

C9	0.1476 (2)	0.6716 (4)	0.3348 (2)	0.0403 (8)
C10	0.0636 (2)	0.6645 (4)	0.3591 (2)	0.0513 (10)
C11	0.0320 (2)	0.5500 (4)	0.3869 (2)	0.0481 (10)
C12	0.0844 (2)	0.4418 (4)	0.3915 (2)	0.0380 (8)
C13	0.1692 (2)	0.4475 (3)	0.3676 (2)	0.0281 (7)

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

Br—C1	1.927 (3)	P—S	1.9348 (11)
P—C2	1.801 (3)	F1—C1	1.343 (4)
P—C8	1.807 (3)	F2—C1	1.341 (4)
P—C1	1.884 (3)		
C2—P—C8	109.04 (14)	F2—C1—F1	106.2 (2)
C2—P—C1	101.57 (14)	F2—C1—P	108.8 (2)
C8—P—C1	105.00 (14)	F1—C1—P	111.6 (2)
C2—P—S	114.42 (10)	F2—C1—Br	108.4 (2)
C8—P—S	115.82 (10)	F1—C1—Br	109.0 (2)
C1—P—S	109.62 (11)	P—C1—Br	112.6 (2)

Data collection: *P3* (Nicolet, 1987). Cell refinement: *P3*. Data reduction: *XDISK* (Nicolet, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Diaza Analogue of Benzo-15-crown-5

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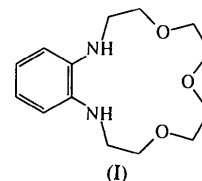
(Received 1 February 1996; accepted 4 March 1996)

Abstract

The title compound, 2,3-benzo-7,10,13-trioxa-1,4-diaza-2-pentadecene, $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$, is a derivative of benzo-15-crown-5 in which the two O atoms flanking the aromatic ring are replaced by NH groups. Except for the rigidly near-planar $\text{OC}_6\text{H}_4\text{O}$ segment, the macrocycle contains *gauche* C—C and a mixture of *gauche* and *anti* C—O and C—N linkages.

Comment

The title compound, (I), was prepared as part of a study of selective complexation of a range of metal ions by crown ethers and their derivatives. Many complexes are known which incorporate 15-crown-5 as a ligand, covering a wide range of over 30 different metal ions; a search of the Cambridge Structural Database (Allen & Kennard, 1993) produced a substantial list.



Substitution of one or more of the O atoms by NH groups alters the complexing ability of the ligand, since the basicity of the NH group in such macrocycles has been found to be lower than that of the replaced O atom (Frensdorff, 1971; Blackborow, Lockhart, Thompson & Thompson, 1978), with even the remaining O atoms showing reduced basicity compared with the parent crown ether (Lockhart, Atkinson, Marshall & Davies, 1979).

Although the Cambridge Structural Database contains around twenty structures related to 15-crown-5 (free or complexed to a metal) in which one O atom has been replaced by NH or NR and almost as many in which two non-adjacent O atoms have been replaced, there are no previous reports of disubstitution in adjacent positions, except where the two N atoms act as bridgeheads in a bicyclic molecule.

The macrocyclic strand of the molecule displays a series of *anti* and *gauche* torsion angles for C—C, O—C and N—C bonds (Fig. 1, Table 2). The individual X—C—X segments are ag^-g^- , ag^-a , ag^+a , and ag^-g^- . For benzo-15-crown-5, which has O atoms in place of NH groups, they are ag^-a , g^-g^-a , ag^+g^+ , and ag^+a (Hanson, 1978). In each case, all of the C—C bonds have a *gauche* conformation. The molecules have no unusual intermolecular interactions. Hydrogen bonding is at best weak, with shortest N...O separations in suitable orientations of 3.688 (5) (intramolecular) and 3.089 (4) Å (intermolecular); the latter is between the N13 and O10ⁱ atoms [symmetry code: (i) 1 - x, 1 - y, 1 - z], with an N13—H13...O10ⁱ angle of 145 (2)° for the freely refined H atom. The N1...O4 intramolecular separation of 2.772 (4) Å is a consequence of the N1—C2—C3—O4 *gauche* conformation; it does not represent hydrogen bonding because the N—H orientation is inappropriate, with an N—H1...O4 angle of only 111 (2)°.

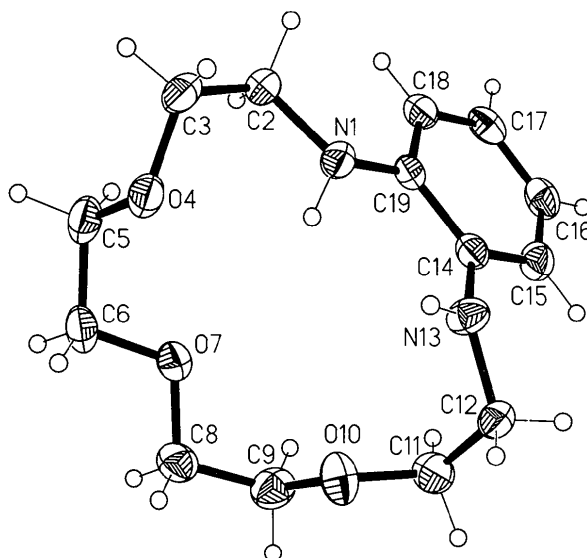


Fig. 1. The molecular structure of (I) shown with 40% probability displacement ellipsoids.

Experimental

The title compound was prepared from 1,2-phenylenediamine (2.08 g, 19.2 mmol), tetraethyleneglycol ditosylate (9.68 g, 19.2 mmol) and potassium carbonate (0.65 g, 48.2 mmol) in dimethylformamide solution (600 ml), heated at 373 K for 48 h. The product was obtained in small quantity after column chromatography (silica gel; ethyl acetate and 4:1 dichloromethane/methanol elution) followed by recrystallization from diethyl ether. Satisfactory elemental analyses (C, H, N) were obtained (Cooper, 1993).

Crystal data

C₁₄H₂₂N₂O₃
M_r = 266.34

Cu Kα radiation
λ = 1.54184 Å

Monoclinic
P2₁/n
a = 8.569 (3) Å
b = 17.316 (6) Å
c = 9.968 (4) Å
β = 109.02 (2)°
V = 1398.3 (9) Å³
Z = 4
D_x = 1.265 Mg m⁻³
D_m not measured

Data collection

Stoe-Siemens diffractometer
ω/θ scans with on-line
profile fitting (Clegg,
1981)
Absorption correction:
none
2174 measured reflections
2174 independent reflections

Cell parameters from 36
reflections
θ = 15.08–19.75°
μ = 0.724 mm⁻¹
T = 240 (2) K
Block
0.70 × 0.60 × 0.50 mm
Colourless

2145 observed reflections
[I > 2σ(I)]
θ_{max} = 65.04°
h = -9 → 9
k = 0 → 20
l = 0 → 11
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F²
R(F) = 0.0508
wR(F²) = 0.1492
S = 1.128
2174 reflections
179 parameters
w = 1/[σ²(F_o²) + (0.0753P)²
+ 0.7825P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.230 e Å⁻³
Δρ_{min} = -0.185 e Å⁻³

Extinction correction:
SHELXL93 (Sheldrick,
1993)
Extinction coefficient:
0.0205 (16)
Atomic scattering factors
from *International Tables
for Crystallography* (1992),
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	U _{eq}
N1	0.2993 (2)	0.31373 (10)	0.5145 (2)	0.0373 (5)
C2	0.1866 (3)	0.26024 (12)	0.4171 (2)	0.0386 (5)
C3	0.2074 (3)	0.26801 (12)	0.2730 (2)	0.0408 (5)
O4	0.1906 (2)	0.34625 (8)	0.22644 (14)	0.0395 (4)
C5	0.0247 (3)	0.37202 (14)	0.1725 (2)	0.0458 (6)
C6	0.0232 (3)	0.45810 (14)	0.1741 (2)	0.0454 (6)
O7	0.0825 (2)	0.48365 (8)	0.31695 (14)	0.0432 (4)
C8	0.0920 (3)	0.56527 (12)	0.3275 (3)	0.0468 (6)
C9	0.1591 (3)	0.58745 (14)	0.4803 (3)	0.0506 (6)
O10	0.3267 (2)	0.56419 (10)	0.5361 (2)	0.0498 (5)
C11	0.3888 (3)	0.56084 (13)	0.6865 (2)	0.0479 (6)
C12	0.5334 (3)	0.50603 (12)	0.7275 (2)	0.0396 (5)
N13	0.4893 (2)	0.42747 (10)	0.6833 (2)	0.0393 (5)
C14	0.3892 (2)	0.38239 (10)	0.7370 (2)	0.0313 (5)
C15	0.3850 (3)	0.39198 (12)	0.8740 (2)	0.0389 (5)
C16	0.2935 (3)	0.34297 (13)	0.9302 (2)	0.0424 (6)
C17	0.2052 (3)	0.28340 (12)	0.8493 (2)	0.0412 (5)
C18	0.2037 (3)	0.27377 (11)	0.7106 (2)	0.0370 (5)
C19	0.2939 (2)	0.32265 (11)	0.6525 (2)	0.0318 (5)
H1	0.295 (3)	0.3583 (14)	0.474 (3)	0.045
H13	0.505 (3)	0.4161 (14)	0.604 (3)	0.047

Table 2. Selected geometric parameters (Å, °)

N1—H1	0.86 (2)	C8—C9	1.492 (3)
N1—C19	1.400 (2)	C9—O10	1.419 (3)
N1—C2	1.457 (3)	O10—C11	1.419 (3)
C2—C3	1.511 (3)	C11—C12	1.508 (3)
C3—O4	1.424 (3)	C12—N13	1.442 (3)
O4—C5	1.419 (3)	N13—H13	0.87 (2)
C5—C6	1.491 (3)	N13—C14	1.390 (3)
C6—O7	1.417 (3)	C14—C19	1.413 (3)
O7—C8	1.418 (3)		
C19—N1—C2—C3	174.4 (2)	C6—O7—C8—C9	-178.6 (2)
N1—C2—C3—O4	-53.2 (2)	O7—C8—C9—O10	67.9 (3)
C2—C3—O4—C5	-78.2 (2)	C8—C9—O10—C11	-162.1 (2)
C3—O4—C5—C6	160.8 (2)	C9—O10—C11—C12	156.6 (2)
O4—C5—C6—O7	-65.4 (2)	O10—C11—C12—N13	-64.4 (2)
C5—C6—O7—C8	177.3 (2)	C11—C12—N13—C14	-65.7 (3)

Isotropic H atoms were refined with a riding model, except for those attached to nitrogen, which were refined freely.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

The authors thank EPSRC and ICI for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: AB1361). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Deoxy-3-C-ethoxycarbonylmethyl-1,2:5,6-di-O-isopropylidene- α -D-allofuranose at 173 K

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Abstract

The furanoid sugar ring in the title compound, C₁₆H₂₆O₇, has a ³T₄ conformation while the two O-isopropylidene rings have envelope conformations, with O(2) and C(5) lying out of the respective ring planes.

Comment

Many naturally occurring compounds which possess interesting biological activities have furofuran structures. Notable among these are azadirachtin (Broughton, Ley, Slawin, Williams & Morgan, 1986; Ley, Santafianos, Blaney & Simmonds, 1987) and miharamycin A and B (Seto *et al.*, 1983). We recently described the synthesis and crystal structure of methyl 2,2'-anhydro-4,6-O-benzylidene-3-deoxy-3-C-[(R)-2-hydroxyethyl]- α -D-allopyranoside (Linden, Lee & Li, 1995). The title compound, (I), is a useful precursor to such ring systems, and we now describe its structure.

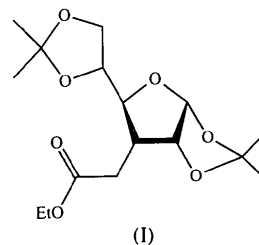


Fig. 1 depicts the correct absolute configuration of (I), which was assigned to agree with the known chirality of D-glucose, from which (I) was synthesized. The bond lengths and angles are normal. The molecule contains three five-membered rings which exhibit various conformations. The furanoid sugar ring has the ³T₄ conformation (Altona & Sundaralingam, 1972), as indicated by the puckering parameters (Cremer & Pople, 1975) $Q = 0.371(4)$ Å and $\varphi_2 = 306.7(6)^\circ$. The 1,2-O-isopropylidene ring has an envelope conformation [$Q = 0.282(4)$ Å, $\varphi_2 = 292.4(7)^\circ$] with O(2) lying 0.42 Å