Structures Optimized by Molecular Mechanics for 15-Crown-5 and Its Water-Accommodating Species

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Synopsis. Optimization of the structure for 15-crown-5 and its water-accommodating species was carried out by a molecular mechanics calculation. Molecular deformation presumed from the Raman spectral feature of 15-crown-5 in aqueous solutions was confirmed by the results of the calculation.

The present author has found that Raman spectra of crown ethers and related polyethylene glycol dialkyl ethers show remarkable features for aqueous solutions, and concluded that molecular deformation takes place by accommodation of water molecules.[1] In the present study, molecular mechanics calculation of 15-crown-5-water systems was made in order to examine whether such a molecular deformation due to accommodation of water is expected from the calculation. For this purpose, information concerning the conformation of 15-crown-5 optimized by molecular mechanics is necessary. However, no molecular mechanics calculation of 15-crown-5 has been reported, in spite of the presence of many reports concerning molecular mechanics calculations and other types of calculations regarding other crowns.[2-9] Therefore, a calculation of 15-crown-5 was also carried out as a first step for calculations of 15-crown-5-water systems.

Calculations

Calculations were carried out with an EWS AV300 work station (Data General Corporation) of the Information Processing Center of Shizuoka University, using the MM2(87) program (VAX version) purchased from QCPE, and written by Allinger.[10] Optimization of 15-crown-5 was started from a conformation with D_{5h} symmetry, in which the molecular skeleton is in a plane (in the following, this structure is designated as "the D_{5h} structure"). For 15-crown-5-water systems, two structures (one in which a water molecule was placed at each side of the D_{5h} structure, and another in which two water molecules were placed instead of one water molecule) were used as starting conformations for optimization. First, these calculations were carried out without the use of a symmetry co-ordinate technique, and confirmed that optimized structures having C_2 symmetry are obtained. Then, the technique was used for optimization. In these systems, the hydrogen bond plays an important role. In the program used for the present study, the potential for a hydrogen bond is included. The HOH bending force constant, and the standard HOH bond angle are not contained in the MM2 program. Thus, values of 0.350 mdyn Å^{-1} and 109.5° were input, respectively, for the present calculations.

Results and Discussion

15-Crown-5. For the purpose of optimization we started from the D_{5h} structure (molecular parameters: r_{CH}=1.09 Å, r_{CC}=1.507 Å, r_{CO}=1.430 Å, ∠CCO=109.47°, ∠HCH=108.00°, ∠HCC=110.91°, ∠HCO=108.74°, ∠COC=110.94°). A slightly deformed conformation having C_2 symmetry was obtained; parameters for the skeleton are shown in Table 1; other parameters are as follows: r_{CH}=1.1141 Å, ∠HCH=109.277°—109.332°, ∠CCH=110.220°—110.257°, ∠HCO=108.268°—108.336°. The energy is 34.9165±0.0028 kcal mol^{-1} (compression=0.8685, bending=5.2115, stretch-bend=0.5737, van der Waals (1,4 energy=17.4822, other=—0.8946), torsional=9.8422, dipole=1.8328). The dipole moment of the conformer is 0.000 Debye.

15-Crown-5-2H_2O System. In the initial structure, one water molecules is located at each side of the D_{5h} structure (the coordinates of a water molecule in the coordinate system in Fig. 1, are O (0, 0, 1.47910), H (0.77667, −0.25236, 0.90196), H (−0.77667, 0.25236,

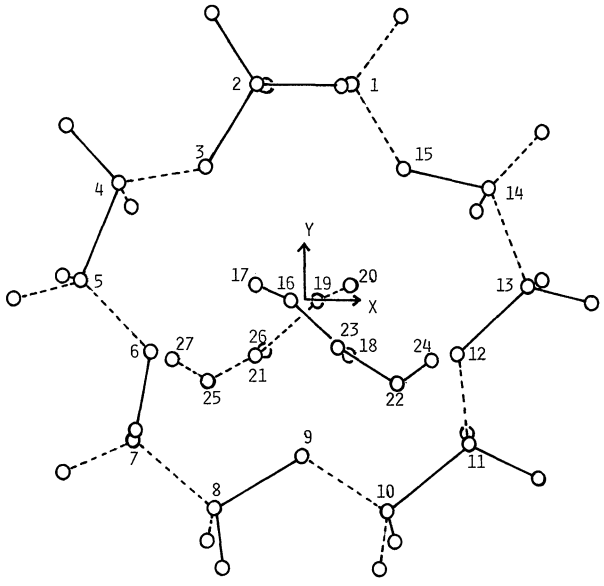

Fig. 1. Projection of the optimized 15-crown-5-4H_2O [II] on the xy plane (for two CH (or OH) bonds from the same carbon (or oxygen) atom, solid line bond is above dotted line bond; C_2 axis passes through the middle point of 1-2 bond and atom, 9, which coincides with y axis; other cartesian axes, x and z, are taken so that the x (or z) coordinates of symmetrically equivalent atoms are opposite in sign and equal in absolute value).

Table 1. Molecular Parameters of Various Structures Optimized by Molecular Mechanics[a)]

Parameters	15-Crown-5	15-Crown-5-2H_2O	15-Crown-5-4H_2O [I]	15-Crown-5-4H_2O [II]
12=CC	1.5235	1.5216	1.5192	1.5219
23=1,15=CO	1.4129	1.4107	1.4116	1.4106
34=14,15=CO	1.4129	1.4110	1.4110	1.4108
45=13,14=CC	1.5235	1.5206	1.5209	1.5209
56=12,13=CO	1.4130	1.4127	1.4114	1.4128
67=11,12=CO	1.4129	1.4121	1.4108	1.4122
78=10,11=CC	1.5235	1.5217	1.5196	1.5220
89=9,10=CO	1.4131	1.4108	1.4111	1.4097
123=21,15=CCO	110.472	107.136	106.771	107.167
234=14,15,1=COC	112.849	114.851	114.165	114.907
345=13,14,15=OCC	110.402	106.482	108.027	106.706
456=12,13,14=CCO	110.381	107.398	111.123	107.471
567=11,12,13=COC	112.871	114.110	114.471	114.168
678=10,11,12=OCC	110.423	108.205	107.643	108.255
789=9,10,11=CCO	110.462	107.723	107.493	107.372
89,10=COC	112.843	114.945	114.007	115.130
t(12)=t(CC)	0.171	−57.899	57.865	61.611
t(23)=t(1,15)=t(CO)	−179.748	176.851	−171.562	−172.674
t(34)=t(14,15)=t(OC)	−179.876	−177.291	−168.249	176.215
t(45)=t(13,14)=(CC)	−0.619	57.058	−47.304	−59.767
t(56)=t(12,13)=t(CO)	−179.885	−169.033	−85.884	166.562
t(67)=t(11,12)=t(OC)	−179.747	175.349	171.875	−177.848
t(78)=t(10,11)=t(CC)	0.114	−43.490	−55.539	42.652
t(89)=t(9,10)=t(CO)	180.000	−160.366	−175.012	164.721

a) ij···bond length of ij bond (in Å). ijk···bond angle of ijk angle (in degree). t(ij)···dihedral angle around bond, ij (in degree).

0.90196); another water molecule is located at the position produced by C_2 operation on the above-mentioned coordinates). The corresponding final coordinates are O (0.05355, −0.01547, 1.44051), H (0.59736, −0.45049, 0.80164), H (−0.68438, 0.34133, 0.97167). The optimized structure has a C_2 symmetry; the parameters for the skeleton are shown in Table 1. Other parameters of 15-crown-5 in the system are the same as the corresponding ones of 15-crown-5, as is the case for the 15-crown-5-4H_2O systems described below.

The energy is 2.4949±0.0033 kcal mol^{-1} (compression=0.6530, bending=6.8619, stretch-bend=0.3844, van der Waals (1,4 energy=12.3606, other=−16.8091), torsional=0.0136, dipole=−0.9696). The dipole moment is 0.224 Debye. The parameters of this system shown in Table 1 are somewhat different from the corresponding ones of 15-crown-5 in the table, showing that the presence of water molecules has considerable effect on the structure of 15-crown-5 in the system.

15-Crown-5-4H_2O System. Two cases, [I] and [II], were studied. In both cases, structures in which two water molecules are located at each side of the D_{5h} structure, were adopted as the starting structures for optimization by molecular mechanics.

[I] The initial co-ordinates of water molecules are shown in Table 2. The optimized structure has the parameters of a skeleton, as shown in Table 1. The energy is −8.9057±0.0038 kcal mol^{-1} (compression = 0.5820, bending=7.5673, stretch-bend=0.4141, van der Waals (1,4 energy=11.8469, other=−24.8358), torsional=1.6051, dipole=−6.0852). The dipole moment is 1.881 Debye. The final coordinates of the water molecules are shown in Table 2.

[II] The initial structure for [II] is that produced by a rotation operation of 90° around the C_2 axis on only water molecules in the initial structure of [I]. The parameters of the skeleton of the optimized structure are shown in Table 1, which are remarkably different from those of 15-crown-5. The energy is =−12.0556± 0.0038 kcal mol^{-1} (compression=0.6611, bending=6.9554, stretch-bend=0.3814, van der Walls (1,4 energy= 12.2781, other=−27.2393), torsional=−0.1124, dipole= −4.9798). The dipole moment is 0.703 Debye. The final coordinates of the water molecules are shown in Table 2, and the arrangement of water molecules are shown in Fig. 1. In this figure, hydrogen bonds are present between the respective pair of atoms shown in Table 3.

Other initial structures produced by a θ° rotation of the water molecules of the initial structure in [I] around the C_5 axis of "the D_{5h} structure" were optimized to the same structure and energy as those of [I] for θ=30°, 50°, 80°, and to the same structure and energy as those of [II] for θ=10°, 20°, 40°, 45° 60°, 70°, respectively.

Measurements of the Raman spectra of 15-crown-5 revealed that remarkable frequency shifts of skeletal vibrations, 825 cm^{-1}→848 cm^{-1}, 548 cm^{-1}→553 cm^{-1}, 319 cm^{-1}→338 cm^{-1}, occur by a state change: pure liquid to an aqueous solution.[1)] This suggests some considerable deformation of 15-cronw-5 by the accommodation of one or more water molecules. The results of the present calculation are in accordance with the experimental results, as follows. The optimized structures, [I] and [II], for 15-crown-5-4H_2O systems

Table 2. Coordinates of Water Molecules (in Å)[a)]

Structure		Initial coordinates			Final coordinates		
		x	*y*	*z*	*x*	*y*	*z*
[I]	O(16)	0.00000	−0.64674	1.47910	−0.04188	−0.06734	1.72102
	H(17)	0.81664	−0.64674	0.90196	0.12185	0.55701	1.03069
	H(18)	−0.81664	−0.64674	0.90196	−0.56897	−0.75752	1.35009
	O(22)	0.00000	0.64674	1.47910	−1.23277	1.56398	2.99388
	H(23)	0.81664	0.64674	0.90196	−0.58252	0.93057	3.24842
	H(24)	−0.81664	0.64674	0.90196	−1.37705	1.39051	2.07729
[II]	O(16)	−0.64674	0.00000	1.47910	−0.16281	−0.01217	1.39051
	H(17)	−0.64674	0.81664	0.90196	−0.66028	0.20052	0.61521
	H(18)	−0.64674	−0.81664	0.90196	0.38677	−0.75478	1.18694
	O(22)	0.64674	0.00000	1.47910	1.30194	−1.15402	2.93763
	H(23)	0.64674	0.81664	0.90196	0.49575	−0.66573	2.98452
	H(24)	0.64674	−0.81664	0.90196	1.80579	−0.79485	2.22538

a) Coordinates of the other two water molecules are produced by C_2 operation on the above coordinates.

Table 3. Important Hydrogen Bonds in 15-Crown-5.4H_2O [II]

Atom pair	Interatomic distance/Å
O(3) ···H(17)	1.8570
O(6) ···H(17)	2.0111
O(6) ···H(21)	1.9133
O(6) ···H(27)	1.8626
O(9) ···H(18)	1.8648
O(9) ···H(21)	1.8648
O(12)···H(18)	1.9133
O(12)···H(20)	2.0111
O(12)···H(24)	1.8626
O(15)···H(20)	1.8570
O(16)···H(20)	2.1785
O(16)···H(23)	1.8444
O(19)···H(17)	2.1785
O(19)···H(26)	1.8444
O(22)···H(18)	2.0154
O(25)···H(21)	2.0154

have energies of −8.9057±0.0038 kcal mol^{-1} and −12.0556±0.0038 kcal mol^{-1}, respectively. This shows the stabilization of the structures compared with the optimized structure of 15-crown-5 having an energy of 34.9165±0.0028 kcal mol^{-1}. This stabilization primarily comes from van der Waals energy other than 1,4 energy (15-crown-5-4H_2O [I]: −24.8358, 15-crown-5-4H_2O [II]: −27.2393), which overcomes any instability due to the bending energy (15-crown-5-4H_2O [I]: 7.5673, 15-crown-5-4H_2O [II]: 6.9554) generated by bond angle changes in the molecular skeleton. As shown in Table 1, these structures, especially [II], have dihedral angles remarkably different from those of the optimized structure of 15-crown-5 given in the table. The difference in the dihedral angles shows a deformation of the molecular skeleton, which is expected to give rise to changes in the skeletal vibration frequencies, as observed in the Raman spectra. Therefore, both the present calculation and the observed Raman spectra suggest such a molecular deformation of 15-crown-5 as to accommodate water molecules. The average number of iterations for each optimization throughout the entire calculation is a rather small value of 155 (max., 306; min., 96), which seems to suggest an effective energy minimization which would lead to reasonable optimized structures.

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