

WATER'S ROLE IN RESHAPING A MACROCYCLE'S BINDING POCKET: CONFORMATION-SPECIFIC INFRARED AND ULTRAVIOLET SPECTROSCOPY OF BENZO-15-CROWN-5-(H₂O)_n-CLUSTERS (*n* = 1, 2)

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Crown ethers are well-studied examples of flexible macrocycles with a high binding selectivity for substrates, especially cations. We investigated the conformational preferences of the singly and doubly complexed water clusters of the crown ethers benzo-15-crown-5 (B15C) and its amino-derivative 4'-aminobenzo-15-crown-5 (ABC) cooled in a supersonic jet expansion. The fluorescence excitation, resonance enhanced two-photon ionization (R2PI), UV-UV holeburning (UVHB), fluorescence-dip infrared (FDIR), resonant ion-dip infrared (RIDIR) and novel IR-IR-UV holeburning¹ spectra allowed for the identification of two B15C-(H₂O)₁ conformers and one ABC-(H₂O)₁ conformer. These conformers are characterized by an all-planar arrangement of the atoms directly bound to the benzene ring in which the crown ether macrocycle opens up to a symmetric structure and accommodates a doubly and triply H-bonded H₂O molecule in two distinct ways, respectively. Two B15C-(H₂O)₂ conformers and one ABC-(H₂O)₂ conformer were identified. One of the B15C-(H₂O)₂ conformers contains a macrocycle configuration identical to that found in the monohydrated clusters with an H-bonding topology in which the H₂O molecules occupy both available sites simultaneously. The second B15C-(H₂O)₂ conformer is assigned to an H-bond pattern in which the two H₂O molecules are concatenated to form an H-bonded bridge involving only three of the four available O-H-bonds (see figure).

(1) V. A. Shubert and T. S. Zwier, *J. Phys. Chem. A*, **2007**, *111*, 13283.

