

6,7-Bis(bromomethyl)-2,11,18,21,24-pentaoxatetracyclo[23.4.0.0^{4,9}.0^{12,17}]-nonacosa-1(25),4(9),5,7,12(17),13,-15,26,28-nonaene

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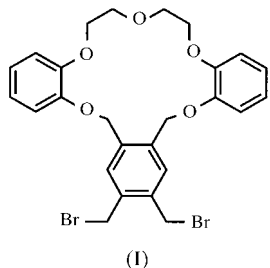
Received 7 June 2000

Accepted 23 November 2000

The 17-crown-5 unit, C₂₆H₂₆Br₂O₅, consisting of a 1,2-bis(bromomethyl) group, three benzo groups and diethylene glycol, was prepared from the reaction of 1,2,4,5-tetrakis(bromomethyl)benzene and bis-phenol in the presence of sodium hydride as a base. This molecule seems to offer an internal cavity for the formation of a host-guest complex.

Comment

Since the first report on the synthesis and properties of crown ether (Pedersen, 1967), there has been tremendous interest in the synthesis and inclusion behaviour of these compounds (Pedersen, 1988; Cram, 1986; Lehn, 1988; Lnoe & Gokel, 1990; Weber *et al.*, 1989). In spite of extensive studies on crown ethers, only a few common-nuclear bis-crown compounds containing a single benzene ring serving as a common aromatic unit have been explored (Loeb & Shimizu, 1992; Lee *et al.*, 1992). In our previous papers, we have reported the synthesis and complexation behaviour of common-nuclear bis-crown ethers (Lee *et al.*, 1992, 1997). In this regard, we now report the preparation of a new crown ether, (I), and its solid-state structure, which could be a precursor of the common-nuclear bis-crown ether bearing a benzene ring.



The title compound with the atomic labelling scheme is shown in Fig. 1. The C—Br bond lengths are not significantly different and average to 1.937 (9) Å. Similarly, the Br—C—C

angles do not differ significantly and average to a value of 111.7 (6)°. In the chain-bridging benzo groups *B* and *C*, the average C—O—C angle is slightly larger than tetrahedral, while the O—C—C angle is very close to tetrahedral. In the *A*-to-*B* ring and *A*-to-*C* ring connectivities, the torsion angles C7—C9—O1—C10 and C6—C26—O5—C25 are 170.8 (11) and 168.5 (12)°, respectively, indicating that the *A* ring is situated *trans* to both the *B* and *C* rings. The two O—C—C—O and four C—O—C—C torsion angles in the diethylene glycol group are *gauche* and *trans*, respectively, because there is one extra atom in the diethylene glycol back bond. Atom positions C12 and C13 in ring *B* and atom positions C21, C22, C23 and C24 atoms in ring *C* are disordered. Consequently, some of their bond lengths and angles differ considerably from the normal values. The interatomic distances O1···O3 of 4.96 (1) Å and O3···O5 of 4.92 (1) Å appear to be sufficient to introduce a guest atom inside the molecule.

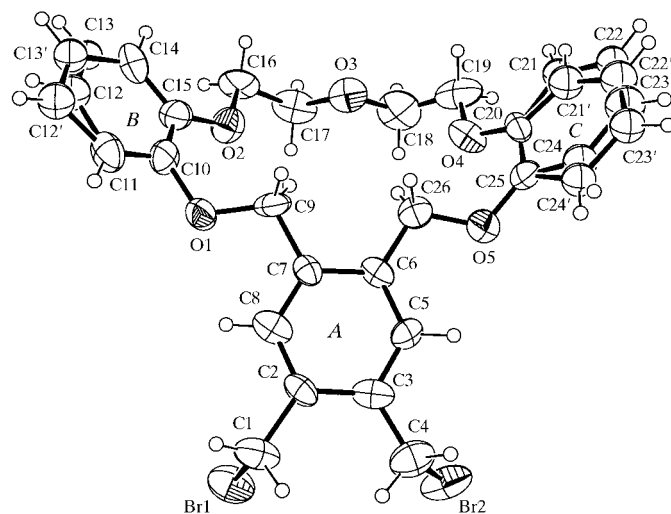


Figure 1

ORTEP (Johnson, 1976) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Some C atoms in phenyl rings *B* and *C* are disordered.

Experimental

To a refluxing suspension of 95% sodium hydride (0.132 g, 5.50 mmol) in tetrahydrofuran (THF; 50 ml) was added dropwise a solution of 1,2,4,5-tetrakis(bromomethyl)benzene (1.00 g, 2.20 mmol) and 1,5-bis(2-hydroxyphenoxy)-3-oxapentane (0.580 g, 2.00 mmol) in THF (50 ml) over 3 h under an N₂ atmosphere. The reaction mixture was refluxed for an additional 24 h. After cooling to room temperature, 10% aqueous hydrochloric acid was added. The solvent (THF) was removed under reduced pressure and the aqueous layer was extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was chromatographed on silica gel using a mixed solvent of ethyl acetate and *n*-hexane (1:1) as eluent, and recrystallized from dichloromethane/*n*-hexane (1:20, *v/v*). Crystalline (I) was obtained in 30% yield (0.35 g), m.p. 455–456 K. Found: C 54.67, H 4.65%; C₂₆H₂₆Br₂O₅ requires C 54.00, H 4.53%; IR (KBr pellet) 2929, 1599, 1506, 1452, 1260, 1212, 1128, 749 and 610 cm⁻¹; ¹H NMR (CDCl₃): δ 7.65 (*s*, 2H, arom.), 7.06–6.85 (*m*, 8H, arom.), 5.20 (*s*, 4H, OCH₂Ar),

4.71 (*s*, 4H, ArCH₂Br), 4.15 (*t*, 4H, ArOCH₂CH₂O) and 3.85 (*t*, 4H, ArOCH₂CH₂O); ¹³C NMR (CDCl₃): δ 150.562, 147.841, 137.211, 135.607, 130.644, 123.331, 120.957, 119.278 and 112.842 (Ar), 70.399, 69.514 and 67.818 (CH₂O), and 30.032 (CH₂Br). MS (*m/z*): 578 (*M*⁺), 307, 182, 154, 136, 107.

Crystal data

C ₂₆ H ₂₆ Br ₂ O ₅	Mo <i>K</i> α radiation
<i>M_r</i> = 578.29	Cell parameters from 25 reflections
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>θ</i> = 11.37–13.75°
<i>a</i> = 8.141 (2) Å	<i>μ</i> = 3.337 mm ⁻¹
<i>b</i> = 13.7976 (16) Å	<i>T</i> = 293 (2) K
<i>c</i> = 21.852 (2) Å	Plate, colourless
<i>V</i> = 2454.6 (7) Å ³	0.528 × 0.363 × 0.132 mm
<i>Z</i> = 4	
<i>D_x</i> = 1.565 Mg m ⁻³	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.013
Non-profiled ω/2θ scans	<i>θ</i> _{max} = 25.0°
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = -2 → 9
<i>T</i> _{min} = 0.247, <i>T</i> _{max} = 0.644	<i>k</i> = -4 → 16
2564 measured reflections	<i>l</i> = -6 → 25
2516 independent reflections	3 standard reflections
1137 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 300 min
	intensity decay: none

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 1.4141P]$
$R[F^2 > 2\sigma(F^2)] = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.011	Δρ _{max} = 0.58 e Å ⁻³
2516 reflections	Δρ _{min} = -0.42 e Å ⁻³
294 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.33 (3)

Atoms C12 and C13 in benzene ring *B* and atoms C21, C22, C23 and C24 in benzene ring *C* were disordered over two positions, and were refined isotropically with an occupancy of 0.49 (6) for the unprimed atoms and 0.51 (6) for the primed atoms using both *TWIN* and *BASF* instructions. All H atoms were fixed geometrically and allowed to ride on their attached atoms and their isotropic displa-

cement parameters were fixed at 1.2 times the equivalent isotropic displacement parameters of their parent atoms. The largest peak in the final electron-density map is 1.24 Å from the Br2 atom.

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, 1990); 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).

This research was fully supported by the Korea Research Foundation (BSRI grant No. 1999-015-DP0203).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1007). Services for accessing these data are described at the back of the journal.

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