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1,3:16,18-Bis(xylyl)-30-crown-8[1]

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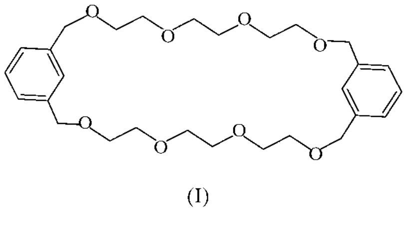
The title crown ether, $C_{28}H_{40}O_8$, crystallizes in an orthorhombic cell with the full molecule generated from crystallographic inversion symmetry. The ring consists of 30 atoms which could potentially influence the size of the ring cavity and the conformational flexibility. Unusual C—O—C—C and O—C—C—O torsion-angle geometries, deviating by as much as 30° from their ideal values, have been observed.

Comment

Macrocyclic compounds such as crown ethers can show selectivity, *via* the O atoms, in complexing with a diverse range of neutral, polar and cationic substrates. The ligand properties can also be modified by altering the number of O atoms, replacing oxygen with other heteroatoms, or changing the length of the aliphatic chains and/or the aromatic groups between the O atoms.

The title crown ether molecule, (I) (Fig. 1), crystallizes in an orthorhombic unit cell, with the full molecule generated by an inversion operation. Selected geometric parameters are presented in Table 1. Bond distances and angles are within normal ranges; Csp^3—O between 1.4149 (18) and 1.4302 (18) Å and C—O—C angles from 110.54 (11) to 113.87 (11)°, these values being comparable with other crown ether complexes based on benzo-annelated systems such as dibenzo-30-crown-10 (Bush & Truter, 1972).



(I)

Torsion-angle analysis around the C—O and aliphatic C—C bonds within the crown ring can provide an insight into the puckering of the ligand. In general, the C—O—C—C torsion angles are expected to lie close to 180° (*trans*) whereas the O—C—C—O torsion angles tend to cluster around 60° (*gauche*). In this molecule, two C—O—C—C torsion angles possess unusual geometries; C8—O1—C7—C6 deviates significantly from the ideal *trans* value, 148.79 (13)°, and C13—O4—C14—C2 is *gauche*, 76.52 (15)°, whilst all other C—O—C—C values group around ±180°. Two O—C—C—O torsion angles adopt their expected *gauche*-type geometries, while the third (belonging to O2—C9—C8—O1) is *trans*, 175.94 (11)°. Smaller rings such as dibenzo-26-crown-8 also display unusual torsion-angle measurements (Buchanan *et al.*, 1997).

The absence of interannular contacts, illustrated by the nonbonding distances O1$\cdots$C8^{i} of 3.835 (2) and C1$\cdots$O3^{i} of 3.529 (2) Å [symmetry code: (i) $-x$, $-y$, $1-z$], results in a small central ring cavity. There seems to be no correlation between the number of atoms in the ring and the size of the cavity as other 30-atom crown species show appreciably larger central cavities (Anelli *et al.*, 1988). Overall, the crown ether is flat, the largest deviation from the mean plane of the 30 ring atoms being 0.890 (2) Å, with slight puckering at the xylyl moiety. The packing efficiency of the compound was analysed using the CALC VOID option in *PLATON* (Spek, 1999). The packing index (Kitajgorodskij, 1973) of this crown is 71%, which is comparable to the values obtained for dibenzo-30-

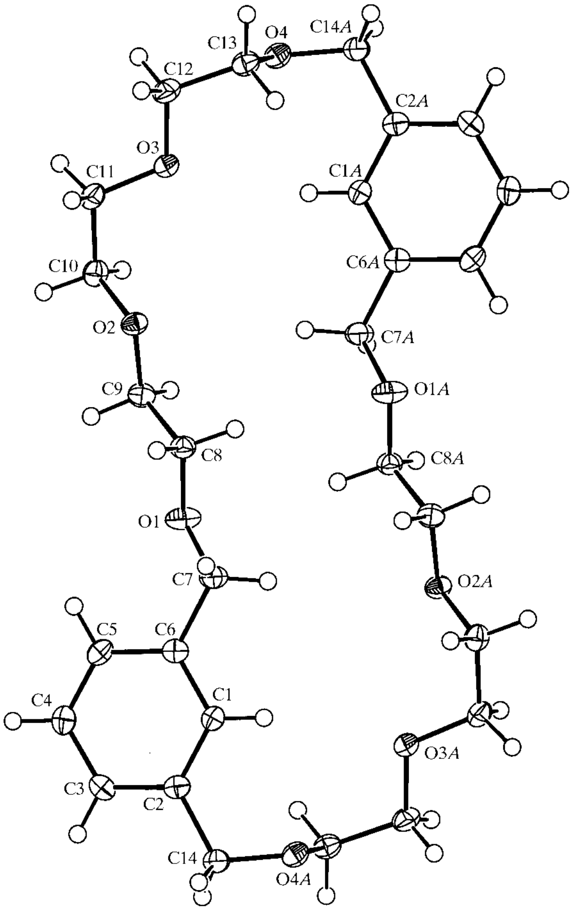


Figure 1
Displacement ellipsoid plot (50% probability) of (I) with the atom-labelling scheme. [Symmetry operation: (*A*) $-x$, $-y$, $1-z$.]

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[1] Systematic name: 3,6,9,12,20,23,26,29-octaoxatricyclo[29.3.1.1^{14,18}]hexatriaconta-1(35),14,16,18(36),31,33-hexaene (CAS No. 57624-54-1).

crown-10, 68% (Bush & Truter, 1972), and 30-crown-10, 67% (Bheda *et al.*, 1994).

The crown ether ring has rearranged on complexation with a diphenyl magnesium substrate (Markies *et al.*, 1994), leading to a change in the torsion angle descriptors and hence the ring conformation. Only three of the four O atoms ligate to the magnesium ions; presumably either steric interactions between diphenyl groups on the magnesium and the 1,3-xylyl units or a relatively long O1$\cdots$O2 distance of 3.577 (2) Å prevents full participation. It would be interesting to see if higher coordination numbers could be achieved with other cationic species such as K^+ or Na^+ (Mercer & Truter, 1973; Owen & Truter, 1979).

Table 1
Selected geometric parameters (Å, °).

O1—C8	1.4163 (17)	O3—C11	1.4140 (18)
O1—C7	1.4180 (18)	O3—C12	1.4203 (17)
O2—C9	1.4175 (17)	O4—C14^i	1.4149 (18)
O2—C10	1.4228 (17)	O4—C13	1.4302 (18)
C8—O1—C7	113.87 (11)	C11—O3—C12	111.74 (11)
C9—O2—C10	110.54 (11)	C14^i—O4—C13	112.25 (11)
C8—O1—C7—C6	148.79 (13)	O2—C10—C11—O3	67.86 (15)
C7—O1—C8—C9	−174.42 (12)	C11—O3—C12—C13	175.10 (12)
C10—O2—C9—C8	179.85 (12)	C14^i—O4—C13—C12	−164.85 (12)
O1—C8—C9—O2	175.94 (11)	O3—C12—C13—O4	66.53 (15)
C9—O2—C10—C11	−176.43 (12)	C13—O4—C14^i—C2^i	76.52 (15)
C12—O3—C11—C10	177.09 (12)		

Symmetry code: (i) $-x, -y, 1 - z$.

Experimental

The dimeric compound was formed as a side product in the synthesis of the monomer 1,3-xylyl-15-crown-4 reported by Gray *et al.* (1976, 1977). Isolation and purification from the oligomeric fraction, followed by repeated crystallization of the crude product from ethanol, produced crystals suitable for X-ray analysis.

Crystal data

$C_{28}H_{40}O_8$
$M_r = 504.60$
Orthorhombic, *Pccn*
$a = 16.9096$ (17) Å
$b = 18.351$ (2) Å
$c = 8.350$ (2) Å
$V = 2591.0$ (8) Å^3
$Z = 4$
$D_x = 1.294$ Mg m^{-3}
Mo $K\alpha$ (Zr-filtered) radiation
Cell parameters from 25 reflections
$\theta = 14.0$–$17.9°$
$\mu = 0.094$ mm^{-1}
$T = 100$ (2) K
Block, colourless
0.58 × 0.45 × 0.42 mm

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans
5946 measured reflections
2976 independent reflections
2337 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 27.48°$
$h = 0 \rightarrow 21$
$k = -23 \rightarrow 23$
$l = 0 \rightarrow 10$
2 standard reflections
frequency: 60 min
intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.109$
$S = 1.025$
2976 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 1.2483P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.562$ e Å^{-3}
$\Delta\rho_{\min} = -0.220$ e Å^{-3}

All H atoms were constrained to ride on their parent C atom with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$; C—H distances refined to 0.95 or 0.99 Å for aromatic CH and CH_2 groups, respectively.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1578). Services for accessing these data are described at the back of the journal.

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