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Stereochemistry of oxygenated 10-membered rings: X-ray crystal structure, theoretical calculations and ¹H and ¹³C NMR studies of benzo-10-crown-3 ether in solution and in the solid phase

G.W. Buchanan*, M. Gerzain, C. Bensimon, R. Ellen, V.M. Reynolds

Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, Ottawa, Canada K1S 5B6

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Abstract

The title molecule crystallizes in space group P21/c, with a = 7.2705(20), b = 10.825(3), c = 12.790(5) Å, $\beta = 93.51(3)^{\circ}$ and Z = 4. The solid phase ¹³C NMR spectrum is discussed in relation to that obtained in solution. A dideuterio derivative has been synthesized to aid in the spectral assignments. Conformational preferences of the 10-membered ring in the solid state are compared with results of molecular mechanics calculations using MM2 and quantum mechanical methods employing the AM1 approach. © 1997 Elsevier Science B.V.

Keywords: Crown ether analog; Conformation

1. Introduction

The X-ray crystal structures for several monobenz-annelated crown ethers are now available. Specifically, the 15-crown-5 [1], 13-crown-4 [2] and 9-crown-3 [3] structures have been reported. In two instances, detailed ¹³C CPMAS spectra have been included [3,4] to illustrate the complementarity of these techniques in examining details of solid state crystal packing phenomena.

Recently we have undertaken a program to examine the structures and complexation features of a number of novel crown ether analogs. Some of these compounds, such as dibenzo-20-crown-6 exhibit unusual geometries in their O-C-C-O and C-C-O-C units [5] and others, such as dibenzo-15-crown-4 exhibit interesting complexation properties [6].

The present report, for benzo-10-crown-3 (1) below, is the first of any kind involving the 10-crown-3 ether ring system.



^{*} Corresponding author.

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Fig. 1. ORTEP diagram for benzo-10-crown-3 ether 1.

Table 1				
Atomic bond	distances	(Å) and	bond	angles (°)

Distances			
01-C1	1.3835(17)	01-C11	1.4410(18)
O2-C6	1.3808(17)	O2-C7	1.4432(19)
O3-C8	1.4282(22)	O3-C9	1.4298(19)
C1-C2	1.3847(21)	C1-C6	1.3971(21)
C2-C3	1.3906(22)	C3-C4	1.3835(23)
C4-C5	1.3862(23)	C5-C6	1.3883(21)
C7-C8	1.5037(24)	C9-C11	1.5071(24)
C10-C11	1.5113(21)		
Angles			
C1-O1-C11	114.79(11)	C6-O2-C7	115.60(11)
C8-O3-C9	114.60(12)	O1-C1-C2	119.19(13)
O1-C1-C6	120.75(12)	C2-C1-C6	120.03(13)
C1-C2-C3	120.15(14)	C2-C3-C4	119.89(14)
C3-C4-C5	120.11(14)	C4-C5-C6	120.38(14)
O2-C6-C1	121.58(13)	O2-C6-C5	118.93(13)
C1-C6-C5	119.42(13)	O2-C7-C8	108.78(13)
O3-C8-C7	114.02(13)	O3-C9-C10	109.31(12)
C9-C10-C11	112.77(13)	O1-C11-C10	107.96(12)

Table 2 Torsion angles (°)

C11-O1-C1-C2	- 106.4(1)	
C1-O1-C11-C10	- 160.4(2)	
C7-O2-C6-C5	-118.2(1)	
C9-O3-C8-C7	69.9(1)	
O1-C1-C2-C3	- 178.4(2)	
C6-C1-C2-C3	-0.6(1)	
O1-C1-C6-O2	-4.4(1)	
C2-C1-C6-O2	177.8(2)	
C1-C2-C3-C4	-0.5(1)	
C2-C3-C4-C5	1.3(1)	
C3-C4-C5-C6	- 1.1(1)	
C4-C5-C6-O2	- 177.1(2)	
02-C7-C8-O3	58.6(1)	
C9-C10-C11-O1	55.5(1)	
C11-O1-C1-C6	75.8(1)	
C7-O2-C6-C1	64.9(1)	
C6-O2-C7-C8	- 148.9(2)	
C8-O3-C9-C10	- 136.3(2)	
O1-C1-C6-C5	178.7(2)	
C2-C1-C6-C5	0.9(1)	
C4-C5-C6-C1	- 0.1(1)	
O3-C9-C10-C11	55.4(1)	

Table 3 Crystallographic data

•	D 14	1	1.	•
Ζ.	Results	and	disc	ussion

Fig. 1 shows the ORTEP diagram for 1, while the ¹³C CPMAS spectra (regular and dipolar dephased) are presented in Fig. 2. Bond lengths and angles are collected in Table 1, while torsion angles for ring skeletal angles are in Table 2. Crystallographic data are in Table 3 and atomic parameters in Table 4. Anisotropic temperature factors and structure factors are available as supplementary data.

2.1. X-ray crystal structure

With regard to experimental determinations of Xray crystal structures of simpler "model" type compounds for 1, rather little is known. One could, however, regard cis-cyclodecene as such a model and this system has been extensively studied with regard to calculations of preferred geometries [7–9]. It has been noted [7] that there are likely to be many possible conformations of comparable energy, and four conformations have been calculated to have energies within 3 kcal mol⁻¹. None of these, however, has any

Formula	$C_{11}H_{14}O_3$
fw	194.23
crystal system	monoclinic
space group	P21/c
a (Å)	7.2705(20)
b (Å)	10.825(3)
<i>c</i> (Å)	12.790(5)
$V(\text{\AA}^3)$	1004.7(6)
Z (molecules/unit cell)	4
$D_{\rm C} (\rm g/cm^3)$	1.284
crystal dimensions (mm)	0.20 x 0.20 x 0.20
Radiation, λ (Å)	Μο Κα, 0.70930
Octants measured	h (-8 to 8), k (0 to 12), l (0 to 15)
Max 2 Θ (°)	49.9
Temperature (°C)	- 100
No. of unique reflections	1768
No. of reflections measured	1912
No. of reflections with $I_{\text{net}} > 2.5\sigma(I_{\text{net}})$	1456
largest shift/error in final least-squares cycle	0.068
R f	0.035
R _w	0.041
GoF	2.11
maximum and minimum residual $e\rho$ in final difference	0.160 and -0.160
Fourier map (e Å ⁻³)	



Fig. 2. (a) ¹³C CPMAS NMR spectrum of 1. (b) Dipolar dephased ¹³C CPMAS NMR spectrum of 1. (c) ¹³C CPMAS NMR spectrum of 1-7d₂. (d) Dipolar dephased ¹³C CPMAS NMR spectrum of 1-7d₂.





Fig. 2. continued.

	x	у	z	Biso	
01	0.49713(13)	0.47425(9)	0.16146(8)	2.43(4)	
02	0.62606(15)	0.22780(9)	0.15770(8)	2.75(4)	
03	0.28505(15)	0.24504(10)	0.03376(9)	3.11(5)	
CI	0.64737(19)	0.43691(13)	0.22531(11)	2.21(6)	
C2	0.73558(22)	0.52202(14)	0.29186(12)	2.68(6)	
C3	0.88958(23)	0.48726(15)	0.35486(12)	2.97(6)	
C4	0.95389(21)	0.36711(15)	0.35159(12)	2.92(6)	
C5	0.86739(21)	0.28209(14)	0.28407(12)	2.67(6)	
C6	0.71406(20)	0.31613(13)	0.22056(11)	2.30(5)	
C7	0.62387(23)	0.25064(15)	0.04647(13)	3.06(7)	
C8	0.4505(3)	0.19653(16)	- 0.00485(13)	3.46(7)	
C9	0.24703(22)	0.37069(15)	0.00553(13)	3.05(6)	
C10	0.18485(21)	0.43939(14)	0.09960(12)	2.87(6)	
C11	0.32163(20)	0.43087(14)	0.19317(12)	2.51(6)	

Table 4 Atomic parameters x, y, z and Biso

Biso is the mean of the principal axes of the thermal ellipsoid.

ESDs refer to the last digit printed.

strong resemblance to the observed conformation of the 10-membered ring in crystalline 1.

A difficulty in using a hydrocarbon model for the conformation of 1, lies in the strong preference of the O-C-C-O unit for a gauche-type geometry regardless of ring size [3,10,11]. Such a preference immediately rules out the existence of a chair-chair form, which is calculated to be one of the preferred cis-cyclodecene conformations [8,9]. Indeed, at -100° C, the 10-membered ring of 1 exhibits an O2-C7-C8-O3 angle of 58.6(1)°, in accord with precedent.

It is also of interest to compare the disposition of C7

relative to the plane of the aromatic ring of 1 with that observed for the two such sites in benzo-9-crown-3 [3]. In 1, C7 is situated ~64° out of the aromatic plane, whereas in benzo-9-crown-3, one such carbon is nearly coplanar ($\Theta = 170.3^{\circ}$), while the other is approaching a perpendicular disposition ($\Theta = 79.9^{\circ}$). Due to the paucity of information in the literature regarding the conformations of oxygenated 10-membered rings, we have carried out a series of theoretical calculations of the preferred geometries of 1. These calculations involve a comparison of results from the classical mechanical and quantum mechanical approaches.

Table 5

Total energies E (kcal mol⁻¹) of conformations **A**–**D** and comparison of selected torsion angles (°) with those determined via X-ray crystallography

Torsional network	X-ray structure	Α	В	С	D	
C2-C1-O1-C11	- 106.4	- 106.0	36.9	30.2	37.4	
C1-O1-C11-C10	- 160.4	- 155.2	116.2	161.4	69.1	
01-C11-C10-C9	55.5	51.9	- 67.1	- 46.7	68.1	
C11-C10-C9-O3	55.4	53.6	58.3	71.9	- 52.9	
C10-C9-O3-C8	- 136.3	- 151.5	75.8	- 157.8	- 84.4	
C9-O3-C8-C7	69.9	77.7	- 117.2	86.7	166.1	
O3-C8-C7-O2	58.6	47.3	- 51.6	59.4	- 59.9	
C8-C7-O2-C6	- 149.8	- 147.2	72.6	- 128.8	- 55.2	
C7-O2-C6-C5	- 118.2	- 105.9	- 160.4	- 108.5	- 81.3	
calculated total energy	E (kcal mol ⁻¹)	10.28	9.95	9.35	6.93	

2.2. Classical mechanical (MM2) results

This molecular mechanics (MM) or force field procedure [12-14] treats the molecule as an array of atoms governed by a set of classical mechanical potential functions. In the present case, the calculated potential energy surfaces spanned a range of conformations of 1 which were controlled by the one or two bond drive technique [14]. Four minimized structures (A-D) were obtained with selected dihedral angles presented in Table 5.

Notably, the most stable structure (**D**) has a remarkably different conformation than that determined by X-ray crystallography. The closest agreement between minimized structures and the crystal structure is for **A**, where the average difference between calculated and observed torsion angles is only 6.6° .

It is useful to examine in detail the contributions to the total conformational energies of forms **A** to **D** and these are presented in Table 6. For each of **B**, **C** and **D** there is a stabilizing dihedral term ranging from 2.4 to 4.8 kcal mol⁻¹ arising from the near coplanarity of one of the lone pairs on O1 with the p orbital on C1. Such an interaction is lacking in structure **A**. Literature precedent for such a stabilization exists in the case of MM2 calculations on 1,4-dioxacyclohepta-2-ene) [15] where minimized structures with good oxygen lone pair–p orbital overlap are stabilized mainly via the dihedral angle term. Principal factors stabilizing conformation **A** are the bond angle and van der Waals terms.

2.3. Quantum mechanical (AM1) results

This approach [16] is a modification of the earlier

Table 6

MM2 calculated contributions to the total energy of conformations A-D (kcal mol⁻¹)

Term	A	B	С	D	-
bond stretch	0.53	0.67	0.56	0.58	-
bond angle	3.44	6.53	4.37	4.10	
improper torsion	0.06	0.01	0.02	0.02	
dihedral	0.06	- 4.71	- 2.35	- 3.93	
electrostatic	0.33	0.44	0.49	0.46	
van der Waals	5.86	7.01	6.26	5.70	
hydrogen bond	0.00	0.00	0.00	0.00	
total energy	10.28	9.95	9.35	6.93	

[17] MNDO method and is based on the core repulsion functions (CRF) which have been expanded by the addition of Gaussian terms. In the present case, the structure for 1 was optimized by considering sets of three to four torsional networks at a time and minimizing the force constants.

Initially, a local minimum energy structure was obtained in which C7 and C11 were on opposite sides of the plane of the aromatic ring, i.e. an "updown" structure. This is in accord with the disposition of these atoms in the X-ray crystal structure. Further refinement, in which the only constraint was a gauche O2-C7-C8-C9 angle (in accord with the present X-ray data) leads to a "refined" minimum energy conformation **E**. Comparison of the key torsion angles in **E** with the X-ray data is shown below.

Network	X-ray structure	structure E	difference
C7-O2-C6-C5	- 118.2	- 119.0	0.8
C8-C7-O2-C6	- 148.9	- 151.4	2.5
02-C7-C8-O3	58.6	66.1	7.5
C9-O3-C8-C7	69.9	65.6	4.3
C10-C9-O3-C8	- 136.3	- 131.2	5.1
C11-C10-C9-O3	55.4	49.9	5.5

Clearly there is quite good agreement, with the difference between calculated and observed angles ranging from 0.8 to 7.5° .

2.4. Solution NMR studies

The ¹H and ¹³C solution NMR spectra of 1 have been recorded as a function of temperature between 300 and 200 K. No coalescence phenomena were observed over this range indicating that all 10-membered ring conformational interconversions are fast on the NMR time scale at these temperatures. Iterative computer analysis of the aliphatic region of the 400 MHz⁻¹H spectrum at 300 K was carried out, treating the C7, C8 protons as an AA'BB' system and the C9, C10, C11 protons as an AA'MM'XX' case. Results are summarized in Table 7. For the C7 and C8 protons, the vicinal coupling constants of 6.39 and 2.29 Hz are similar to those found in related molecules [3.5] and are consistent with a situation in which there is rapid interconversion between rotamers in which the oxygen atoms are in a gauche relationship. The four vicinal couplings in the C9-C10-C11 unit

Proton	$\partial_{\rm H}$ (ppm from TMS ± 0.001)	^{2}J (Hz ± 0.01)	³ J (Hz)	
7,7'	4.181	- 12.37	6.39, 2.29	
8,8′	3.799	- 10.23	6.39, 2.29	
9,9′	3.897	- 12.52	5.41, 5.20	
10,10'	1.885	- 14.25	5.41, 5.20 5.07, 4.49	
11,11'	4.199	- 14.35	5.07, 4.49	

Table 7 ¹H NMR data for aliphatic protons of **1**

are conformationally averaged to values of 5.41, 5.20, 5.07 and 4.49 Hz.

Signal assignments in the ¹H spectrum were facilitated by results of a NOESY experiment, in which correlations were noted between the more shielded aromatic proton resonances for H2 and H5 and the most deshielded set of aliphatic resonances appearing at \sim 4.2 ppm. Hence the protons at C7 and C11 must give rise to the partially overlapping multiples (4H) near 4.2 ppm. Distinction between H7 and H11 resonances can be made on the basis of COSY results, since H11 correlates to the most shielded aliphatic protons on the C10 site. This assignment was verified by synthesis of $1-7d_2$. With the ¹H assignments in hand, the ${}^{1}J$ HETCOR experiment gives shifts for the bonded carbons directly. The ¹³C NMR solution data are presented in Table 8. A long range HETCOR experiment permitted distinction between the quaternary aromatic carbons.

2.5. Solid phase ¹³C chemical shifts

The ¹³C CPMAS spectra are illustrated in Fig. 2. Assignments shown in Table 8 are made by analogy

Table 8 ^{13}C NMR chemical shifts for 1 (∂_C from TMS \pm 0.1)

	Solution (0.1M in CDCl ₃)	Solid phase
CI	151.3	152.2
C2	122.4	125.8
C3	123.9	125.8
C4	124.2	128.0
C5	121.7	123.4
C6	151.7	153.7
C7	73.7	71.9
C8	69.5	67.5
C9	66.6	61.2
C10	29.9	29.4
C11	71.1	70.7

with the solution data and by examination of spectra for the 7-d₂ derivative. For the aliphatic carbons, the range of shifts in the solid phase (10.1 ppm) is considerably larger than in solution (7.1 ppm) presumably due to the lack of conformational averaging in the solid. In particular C9 shows the largest shift difference (5.4 ppm) between solid phase (61.2 ppm) and solution (66.6 ppm) values. The upfield solid phase shift may be due in part to the torsion angle of $55.5(1)^{\circ}$ between C9 and O1 in the C9-C10-C11-O1 network. Such gauche-steric interactions are well known to result in upfield shifts for the terminal carbon atom [18]. In the dipolar dephased spectra, the protonated carbon resonances disappear completely, indicative of a lack of any large amplitude conformational motion in the 10-membered ring of solid 1.

3. Experimental

3.1. Spectra

All solution NMR spectra were recorded using a Bruker AM-400 spectrometer equipped with a 5 mm inverse probe and an Aspect X32 computer. An Aspect 3000 process controller was employed and all standard microprograms used are in the Bruker Software Library.

For the NOESY experiment, the mixing time used was selected to be consistent with the $1/T_1$ criterion [19], and in the present case it was set to 0.3 s. For the ¹H¹³C HETCOR experiment, the free induction decays were acquired over 1024 data points for each of the 512 values of the evolution time, with a digital resolution of ~8 Hz point⁻¹ in F2 and 4 Hz point⁻¹ in F2. The raw data were zero filled in F1 prior to transformation using the qsine window function for both F1 and F2. The proton relaxation delays were set to 1 s. Delays were chosen to emphasize J values of 135-140 Hz. For the long range HETCOR experiment, delays were chosen to emphasize a coupling of 7.5 Hz.

The ¹H¹H COSY experiments were run using Ntype phase cycling with a 450 mixing pulse. The free induction decays were acquired over 1024 data points for each of the 256 values of the evolution time, with a digital resolution of 5 Hz point⁻¹. The raw data were zero filled in F1 prior to transformation using the qsine window function for both F1 and F2. The data were symmetrized about the diagonal.

The solid phase ¹³C CPMAS NMR spectra were recorded at 50.3 MHz using a Bruker ASX-200 solid state NMR spectrometer equipped with a Bruker 7 mm triple resonance MAS probe. The magic angle was set accurately [20] using the ⁷⁹Br resonance of KBr and maximizing the number of rotational echoes in the FID. Magic angle spinning rates were ~4 kHz. ¹H 90° pulse widths were $3.5-3.8 \ \mu$ s with contact times of 1 s. Chemical shifts were referenced to the ¹³C resonance of tetrakistrimethylsilyl silane, $Si(Si(CH_3)_3)_4$, which has a chemical shift of 3.7 ppm relative to TMS.

3.2. X-ray crystallographic measurements and structure solution

A summary of the crystallographic data is given in Table 4. Diffraction intensifies were collected on a Rigaku diffractometer using Mo K α , radiation at -100°C. The $\Theta/2\Theta$ scan technique was used to a maximum 2Θ value of 49.9°.

The space group was determined by systematic absences. Unit cell parameters were obtained from least-squares refinement using the setting angles of 24 reflections in the range $40 < 2\Theta < 50$. The data were corrected for Lorentz and polarization effects. No absorption correction was made. The structure was solved by direct methods plus Fourier maps and was refined by full-matrix least-squares analysis with weights based on counting statistics. Non-H atoms were refined anisotropically and H atoms



Fig. 3. Synthetic scheme for preparation of 1.

isotropically. No crystal decay was noted during data collection. All calculations were performed using the NRC VAX Crystal Structure programs [21]. Structure factor tables and anisotropic temperature factors are available as supplementary data.

3.3. Materials

The synthetic scheme for preparation of benzo-10crown-3 is shown in Fig. 3. Procedures for individual steps are described below.

3-chloro-1-propanol (Aldrich), **A**, 4.7 g (0.05 moles) was dissolved in 50 mL of dichloromethane and mixed with ethyldiazoacetate (Aldrich), 5.7 g (0.05 moles) in a 250 mL round bottom flask under argon. The reaction flask was cooled in an ice bath, and 5 drops of the catalyst, BF₃·Et₂O were added via a septum dropwise with stirring. A highly exothermic reaction occurred with rapid nitrogen release. After stirring for 3 h, the mixture was allowed to come to ambient temperature. The solvent was then removed by rotoevaporation and the product purified by distillation under reduced pressure to give **B**, bp 88–92°C/4 mm Hg in 75% yield. ¹³C NMR in CDCl₃ $\partial = 170.1$, 68.3, 68.0, 60.7, 41.8, 32.5 and 14.1 ppm.

Conversion of **B** to 6-chloro-3-oxahexan-1-ol was accomplished as follows: a suspension of LiAlH₄, 1.47 g (0.039 moles), in 250 mL anhydrous THF was prepared under argon and cooled in an ice-salt bath. To this was added **B**, 6.34 g (0.035 moles) dropwise with stirring. The reaction mixture was stirred for 12 h and allowed to reach ambient temperature. Following addition of 2 mL of water and 10 mL of 20% H₂SO₄, the precipitate was removed by filtration. The solvent was removed by rotoevaporation and the crude product was taken up into CH₂Cl₂ and extracted into water. The water was subsequently removed in vacuo at 50°C to provide 6-chloro-3-oxa-hexan-1-ol in 95% yield. ¹³C NMR (CDCl₃); $\partial = 72.0, 67.4, 61.4,$ 41.6 and 32.3 ppm.

C was produced via reaction of the 6-chloro-3-oxahexan-1-ol with a 10% molar excess of thionyl chloride in the absence of solvent at 0°C. After the addition of the thionyl chloride, the reaction mixture was allowed to reach room temperature and it was then stirred overnight at 50°C. The crude product was subsequently taken up into CH_2Cl_2 and washed with water. After drying over anhydrous Na_2SO_4 , the solvent was removed by rotoevaporation to yield C in 80% yield.

¹³C NMR (CDCl₃); ∂ = 72.0, 67.4, 43.1, 42.0 and 32.3 ppm.

For the preparation of 1, catechol (Aldrich), 1.83 g (0.017 moles) was placed in a 1 L 3-necked round bottom flask along with 400 mL distilled water and $LiOH \cdot H_2O$, 1.43 g (0.034 moles). This mixture was then stirred at 40°C for 1 h. To this mixture was added C, 2.67 g (0.017 moles) dropwise with stirring and the mixture was refluxed for 6 days. After cooling to room temperature, the mixture was acidified to pH 1-2 by addition of 6M HCl and extracted with CH_2Cl_2 (3 × 100 mL). The organic extracts were washed carefully with 2% aqueous KOH and dried over Na₂SO₄. Following solvent removal via rotoevaporation, the crude oily product was purified by column chromatography on silica gel using 3:1 hexane : acetone as eluent. Recrystallization from cold pentane gave 1, mp 30-31°C in 12.2% yield.

Preparation of $1-7d_2$ was carried out in an analogous manner using LiA1D₄ for the reduction of **B**.

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