Intramolecular sp^2-CH···O Interaction in the Single Crystal of Macrocyclic Polyethers with an Isobutenyl Group

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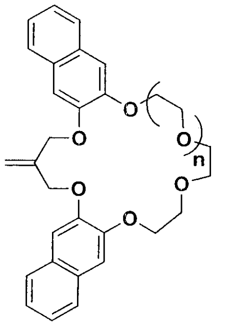
Effects of the ring size on the conformation in the macrocyclic polyethers with an isobutenyl group have been studied by X-ray crystallography: the intramolecular CH···O interaction has been observed in the compound having 22 membered macrocyclic ring.

In the field of molecular recognition for macrocyclic ring in host molecules, not only ring size but also conformation of the molecule play important roles. The effect of ring size on molecular recognition is well known in capture of metal ions in crown ethers and of organic molecules in cyclodextrins.[1,2] Molecular recognition properties in calixarenes are greatly affected by conformation of benzene rings.[3] We recently reported that crownophanes having two phenolic hydroxyl groups can be synthesized from the corresponding macrocyclic polyethers having an isobutenyl group via tandem Claisen rearrangement.[4] It has been found that the rate of the formation of crownophanes via tandem Claisen rearrangement depends on the ring size of macrocyclic ethers by using NMR method.[5] Herein, we describe the relation between ring size and conformation of the macrocyclic polyethers having an isobutenyl group with different macrocyclic rings (**1** and **2**) in solid states by using X-ray crystallography.



1 : n = 1
2 : n = 2

Macrocyclic polyethers (**1** and **2**) were synthesized by using 3-chloro-2-(chloromethyl)-1-propene, 2,3-dihydroxynaphthalene, and oligoethyleneglycol di-*para*-tosylate in the similar manner as previously reported.[4] The products were identified by IR, ^{1}H NMR, and precise mass spectrometry.

Single crystals of **2** were obtained from acetonitrile solution at 295 K. The X-ray crystal structure of these crystals was determined and is shown in Figure 1.[6] The packing of the molecules in the crystal of **2** reveals normal intermolecular contacts equal to the sum of the van der Waals radii. Space group *Pnma* has 8-fold general positions. However, there are four molecules in the unit cell, so the molecule is required to have twofold symmetry in the crystal of **2**. There exists mirror plane along the double bond in the isobutenyl group and the molecule has *Cs* symmetry. Both of the methylene hydrogens in the isobutenyl group, which attach to the oxygen atom, are on the same side, opposite to the exo-methylene group. The exo-methylene group of **2** exists in the cavity, facing the oxyethylene moiety in the crystal. The torsion angle O(4)–C(15)–C(16)–C(17) is 2(1)°, which shows that the isobutenyl group and oxygen atoms attached to it are almost planar. Since the torsion angle C(1)–O(4)–C(15)–C(16) is 151.0(6)°, the naphthalene ring deviates from the plane of isobutenyl group by ca. 30°. The non-bonding distances of C(17)–O(4) and H(C(17))–O(4) are 2.73 (1) Å and 2.38 Å, respectively. The atoms O(4), C(15), C(16), C(17), and H(C(17)) exist in almost planar plane and make a pseudo five membered ring. The very short distance indicates that there exists CH···O hydrogen bonding between H(C(17)) and O(4). The hydrogen atoms of the exo-methylene group are spatially directed to the oxygen atoms of oxyethylene groups. The non-bonding distance C(17)–O(1) is 3.95 (1) Å. The range of non-bonding distance between carbon and oxygen atoms is 3.0–4.0 Å in the case of CH···O hydrogen bond.[7] The relatively short distance suggests that CH···O intramolecular interaction also exists between H(C(17)) and O(1). Although such CH···O intramolecular interaction of macrocyclic polyether has also been reported in uncomplexed 18-crown-6,[8] it is the first example that hydrogen atoms attached to sp^2 carbon interact with ether oxygen atoms intramolecularly to our knowledge.[9]

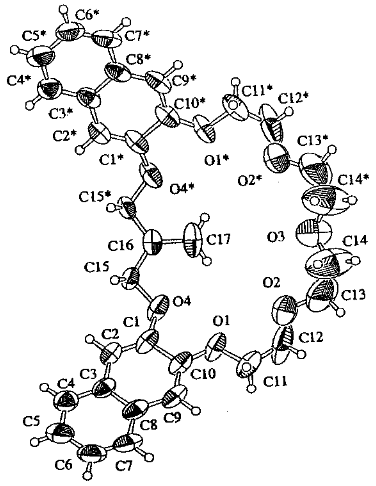


Figure 1. ORTEP drawing of **2** with the numbering scheme. Ellipsoids are represented with 40% probability.

Single crystals of **1** were also obtained from acetonitrile solution at 295 K, and the structure was characterized by X-ray

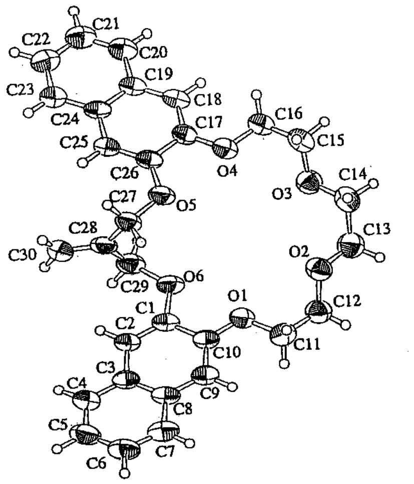


Figure 2. ORTEP drawing of **1** with the numbering scheme. Ellipsoids are represented with 40% probability.

crystallography (Figure 2).[10] In the case of **1**, contrary to the crystal structure of **2**, the terminal methylene group is directed to the outside of the hole. Though there is nothing inside the cavity, the macrocyclic ring seems to have a round shape, of which cavity size are almost the same as that of 18-crown-6. This cavity is too small for exo-methylene group to exist inside the macrocyclic ring. The torsion angles O(5)–C(27)–C(28)–C(30) and O(6)–C(29)–C(28)–C(30) are –140.1(4)° and –133.5(4)°, respectively, which shows that the isobutenyl group and oxygen atoms attached to it are not planar but twisted. This molecule has approximately C_2 symmetry, since the hydrogens of both methylene carbons, attached to oxygen atoms, of isobutenyl group in **1** are on the opposite sides each other. There is no CH···O interaction concerning the exo-methylene group in **1**. Thus, the conformation of **1** is quite different from that of **2**. Only one oxy-ethylene moiety causes great conformational change in the macrocyclic structure.

From these results, it is concluded that the exo-methylene group exists in the cavity, facing the oxyethylene moiety in solid states of **2**. The weak intramolecular interaction as CH···O between exo-methylene hydrogen atoms and ether oxygen atoms exists in these compounds. The cavity of **1** is too small for the isobutenyl group to be located inside. As reported, macrocyclic polyethers having isobutenyl ether units might rearrange to the corresponding crownophanes having plural phenolic hydroxy groups by thermal reaction. The information of their structure will lead to the sophisticated molecular design and synthesis to make high-performance functional host molecules or supramolecular systems. We are now in due course to make highly-designed molecular systems.

References and Notes

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5 Unreported result: for example, the half life of **1** is two times longer than that of **2** at 160 °C.

6 Crystal Data for **2**: $C_{32}H_{34}O_7$, *M*w = 530.62, orthorhombic, $a = 10.519(3)$, $b = 31.741(4)$, $c = 8.195(2)$ Å, $U = 2736.3(9)$ Å^3, $T = 295$ K, space group *Pnma* (no. 62), $Z = 4$, μ(Cu Kα) = 7.37 cm^{-1}, 2782 reflections measured, 2066 unique (R_{int} = 0.025) reflections of which 1127 were observable ($I > 2.00\sigma(I)$). Solution by direct method with SIR92. Full-matrix least-square refinement on *F* with all non-hydrogen atoms anisotropic and hydrogen atoms included but not refined. Final *R* and R_w values on observed data were 0.078 and 0.108, respectively.

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10 Crystal Data for **1**: $C_{30}H_{30}O_6 + 2CH_3CN$, *M*w = 568.67, monoclinic, $a = 9.097(1)$, $b = 16.423(1)$, $c = 41.899(4)$ Å, $\beta = 93.250(5)^\circ$, $U = 6249.2(9)$ Å^3, $T = 295$ K, space group $P2_1/c$ (no. 14), $Z = 8$, μ(Cu Kα) = 6.74 cm^{-1}, 10185 reflections measured, 8448 unique (R_{int} =0.023) reflections of which 5269 were observable ($I > 3.00\sigma(I)$). Solution by direct method with SIR92. Full-matrix least-square refinement on *F* with all non-hydrogen atoms anisotropic and hydrogen atoms included but not refined. Final *R* and R_w values on observed data were 0.061 and 0.071, respectively.