C(1)—C(6)	116.77 (25)	C(1)—C(6)—C(5)	118.5 (3)
C(2)—C(1)—C(6)	121.4 (3)	C(1)—C(6)—C(8)	119.39 (24)
C(1)—C(2)—C(3)	119.2 (3)	C(5)—C(6)—C(8)	122.14 (24)
C(1)—C(2)—C(7)	120.4 (3)	O(2)—C(7)—C(2)	112.51 (23)
C(3)—C(2)—C(7)	120.4 (3)	O(3)—C(8)—C(6)	109.16 (23)
C(2)—C(3)—C(4)	119.1 (3)	O(2)—C(9)—C(10)^i	108.77 (24)
Cl—C(4)—C(3)	119.30 (23)	O(3)—C(10)—C(9)^i	113.74 (24)
C9—O2—C7—C2	71.8 (2)	C1—C2—C7—O2	43.9 (2)
C7—O2—C9—C10^i	−168.0 (3)	C1—C6—C8—O3	−158.2 (3)
C10—O3—C8—C6	−167.7 (3)	O2—C9—C10^i—O3^i	62.1 (2)
C8—O3—C10—C9^i	−69.7 (2)		
O(1)···O(2)	2.735 (3)		

Symmetry code: (i) $-x, -y, -z$.

Data collection and cell refinement: Enraf–Nonius CAD-4 software. The θ-scan width was $(0.6+0.35\tan\theta)°$ with a θ-scan rate of 3.3° min^{-1} and background counts for 15 s on each side of every scan. The systematic absences ($0kl$ absent if $l = 2n+1$, $h0l$ absent if $h = 2n+1$, $hk0$ absent if $k = 2n+1$) determine centrosymmetric space group *Pcab* uniquely. Data reduction, program used to solve and refine the structures, software used to prepare material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The diagrams were prepared using *ORTEP*II (Johnson, 1976). In the refinement process, H atoms were included but not refined (with U_{iso} 0.06 Å^2) at positions determined from a difference map computed after initial anisotropic refinement.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55347 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1019]

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Structure of a (1:2) Adduct of 1,1-[Bis(3,3,3-trifluoropropynyl)]ethyl Acetate and Furan

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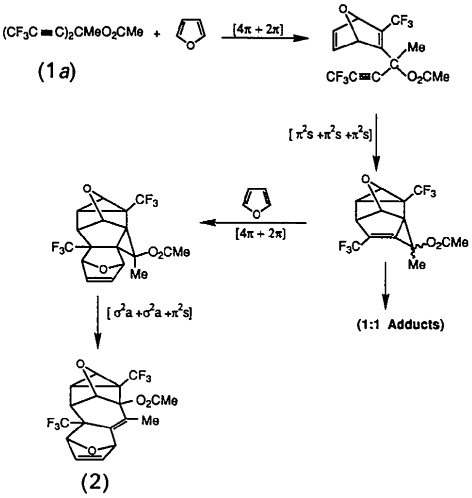
Abstract

Crystallographic characterization of the (1:2) adduct 3-methyl-5,11-bis(trifluoromethyl)-8,15-dioxahexacyclo[10.2.1.0.^{2,11}0.^{4,9}0.^{5,7}0^{6,10}]pentadeca-2,13-dien-4-yl acetate (2) has assisted in establishing mechanistic pathways. The most strained feature of this novel ring system (besides the three-membered ring) is at C11 where the longest bonds are found [C11—C12 = 1.570 (9), C11—C22 = 1.568 (9) Å]. In addition, the six C—C—C angles at C11 vary from 98.7 (6) to 122.0 (6)° and the CF_3 substituent at this position has disordered F atoms.

Comment

When 1,4-diynyl esters $(CF_3C{\equiv}C)_2CROCOR$ [(1*a*), *R* = Me; (1*b*), *R* = Ph] undergo Diels–Alder reactions with furan, both (1:1) and (1:2) adducts can be isolated (Barlow, Tajammal & Tipping, 1989). Crystallographic identification of (2) has assisted in the elucidation of the complex reaction mechanism along with the determination of the structures of the two (1:1) adducts (with *R* = Ph) already reported (Barlow *et al.*, 1992). Details of the preparation of (2) have been described by Tajammal (1991). After chromatographic separation from an initial solid, (2) was recrystallized slowly from a mixture of petroleum ether (b.p. 313–343 K) and dichloromethane (1:3 *v*/*v*).



No other crystal structure with the ring system of (2) appears to have been reported.

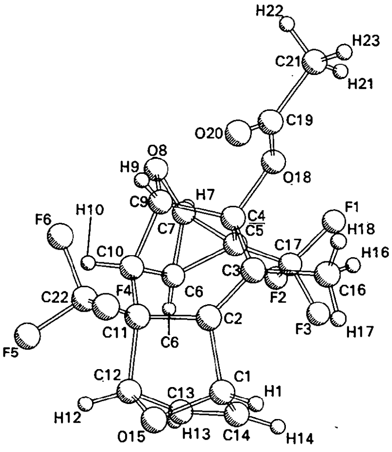


Fig. 1. View of (2) showing the labelling of the atoms; F7, F8 and F9 (the lesser components of the disordered CF_3 at C11) are omitted for clarity.

Experimental

Crystal data

$C_{18}H_{14}F_6O_4$

M_r = 408.30

Mo *Kα* radiation

λ = 0.71069 Å

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