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High-Resolution Rotational Spectroscopy of a Cyclic Ether

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Ⓢ *Supporting Information*

ABSTRACT: The conformational landscape of crown ethers has constituted a central topic in the development of host−guest supramolecular chemistry. We report a high-resolution rotational study of a crown ether, 1,4,7,10,13-pentaoxacyclopentadecane (15-*crown*-5), by means of molecular beam Fourier transform microwave spectroscopy. The considerable size and the broad range of conformations allowed by the flexibility of the cyclic backbone of this ether pose important challenges to spectroscopy approaches. In this investigation, three stable rotamers of the 15-*crown*-5 ether have been identified and characterized through their rotational constants and centrifugal distortion coefficients. Ab initio quantum calculations at the MP2 level predict these conformers as the most stable ones for the title system and reproduce accurately their distinct structural features. The results pave the ground for an extensive survey of the conformational landscape of the 15-*crown*-5 and related cyclic ethers in the near term.

SECTION: Kinetics, Spectroscopy
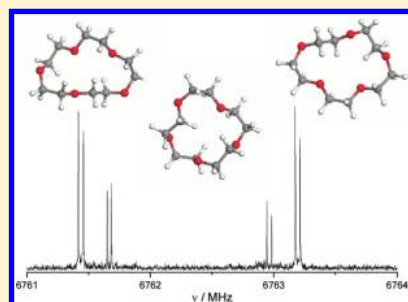
Crown ethers stand as one cornerstone molecular class in host−guest supramolecular chemistry and are the building blocks of a broad range of modern materials in separation and catalytic science.[1,2] The most remarkable feature of crown ethers is the ability of their flexible backbone of adopting a broad range of open (ring-like) and folded (cage-like) coordination structures with metal and molecular cations.[3−7] The stability of the cationic complexes of crown ethers is sustained by the net negative charge conferred to the crown cavity by the lone-pair orbitals of the ether oxygens. This is in marked contrast with the structures displayed by uncomplexed crown ethers, in which part of the oxygen sites are oriented outward from the ring.[8] In this way, the mutual electrostatic repulsions between the oxygens are minimized, and weak intramolecular C−H···O bonds are allowed to form across the crown cavity. Hence, the stabilization of the cationic complex involves a "conformational switch" of the crown ether backbone between two qualitatively different structures well-separated in conformational space: concerted turns of several dihedral angles of the initially free crown ether are required to build an optimum coordination arrangement of the oxygen sites around the cation. The barriers between the free and complexed conformations can be expected to drive the kinetics of the cation binding process.

Given the ability of crown ethers to form molecular complexes easily, it is advantageous to characterize their intrinsic preferred structures under isolation conditions. A low internal temperature of the molecules is also essential because the flexibility of crown ethers leads to a distribution of their equilibrium population among a wealth of low-energy conformers.[8] The preparation of molecules in supersonic jets fulfills both of these requirements.[9] In the jet, the individual conformers are internally cooled, but the conformer distribution before the expansion is roughly preserved, provided that interconversion barriers between conformers are sufficiently high.[10] Under these conditions, the spectroscopic properties of the different conformers can be probed in a local environment of virtual isolation. Previous studies on neutral crown ether systems in supersonic expansions have explored the vibronic spectra of benzo-15-*crown*-5[11] and dibenzo-18-*crown*-6[12] and of their complexes with solvent molecules,[13,14] by means of laser-induced fluorescence and double-resonance laser techniques.

We report here what to our knowledge constitutes the first high-resolution rotational study of a crown ether. Microwave spectroscopy is applied in combination with quantum calculations to characterize the most stable rotamers of the 15-*crown*-5 molecule (henceforth, 15c5; systematic name: 1,4,7,10,13-pentaoxacyclopentadecane). The different conformational species have unique moments of inertia and give rise to separate rotational spectra. Even in conformationally challenging systems as the title one they can be distinguished by rotational spectroscopy. This has been recently illustrated for amino acids[15] and with the assignment of nine low-energy conformers in γ-aminobutyric acid.[16]

The molecular-beam Fourier transform microwave spectrometer (MB-FTMW) employed in this study has been described elsewhere.[17] A supersonic jet of 15c5 in a Ne seeding bath is generated by vaporizing the crown ether at 120 °C. The supersonic expansion relaxes the internal energy of the 15c5

molecules and carries them into the 55 cm confocal spherical mirror Fabry−Perot resonator. A short microwave pulse (0.3 μs, 10−300 mW) polarizes the species in the jet, and the subsequent coherent transient emission is recorded in the time domain (typically over ca. 400 μs at 40−100 ns intervals) and Fourier-transformed to the frequency domain. The frequency accuracy of the experiment is better than 5 kHz.

The computational study involved an extensive survey of the conformational space of the isolated 15c5 by means of simulated annealing. The resulting low-energy molecular structures were optimized with the ab initio second-order Møller−Plesset (MP2) method and the basis set 6-311+ +G(d,p). As many as 15 stable conformers are predicted with MP2 free-energy differences within 8 kJ mol^{-1}, corresponding to asymmetric rotors with a broad range of positive (oblate) and negative (prolate) values of the asymmetry parameter $\kappa = (2B - A - C)/(A - C)$ and a variety of electric dipole moment values.

Wide frequency scans were conducted to search for K_{-1} and K_{+1} doublet patterns that provide identifiable signatures for individual conformers. (See Figure 1 for examples of rotational
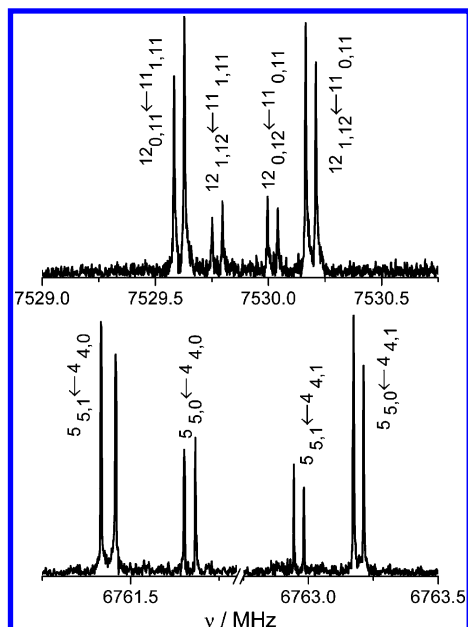

Figure 1. Typical $J'_{K'_{-1},K'_{+1}} \rightarrow J''_{K''_{-1},K''_{+1}}$ rotational lines measured for 15-crown-5 in this work. The $J' = 12 \leftarrow J'' = 11$ and $J' = 5 \leftarrow J'' = 4$ progressions are assigned to rotamers 1 and 3, respectively. Each line displays a Doppler splitting of ca. 40 kHz. The absolute center-frequency of each transition is determined from the half-sum of the two Doppler components with an accuracy better than 5 kHz.

lines illustrative of the overall spectral resolution.) In this way, the spectra of three different rotameric structures of the 15c5 crown ether, labeled 1, 2, and 3, were identified. Ensembles of several tens of lines were measured for each rotamer within the frequency range 4−10 GHz, probing rotational states $J = 4$−16. A list of the complete set of rotational transitions observed is provided as Supporting Information. The assignment of the experimental lines to rotational transitions of a specific conformer was performed through an iterative measurement/ fit procedure based on Watson's semirigid rotor Hamiltonian[18−20] up to quartic terms. In the final fits, the asymmetric top reduction of the Hamiltonian in the I^r representation was

used for the prolate top rotamers 1 and 3, whereas the similar reduction in the III^l representation was employed for the oblate top rotamer 2. For this latter rotamer, the centrifugal distortion constants δ_J and δ_K were found to be nondeterminable and were kept fixed to zero. The fitted transitions match the experimental lines within a standard deviation of $\sigma_{\text{FIT}} < 2$ kHz. The best-fit rotational constants and centrifugal distortion coefficients of the three rotamers identified in this study are given in Table 1. It must be remarked that the small values of the rotational constants that characterize the 15c5 rotamers constitute an important challenge for their spectroscopic study in the gigahertz range.

The observed rotamers of 15c5 have been assigned to the three lowest energy conformers predicted by the ab initio computations. These conformers are represented in Figure 2 and are described through their rotational parameters and dipole moments in Table 1. (Further structural parameters, interatomic distances, and bond angles are provided in Table S4 as Supporting Information.) The principal rotational constants of the computational conformers 1, 2, and 3 (labeled in order of increasing free energy) resemble closely those of the three rotamers characterized in the experiments. None of the other MP2 conformers found in our study matched the rotational constants of the experimental rotamers with a comparable level of accuracy. Quite good agreement exists as well between the experimental and MP2 values for the quartic centrifugal distortion coefficients. Also importantly, the components of the dipole moment of each conformer are consistent with the type and intensities of the lines observed experimentally. For rotamers 1 and 3, strong μ_b-type rotational transitions are detected, in agreement with a dipole moment aligned along the b principal axis. In addition, weaker transitions of μ_a type for rotamer 1 and of μ_c type for rotamer 3 could be assigned, again in consonance with the relative magnitude of the dipole moment components. Finally, rotamer 2 displayed strong μ_a-type transitions, in accord with a dominant component of the dipole moment along the a axis.

The MP2 calculation predicts conformer 1 to have a Gibbs free energy lower by only 1.1 and 1.6 kJ mol^{-1} (87 and 137 cm^{-1}) than the next higher conformers 2 and 3, respectively. These conformers are illustrative of the remarkable diversity of energetically similar structures that the 15c5 ether can adopt. Conformers 1 and 2 are coincident with the conformers 1 and 11, respectively, reported by Hill and Feller.[8] Conformer 3 had not been described in any previous work. The particularly small value for the rotational constant C for the three conformers is related to open ring conformations of the ether backbone, providing a relatively large moment of inertia with respect to the principal axis perpendicular to the ring.

The two prolate conformers 1 and 3 have similar features, as reflected in the values of the experimental rotational constants. Each of these conformers displays significant differences between its three planar inertial moments. This is indicative of different mass distributions out of each of the inertial planes. The small values of the planar inertial moment $P_{cc} = (I_a + I_b - I_c)/2 = \sum_i m_i c_i^2$ (m_i and c_i are the mass and c coordinate of atom i), which gives the mass extension out of the ab inertial plane, indicate that the heavy atoms (O and C) lay at positions not far from that plane. Similarly, the comparably large values found for P_{aa} indicate that the mass distribution is extended mainly out of the bc plane. Conformers 1 and 3 also have in common a roughly coplanar arrangement of the O_4−C−C−O_5 segment of the ring (see atom numbering in Figure 2). Such arrangement

Table 1. Effective Rotational Constants (A, B, C), Anisotropy Parameter ($\kappa = (2B - A - C)/(A - C)$), Planar Inertial Moments ($P_{aa} = (I_b + I_c - I_a)/2$, etc.) and Quartic Centrifugal Distortion Coefficients (Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K) in the A-Reduced I^r Representation for Conformers 1 and 3 (Prolate Asymmetric Tops) and in the A-Reduced III^l Representation for Conformer 2 (Oblate Asymmetric Top)^a

	conformer 1		conformer 3		conformer 2	
	exp	MP2	exp	MP2	exp	MP2
A/MHz	806.82516(19)^b	828.5	710.44967(14)	725.3	595.89572(45)	602.9
B/MHz	417.16283(22)	416.9	434.54680(15)	433.2	560.83329(32)	565.6
C/MHz	303.779894(42)	307.7	287.053113(37)	289.2	342.00682(13)	347.9
κ	−0.549210(1)	−0.582	−0.303280(2)	−0.339	0.723797(5)	0.710
P_{aa}/(amu Å^2)	1124.36153(51)	1122.3	1106.11432(38)	1108.7	765.35204(86)	754.0
P_{bb}/(amu Å^2)	539.27424(51)	520.1	654.46265(38)	638.8	712.33479(86)	698.7
P_{cc}/(amu Å^2)	87.10570(51)	89.9	56.88837(38)	57.9	135.76814(86)	139.6
Δ_J/kHz	0.0103(10)	0.0098	0.01017(571)	0.0100	0.0820(37)	0.0883
Δ_{JK}/kHz	0.0608(48)	0.0675	0.0435(25)	0.0486	−0.1345(90)	−0.146
Δ_K/kHz	0.1212(43)	0.112	0.0731(318)	0.066	0.0663(51)	0.0715
δ_J/kHz	0.00147(47)	0.0064	0.00352(28)	0.0034	[0.0]^c	−0.010
δ_K/kHz	0.0534(58)	0.0522	0.0426(21)	0.046	[0.0]	0.129
$|\mu_a|$/D		0.9		0.1		3.7
$|\mu_b|$/D		2.3		4.2		0.1
$|\mu_c|$/D		0.6		1.6		0.8
number of lines	55		61		46	
σ_{FIT}/kHz	1.3		1.3		1.7	

^{a}Number of experimental lines and the standard deviation, σ_{FIT}, of the fits are indicated in the bottom entries. The theoretical rotational constants, centrifugal distortion coefficients, and components of the dipole moment (μ_a, μ_b, μ_c) of the MP2/6-311++G(d,p) conformers are indicated next to the values of the corresponding experimental rotamers. ^{b}Standard error in parentheses in units of the last digit. ^{c}Values in square brackets were kept fixed in the fit.
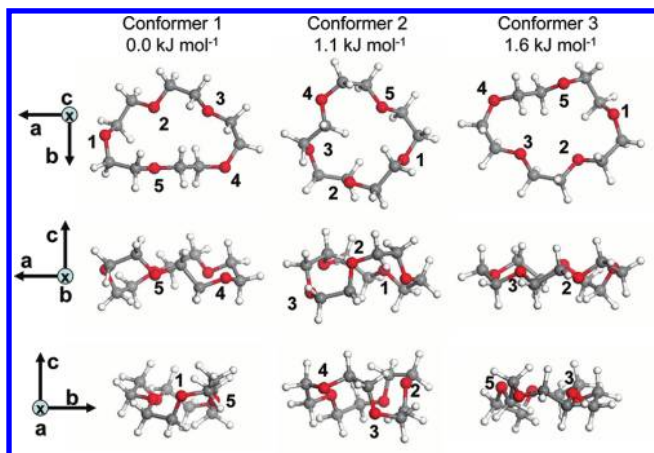

Figure 2. Representation of the MP2/6-311++G(d,p) conformers of the isolated 15-*crown*-5 ether, which are unequivocally identified as the rotamers 1, 2, and 3 characterized in the present microwave rotational spectroscopy experiments. Three orientations according to the principal axis (a, b, c) of the conformers are shown. Some relevant structure parameters are provided in Table 1 and in Table S4 of the Supporting Information.

orients one of the oxygens toward the outside of the ring cavity and places it at a particularly large distance from the other oxygen sites. A detailed inspection of these conformers also reveals differences in the location of the polar oxygen atoms along the ether backbone in each case, which results in noticeable differences in the values of the electric dipole moments.

Conformer 2 is qualitatively different from conformers 1 and 3 and corresponds to an oblate asymmetric top. This conformer is characterized by a remarkable degree of folding of the cyclic backbone, as can be appreciated in Figure 2. Correspondingly,

the value of P_{cc} is larger than those of the two prolate conformers. This renders a unique compact structure that features by far the largest B and C rotational constants and κ parameter among the lowest 15 conformers predicted by the MP2 computations. Such structure provides a homogeneous ensemble of distances between the oxygens (2.9 to 3.1 Å) and allows for efficient C−H···O interactions. It is interesting to note that Δ_J for conformer 2 is significantly higher than it is for the other two conformers. This result is found irrespective of the representation and type of Watson's reduction employed to analyze the complex; for example, the analysis in the I^r representation gives a value of Δ_J of 0.0362(55) kHz (ab initio 0,032 kHz), which is still more than three times higher than found for conformers 1 and 3 in the same representation.

It is interesting to evaluate the magnitude of the conformational "switch" that the free 15c5 ether structures described above must undergo to form their typical cationic complexes. The open structures of conformers 1 and 3 of the free 15c5 ether resemble to some extent the features of the 15c5 backbone in the complexes with cations of relative large size, such as the heavier alkali metals[4] or with the molecular cations HO_3^+ and NH_4^+.[5] Conformer 2 would be a priori closer to the folded structures adopted by the native crown ethers in their complexes with cations smaller than the cavity.[3,21] Nevertheless, significant rearrangement of the ether backbone is still required to bring all oxygens to the interior of the cavity when forming the complex. In particular, cation binding leads to a significant shortening of the distances between consecutive oxygens in the ring. For instance, the 15c5−K$^+$ complex displays an average O−O distance of 2.85 Å,[4] in comparison with 3.0 to 3.1 Å for the conformers of the isolated 15c5 presently described.

Crown ethers can display a variety of qualitatively different conformations within a narrow energetic range. Each of such

conformations finds an optimum balance between the flexibility of the ether backbone and the intramolecular O⋯O repulsions and CH⋯O attractions. This study has shown that MB-FTMW spectroscopy and quantum MP2 methods constitute powerful tools to unveil the fine aspects of the conformational landscape of these systems. In the present experiments, there was an ensemble of weaker unassigned lines remaining in the spectra that are likely to belong to conformers of the 15-crown-5 ether lying higher in energy than the three ones characterized here. Current work is being devoted to the identification of such conformers. This task will involve a considerable extension of the spectroscopic survey and will be the topic of a comprehensive report in the near future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete list of the experimental lines measured for the three 15c5 rotamers characterized in this work and selected geometrical parameters of the MP2 conformers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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