

MITHRIL (Gilmore, 1983) in *TEXSAN*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1086). Services for accessing these data are described at the back of the journal.

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Benzophenone Crown Ether Acetals with 14- and 17-Membered Rings

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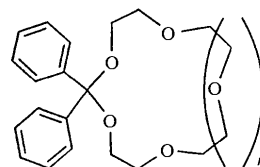
Abstract

The 14-membered ring of 2,2-diphenyl-1,3,6,9,12-pentaoxacyclotetradecane, C₂₁H₂₆O₅, is greatly distorted from a rectangular structure. By contrast, the homologous 17-membered ring of 2,2-diphenyl-1,3,6,9,12,15-hexaoxacycloheptadecane, C₂₃H₃₀O₆, with an additional oxyethylene unit, adopts an approximately rectangular structure and the cavity has an unsymmetrical shape.

Comment

Crown ether acetals have ring-contracted structures, each containing one methylene unit, as compared with usual crown ethers possessing the same number of O atoms. In view of the cation-binding capability, several workers have examined the alkali metal ion extractability of these macrocyclic polyethers (Kawakami *et al.*, 1978; Ouchi *et al.*, 1984). However, little is known about their structural details because of their intrinsic acid-sensitive properties coupled with a lack of general and useful synthetic methods (Pedersen, 1970; Kawakami *et al.*, 1977; Oshima *et al.*, 1982).

In our previous paper, we reported that the 11-membered-ring benzophenone crown ether acetal 2,2-diphenyl-1,3,6,9-tetraoxacycloundecane, (I), adopts a planar–chiral conformation for the largely twisted macrocyclic ring (Tamura *et al.*, 1997). We have extended the X-ray crystal structure analyses to the higher homologues, namely the 14- and 17-membered benzophenone crown ether acetals 2,2-di-



- (I) $n=0$
 (II) $n=1$
 (III) $n=2$

phenyl-1,3,6,9,12-pentaoxacyclotetradecane, (II), and 2,2-diphenyl-1,3,6,9,12,15-hexaoxacycloheptadecane, (III), in order to gain a better understanding of the ring conformations.

The molecular structures of the two crown ether acetals, (II) and (III), are shown in Figs. 1 and 2, respectively. In the complex [Y(OH₂)₈]Cl₃·(15-crown-5), (IV), the crown ether does not have a rectangular structure; likewise, the 14-membered crown ether acetal (II), also with five O atoms, does not adopt a rectangular structure (unfortunately, the X-ray structure of uncomplexed 15-crown-5 has not been determined yet) (Rogers & Kurihara, 1986). The ring of (II) is more distorted than the 15-membered ring of (IV). The deviations of the angles from typical *gauche* or *trans* conformations are |1.8|–|55.2|° for (II), while they are |1.8|–|23.4|° for (IV). In contrast, benzo-15-crown-5 (Hanson, 1978), containing a fused benzene ring, has a nearly rectangular structure because the rigid aromatic nucleus fits well into the space between two adjacent O atoms and partly restricts the ring conformation.

The 17-membered crown ether acetal (III), with six O atoms, adopts a nearly rectangular structure, as in 18-crown-6 (Dunitz & Seiler, 1974). A more careful perusal of both conformations shows that the cavity of (III) has an unsymmetrical shape, with a C2···O5 distance of 3.686(2) Å and a C8···O2 distance of 3.886(2) Å, while the cavity of 18-crown-6 is centrosymmetric in shape, with an O7···C9' distance of 3.746 Å.

The O(acetal)—C(acetal)—C(aromatic)—C(aromatic *o*-position) torsion angles are |6.2(3)|–|20.9(1)|° in (II)

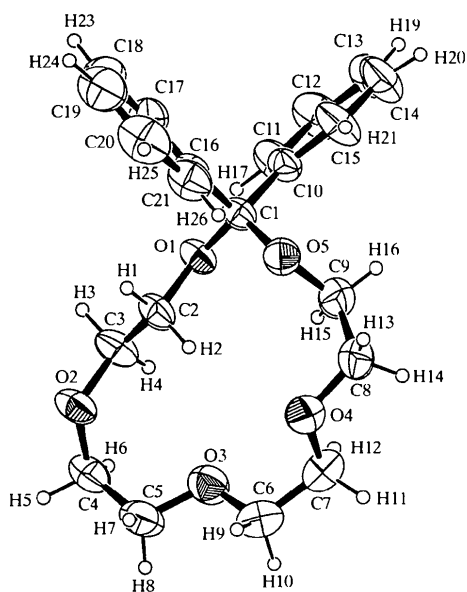


Fig. 1. ORTEP (Johnson, 1976) plot of the molecule of 2,2-diphenyl-1,3,6,9,12-pentaoxacyclotetradecane, (II), with the atom-numbering scheme. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.

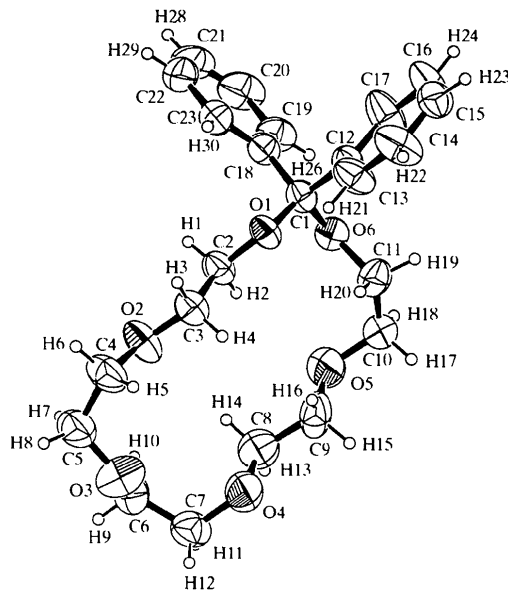


Fig. 2. ORTEP (Johnson, 1976) plot of the molecule of 2,2-diphenyl-1,3,6,9,12,15-hexaoxacycloheptadecane, (III), with the atom-numbering scheme. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level. The O5' and C9' sites have been omitted for clarity.

and (III), similar to those in (I) [|11.6(3)|–|18.2(3)|°]. Furthermore, intramolecular C—H···O contacts within the sum of the van der Waals radii (2.4 Å) are observed between the acetal O atom and the phenyl C—H bond; the O···H distances range from 2.31 to 2.37 Å and the relevant O···C distances are 2.662(2)–2.703(1) Å for (II) and (III).

Experimental

The title compounds, (II) and (III), were prepared according to the procedure described by Oshima *et al.* (1982) and were recrystallized from hexane–diethyl ether solutions at room temperature.

Compound (II)

Crystal data

C₂₁H₂₆O₅
M_r = 358.43
 Monoclinic
*P*2₁/*a*
a = 13.367(3) Å
b = 10.019(2) Å
c = 15.554(2) Å
 β = 109.56(1)°
V = 1962.8(7) Å³
Z = 4
D_x = 1.213 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 10.2–12.1°
 μ = 0.086 mm⁻¹
T = 296 K
 Prismatic
 0.40 × 0.30 × 0.20 mm
 Colourless

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
 Absorption correction:
 ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.969$, $T_{\max} = 1.000$
 6251 measured reflections
 6023 independent reflections

Refinement

Refinement on F^2
 $R = 0.050$
 $wR = 0.057$
 $S = 1.71$
 2687 reflections
 235 parameters
 H atoms riding, $U(H) = 1.2U_{eq}(C)$

2687 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\text{max}} = 30^\circ$
 $h = 0 \rightarrow 18$
 $k = 0 \rightarrow 14$
 $l = -21 \rightarrow 20$
 3 standard reflections
 every 150 reflections
 intensity decay: 19.90%

$w = 1/[\sigma^2(F_o) + 0.0001|F_o|^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.03$
 $\Delta\rho_{\text{max}} = 0.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (II)

O1—C1	1.420 (2)	O4—C8	1.418 (3)
O1—C2	1.438 (2)	O5—C1	1.409 (2)
O2—C3	1.424 (3)	O5—C9	1.426 (3)
O2—C4	1.421 (3)	C2—C3	1.481 (3)
O3—C5	1.415 (3)	C4—C5	1.491 (4)
O3—C6	1.413 (3)	C6—C7	1.485 (4)
O4—C7	1.419 (3)	C8—C9	1.505 (4)
O1—C1—O5—C9	65.1 (2)	C1—O5—C9—C8	-159.5 (2)
O1—C2—C3—O2	176.5 (2)	C2—C3—O2—C4	-124.8 (2)
O2—C4—C5—O3	-67.1 (3)	C3—O2—C4—C5	96.4 (2)
O3—C6—C7—O4	75.0 (3)	C4—C5—O3—C6	173.5 (2)
O4—C8—C9—O5	77.9 (3)	C5—O3—C6—C7	-166.0 (2)
O5—C1—O1—C2	53.0 (2)	C6—C7—O4—C8	-168.2 (2)
C1—O1—C2—C3	178.2 (2)	C7—O4—C8—C9	93.6 (3)

Compound (III)**Crystal data**

$\text{C}_{23}\text{H}_{30}\text{O}_6$
 $M_r = 402.49$
 Monoclinic
 $P2_1/n$
 $a = 13.948 (2) \text{ \AA}$
 $b = 11.703 (2) \text{ \AA}$
 $c = 14.725 (2) \text{ \AA}$
 $\beta = 116.753 (8)^\circ$
 $V = 2146.2 (5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.246 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Rigaku AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction:
 ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.973$, $T_{\max} = 1.000$
 5375 measured reflections
 4922 independent reflections

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 10.6\text{--}12.3^\circ$
 $\mu = 0.089 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Prismatic
 $0.50 \times 0.30 \times 0.20 \text{ mm}$
 Colourless

Refinement

Refinement on F^2
 $R(F) = 0.051$
 $wR(F^2) = 0.141$
 $S = 1.16$
 4922 reflections
 271 parameters
 H atoms riding, $U(H) = 1.2U_{eq}(C)$

$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 0.58P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.068$
 $\Delta\rho_{\text{max}} = 0.58 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (III)

O1—C1	1.406 (1)	O5—C10	1.416 (2)
O1—C2	1.431 (1)	O6—C1	1.423 (1)
O2—C3	1.386 (1)	O6—C11	1.433 (1)
O2—C4	1.420 (2)	C2—C3	1.489 (2)
O3—C5	1.402 (2)	C4—C5	1.492 (2)
O3—C6	1.396 (2)	C6—C7	1.482 (2)
O4—C7	1.441 (2)	C8—C9	1.483 (2)
O4—C8	1.365 (2)	C10—C11	1.493 (2)
O5—C9	1.408 (2)		
O1—C1—O6—C11	-62.6 (1)	C2—C3—O2—C4	-169.4 (1)
O1—C2—C3—O2	176.24 (9)	C3—O2—C4—C5	-153.7 (1)
O2—C4—C5—O3	75.6 (1)	C4—C5—O3—C6	-116.5 (1)
O3—C6—C7—O4	-66.1 (1)	C5—O3—C6—C7	162.0 (1)
O4—C8—C9—O5	-174.5 (1)	C6—C7—O4—C8	-72.5 (2)
O5—C10—C11—O6	-61.0 (1)	C7—O4—C8—C9	-177.7 (1)
O6—C1—O1—C2	-58.9 (1)	C8—C9—O5—C10	-179.9 (1)
C1—O1—C2—C3	172.82 (8)	C9—O5—C10—C11	-85.9 (1)
C1—O6—C11—C10	153.60 (8)		

In (III), the O5 and C9 atoms of the 17-membered ring are both disordered over two positions. The major component was refined with anisotropic displacement parameters, and the minor component (indicated by primed labels) with isotropic displacement parameters. The occupancy factor of O5 was constrained to be the same as that of C9, and the occupancy factor of O5' the same as that of C9'. Refined occupancy factors were 0.749 (1) and 0.251 (1), respectively. H atoms of the major component were calculated geometrically. The O5—C10 distance was restrained to be the same as O5'—C10, and C8—C10 was restrained to be the same as C8—C9', with $\sigma(\text{distance}) = 0.03$.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structures: *TEXSAN* for (II); *SHELXL93* (Sheldrick, 1993) for (III). For both compounds, software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1043). Services for accessing these data are described at the back of the journal.

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