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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
Disorder in main residue
 R factor = 0.045
 wR factor = 0.107
Data-to-parameter ratio = 11.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.2,11,18,21,24-Pentaoxatetracyclo[23.4.0.0^{4,9}.0^{12,17}]-nonaica-1(25),4(9),5,7,12(17),13,15,26,28-nonaene

The title 17-crown-5 unit, $\text{C}_{24}\text{H}_{24}\text{O}_5$, comprising three benzo groups and diethylene glycol was prepared from the reaction of α, α' -dibromo-*o*-xylene and bisphenol in the presence of sodium hydride as base. This molecule offers a cavity suitable for host-guest complexes.

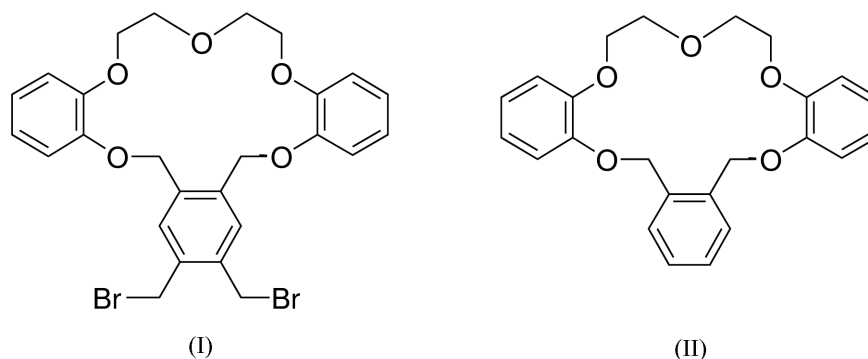
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Comment

Since the first report on crown ethers (Pedersen, 1967), a great number of crown compounds containing one or more aromatic subunits have been investigated (Gokel & Korzeniowski, 1982; Izatt & Christensen, 1978, 1979, 1981; Vögtle & Weber, 1985; Lindoy, 1989; Weber *et al.*, 1989). A number of crown compounds bearing two macrocyclic polyether rings within the molecule, which are referred to as biscrowns, have also been synthesized (Timko *et al.*, 1974; Frensch & Vögtle, 1979; Rebek *et al.*, 1980; Lee *et al.*, 1992). In our previous paper, we reported the preparation of a new crown ether, (I), and its solid-state structure, which could be a precursor of the common-nuclear biscrown ether, bearing a benzene ring (Sim *et al.*, 2001).



We now report a new preparation of crown ether (II), the parent crown ether unit of (I), and its solid-state structure, which is the parent crown ether unit of (I). The preparation of (II) has been reported by Weber and Vögtle (1976), but the yield was rather low when KOH with dimethylformamide (DMF) was used. Therefore, alternative reaction conditions were examined so as to optimize the cyclization yield. In the reaction of α, α' -dibromo-*o*-xylene with 1,5-bis(2-hydroxyphenoxy)-3-oxapentane, the use of *n*-BuLi with tetrahydrofuran (THF) gave a 65% yield. Sodium hydride and THF provided a 72% yield but potassium *tert*-butoxide with THF gave only a moderate 50% yield. Herein, we report the optimized reaction conditions (sodium hydride and THF) for (II), as well as its solid-state structure.

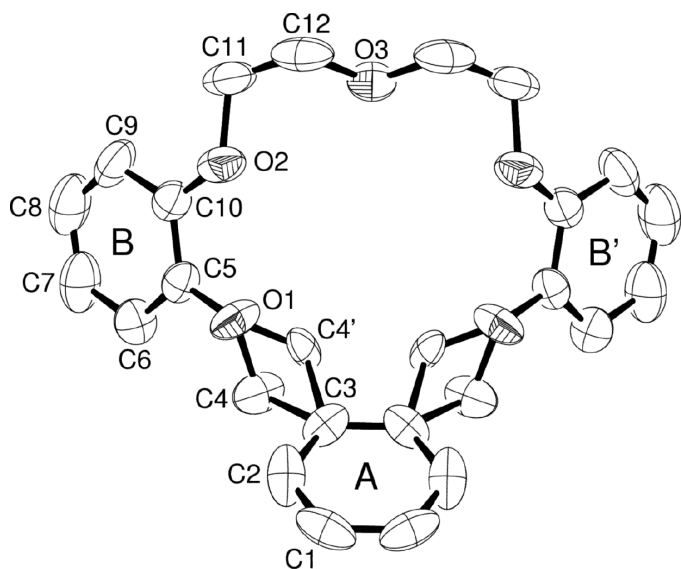


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of (II) showing 35% probability displacement ellipsoids. C atoms are expressed with ellipsoids with only enveloping ellipses and the rest with ellipsoids with octant shading. H atoms have been omitted for clarity. The C4 atom is disordered over two positions.

Compound (II), with the atomic labelling scheme, is shown in Fig. 1. There is crystallographic mirror symmetry in (II) so that half a molecule comprises the asymmetric unit. In the diethylene glycol chain-bridging benzo groups *B* and *B'*, the C10–O2–C11 [116.5 (4)°] and C12–O3–C12ⁱ [111.3 (5)°] angles are slightly greater than tetrahedral, while the O2–C11–C12 [106.7 (5)°] and O3–C12–C11 [108.5 (3)°] angles are very close to tetrahedral [symmetry operation: (i) 2 – *x*, *y*, *z*]. The dihedral angle between rings *B* and *B'* is 83.4 (1)°. In the *A*-to-*B* ring connectivity, the C3–C4–O1–C5 torsion angle is 174.9 (5)° [for the minor component of the disorder associated with C4, C3–C4'–O1–C5 is –148.6 (5)°] which indicates that ring *A* is situated *trans* to ring *B*, with a dihedral angle of 69.2 (1)° between them. In the diethylene glycol group, the O–C–C–O and two C–O–O–C torsion angles are *gauche* and *trans*, respectively, as there is one extra atom in the diethylene glycol backbone. All these conformations are very similar to those found in (I) (Sim *et al.*, 2001). The interatomic distances O1...O3 of 4.580 (5) Å, O1...O2ⁱ of 5.344 (5) Å and O2...O2ⁱ of 4.941 (6) Å suggest sufficient room for the introduction of a guest atom/molecule inside the cavity. The closest intermolecular distance of 2.41 Å occurs between H11^b and H12^bⁱⁱ which suggests that the molecular packing is governed by van der Waals forces [symmetry operation: (ii) *x*, 1 – *y*, $\frac{1}{2}$ + *z*].

Experimental

To a refluxing suspension of sodium hydride (15.2 mmol) in THF under nitrogen was added dropwise a solution of α,α' -dibromo-*o*-xylene (3.79 mmol) and 1,5-bis(2-hydroxyphenoxy)-3-oxapentane (3.79 mmol) in THF over a period of 3 h. The mixture was then refluxed for an additional 24 h. After cooling to room temperature, 10% aqueous hydrochloric acid was added. The solvent was removed

under reduced pressure and the residual mixture was extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated *in vacuo*. The crude product was chromatographed on a silica-gel column using a mixed solvent of ethyl acetate and *n*-hexane (1:1) as eluent, and recrystallization from dichloromethane/*n*-hexane (1:20, *v/v*) gave (II) as a crystalline solid in 72% yield (m.p. 398–400 K). IR (KBr pellet) 3065, 2880, 1596, 1498, 1258, 1119, 949 and 741 cm⁻¹. ¹H NMR (CDCl₃): δ 7.65–7.39 (*m*, 4H, Ar-H), 7.10–6.88 (*m*, 8H, Ar-H), 5.31 (*s*, 4H, OCH₂Ar), 4.20 (*t*, 4H, OCH₂CH₂O) and 3.92 (*t*, 4H, OCH₂-CH₂O).

Crystal data

C₂₄H₂₄O₅
M_r = 392.43
 Orthorhombic, *Cmc*2₁
a = 21.585 (4) Å
b = 11.675 (3) Å
c = 8.092 (2) Å
V = 2039.3 (8) Å³
Z = 4
D_x = 1.278 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 20 reflections
 θ = 11.4–14.1°
 μ = 0.09 mm⁻¹
T = 293 (2) K
 Block, colorless
 0.37 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled $\omega/2\theta$ scans
 1650 measured reflections
 1597 independent reflections
 708 reflections with *I* > 2σ(*I*)
R_{int} = 0.011

θ_{\max} = 30.0°
h = 0 → 30
k = 0 → 16
l = –11 → 5
 3 standard reflections
 frequency: 300 min
 intensity decay: 1%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.045
wR(*F*²) = 0.107
S = 0.98
 1597 reflections
 144 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0360P)^2 + 0.0439P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.11 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.14 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0098 (9)

C4 was disordered over two positions and their sites were refined anisotropically using the *PART* command in *SHELXL97* (Sheldrick, 1997). All H atoms were located in their idealized positions with *U*_{iso} constrained to be 1.2 times the equivalent isotropic displacement of the parent atoms. The number of Friedel pairs measured is 180 and the fraction of Friedel pairs measured is 0.113. As there are no heavy-atom, *i.e.* *Z* > Si, types present, the absolute structure was not determined.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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