

Solid-state Structures for 2-Methoxy-1,3-xylyl-18-crown-5 and 2-Methoxy-1,3-xylyl-21-crown-6: A Search for C–H···O Interactions

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Abstract

Solid-state structures have been determined for 2-methoxy-1,3-xylyl-18-crown-5 (**4**) (monoclinic, $P2_1/n$, $a = 11.361(3) \text{ \AA}$, $b = 8.352(3) \text{ \AA}$, $c = 18.627(4) \text{ \AA}$, $\beta = 91.05(2)^\circ$, $Z = 4$) and 2-methoxy-1,3-xylyl-21-crown-6 (**5**) (monoclinic, Pc , $a = 9.996(2) \text{ \AA}$, $b = 11.321(2) \text{ \AA}$, $c = 8.642(2) \text{ \AA}$, $\beta = 100.095(4)^\circ$, $Z = 2$). In both molecules, the aromatic units are tilted with respect to the polyether ring and the methoxyl methyl hydrogens are oriented toward ether oxygen atoms of the rings. The interatomic distances, particularly the H···O distance and angles provide important information regarding the strength of the C–H···O interactions.

Introduction

Incorporation of substituents onto the aromatic rings of benzo- and dibenzocrown ethers has been utilized to increase their lipophilicity and influence their cation binding behavior [1–3]. Although 1,2-benzo units are the most common in benzo- and dibenzocrown ethers, macrocyclic polyethers with 1,3-benzo units have received some attention [4–7]. Of particular interest has been investigation of 1,3-benzo-type crown ethers with intraannular substituents attached at the 2-position. Solid-state structures have been reported for 2-X-1,3-xylylcrown ethers **1–3** in which the X is a carboxylic acid [4], phenolic hydroxyl [5] and sulfinic acid [6] group, respectively (Figure 1). In each case, there is evidence for O–H···O hydrogen bonding of the intraannular acidic group with one of the polyether ring oxygens.

In our continuing investigation of crown ether compounds and their cation binding abilities, we have now prepared 2-methoxy-1,3-xylyl-18-crown-5 (**4**) and 2-methoxy-1,3-xylyl-21-crown-6 (**5**) and determined their solid-state structures to determine if interactions of the intraannular group with a polyether oxygen can be detected. Such interactions would involve much less common C–H···O hydrogen bonding [8–12].

Experimental

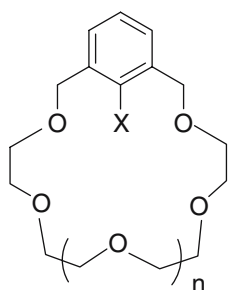
Synthesis and crystal growth

Crown ethers **4** and **5** were prepared by the reported methods [5]. Crystals of **4** and **5** suitable for structure determination were grown in dichloromethane-hexane.

Solid-state structure determination

Crystal data and experimental details for the solid-state structure refinement of **4** and **5** are presented in Table 1. Single crystal intensities for **4** were collected with a Siemens R3 m/V automated diffractometer with Mo radiation, while similar data for **5** were obtained with a Bruker-Nonius FR-591 rotating anode diffractometer using Cu radiation. The two structures were solved using direct methods. Positions for all hydrogen atoms in the two structures were calculated except for those bonded to the methoxy carbon. It was possible to determine positions for H(1A) and H(1B) bonded to C(1) in **4** and all three hydrogens bonded to C(1) in **5** in the difference maps. After locating the two methoxyl hydrogens in **4**, the position of H(1C) was calculated using HFIX3. All non-hydrogen atoms for the two structures were refined anisotropically with a full-matrix, least-squares procedure based on F^2 using SHELXTL [13]. Hydrogen atoms were refined using a riding model.

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	\bar{n}	\bar{X}
1	1	CO ₂ H
2	2	OH
3	0	SO ₂ H
4	1	OCH ₃
5	2	OCH ₃

Figure 1. Structures of 2-X-1,3-xyllyl crown ether compounds.

Results and discussion

When viewed from above, the structures for compounds **4** (Figure 2) and **5** (Figure 3) appear to be similar. Figures 4 and 5 more clearly illustrate the orientation of the methoxyl methyl groups towards the polyether rings. The dihedral angles between the least-squares planes of the aromatic portion of the molecule and the least-squares plane of the ring oxygen atoms are 54° in **4** and

22° in **5**. As a result of this difference, H(1A) and H(1B) interact with polyether ring oxygens in **4**, while H(1C) interacts with a crown ether ring oxygen of a symmetry-related molecule. With the larger crown ether ring in **5**, all three methoxyl methyl hydrogen atoms interact with polyether ring oxygens.

The most significant data regarding the strength of the C–H···O interactions is the H···O interatomic distance. Taylor and Kennard [9] suggest that the limiting H···O distance for a C–H···O bond is 2.40 Å, which is approximately 0.3 Å less than the sum of the van der Waals radii of H and O atoms. Some liberty should be allowed in this limiting distance due to the difficulty in locating accurate hydrogen atom positions using X-ray data. The data presented in Table 2 suggest that only three of the interactions listed should be considered to be hydrogen bonds and they are all found in **4**. All of the interactions in **5** are weak. All of the intramolecular interactions listed in the Table 2 are bifurcated including the two strongest hydrogen bonds, both of which involve H(1B) in **4**. The other apparent hydrogen bond is C(1)–H(1A)···O(18). The remainder of the possible interactions do not qualify as hydrogen bonds. They are likely weak interactions, particularly for those in which the C–H···O angle is 140° or greater.

Earlier we reported the solid-state structures of 2-methoxy-1,3-benzo-16-crown-5 (**6**) and 2-methoxy-1,

Table 1. Crystal data and structure refinement for compounds **4** and **5**

Compound	4	5
Empirical formula	C ₁₇ H ₂₆ O ₆	C ₁₉ H ₃₀ O ₇
Formula weight	326.38	370.43
Temperature, (K)	293(2)	293(2)
Wavelength, (Å)	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	Pc
<i>a</i> (Å)	11.361(3)	10.038(2)
<i>b</i> (Å)	8.352(2)	11.384(2)
<i>c</i> (Å)	18.627(4)	8.693(2)
β (°)	91.05(2)	100.17(3)
Volume (Å ³)	1767.2(7)	977.9(3)
<i>Z</i>	4	2
Density (calculated) (mg/m ³)	1.227	1.258
Absorption coefficient (mm ⁻¹)	0.092	0.789
F(000)	704	400
Crystal size (mm)	0.4×0.3×0.2	0.24×0.15×0.15
θ range (°)	2.08–25.05	3.88–67.46
Limiting indices	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 9, –22 ≤ <i>l</i> ≤ 22	–11 ≤ <i>h</i> ≤ 11, –13 ≤ <i>k</i> ≤ 8, –10 ≤ <i>l</i> ≤ 10
Reflections collected	3284	7577
Independent reflections	3116 (<i>R</i> _{int} = 0.0286)	3201 (<i>R</i> _{int} = 0.0233)
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	3116/0/210	3201/2/247
Goodness of fit on F ²	0.995	1.029
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0577, <i>wR</i> 2 = 0.1075	<i>R</i> 1 = 0.0332, <i>wR</i> 2 = 0.0858
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.1566, <i>wR</i> 2 = 0.1404	<i>R</i> 1 = 0.0346, <i>wR</i> 2 = 0.0876
Extinction coefficient	0.0081(11)	0
Largest diff. map peak and hole (e Å ⁻³)	0.251, –0.147	0.122, –0.138

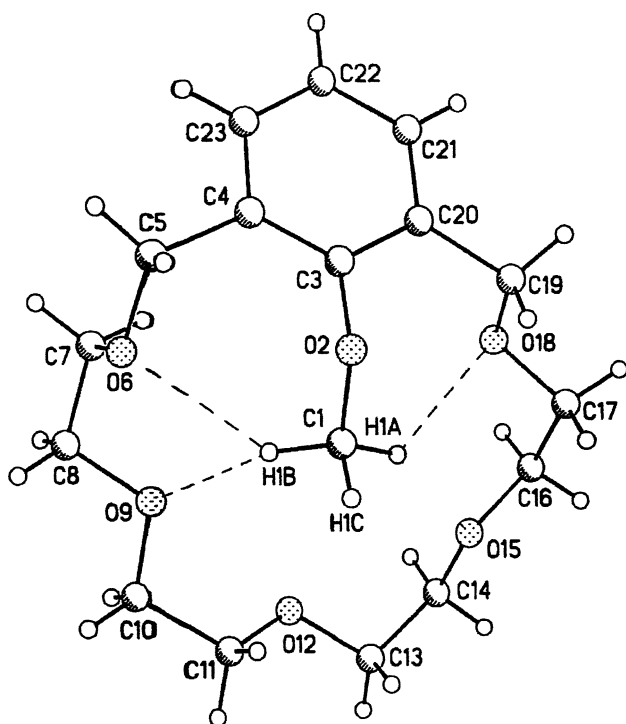


Figure 2. Top view of solid-state structure for 2-methoxy-1,3-xylyl-18-crown-5 (4).

3-benzo-19-crown-6 (7) [14]. In both 6 and 7, the methoxy methyl groups are oriented toward the polyether rings (Figure 6). However, none of the O \cdots H distances were short enough to qualify as a C–H \cdots O hydrogen bond.

In 6 and 7, the carbon atoms of the methoxyl groups were found to deviate from the planes of the aromatic units by 1.131 and 1.099 Å, respectively. In the larger-

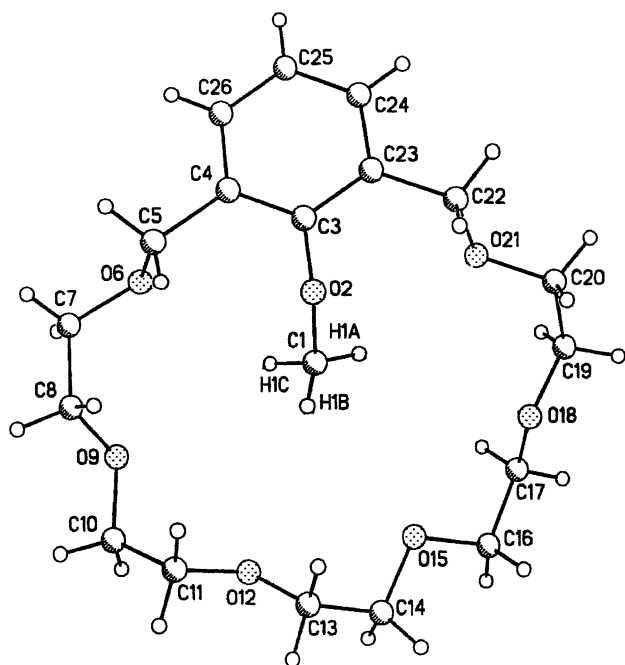


Figure 3. Top view of solid-state structure of 2-methoxy-1,3-xylyl-21-crown-6 (5).

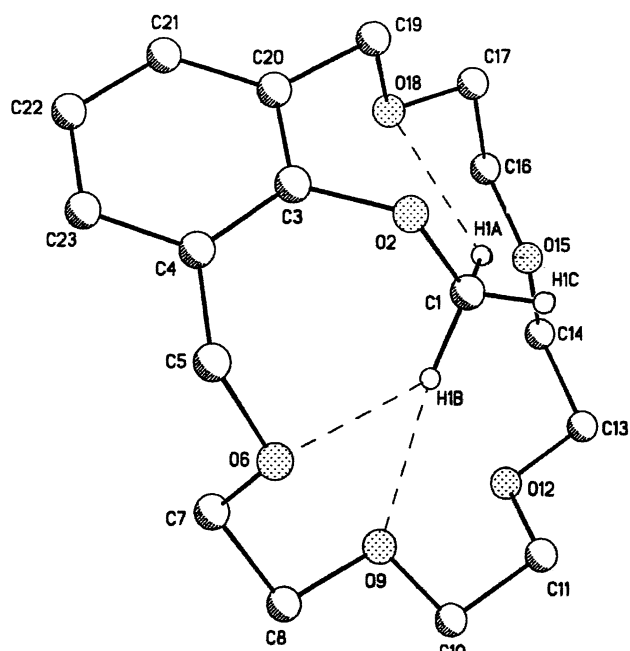


Figure 4. Solid-state structure of 2-methoxy-1,3-xylyl-18-crown-5 (4).

ring analogues 4 and 5, these deviations are 1.024 and 1.117 Å, respectively. Thus the carbon of the methoxyl group in 4 is much closer to the plane of the aromatic ring than those in compounds 5–7.

Conclusions

In conclusion, we have determined the solid-state structures of 2-substituted-1,3-xylyl crown ethers 4 and 5, which have intraannular methoxyl groups. For both compounds, the aromatic units are tilted substantially with respect to the plane of the polyether oxygens and the methoxyl groups are oriented toward the crown

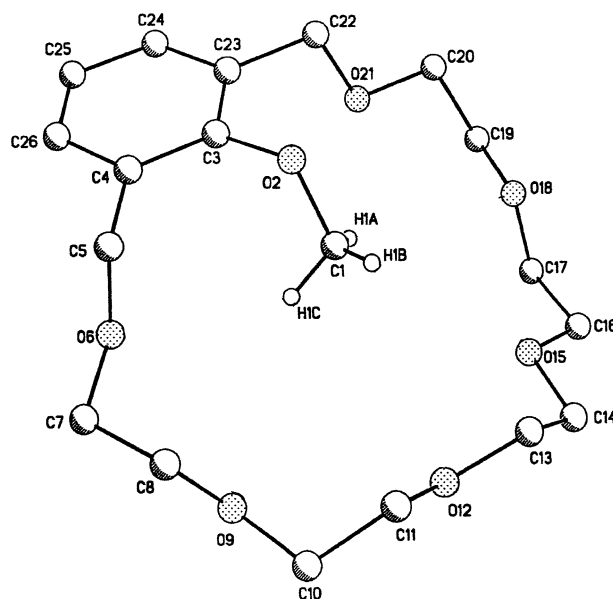


Figure 5. Solid-state structure of 2-methoxy-1,3-xylyl-21-crown-6 (5).

Table 2. Possible C–H···O Hydrogen Bonding Interactions in **4** and **5**

C	H	O	C–H, Å	H···O, Å	C–O, Å	C–H···O, °
Molecule 4						
C(1)	H(1A)	O(15)	1.07	2.59	3.599	156
C(1)	H(1A)	O(18)	1.07	2.45	3.257	131
C(1)	H(1B)	O(6)	1.08	2.37	3.157	128
C(1)	H(1B)	O(9)	1.08	2.28	3.303	156
C(1)	H(1C)	O(15 ^a)	0.96	2.77	3.699	164
Molecule 5						
C(1)	H(1A)	O(18)	0.99	3.18	4.043	146
C(1)	H(1A)	O(21)	0.99	2.65	3.489	143
C(1)	H(1B)	O(12)	0.92	3.27	3.531	99
C(1)	H(1B)	O(15)	0.92	3.15	3.714	122
C(1)	H(1C)	O(6)	0.98	2.61	3.361	134
C(1)	H(1C)	O(9)	0.98	3.18	3.963	138
C(1)	H(1C)	O(12)	0.98	3.23	3.532	100

^aO15 in a symmetry related molecule

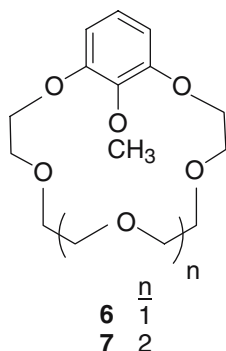


Figure 6. Structures for 2-methoxy-1,3-benzocrown ethers **6** and **7**.

ether rings. Weak intramolecular interactions of the methoxyl methyl hydrogens with oxygens of the polycyclic ether rings are evident. Of the possible interactions in **4**, three H···O bond distances are short enough to qualify as C–H···O hydrogen bonding. For **5**, none of the interactions qualify.

Supplementary material

Crystallographic data for compounds **4** and **5** have been deposited with CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and are identified by deposition numbers of CCDC 612717 and 612716, respectively. Copies of this information can be obtained free of charge on request by e-mail at deposit@ccdc.cam.ac.uk or at <http://www.ccdc.cam.ac.uk>.

Acknowledgement

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