CONFORMATION-SPECIFIC ELECTRONIC AND VIBRATIONAL SPECTROSCOPY OF DIBENZO-15-CROWN-5 ETHER IN A SUPERSONIC JET.

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Crown ethers are oxygen containing cyclic structures noted for their ability to preferentially bind substrates such as ions and water. Despite the high symmetry inherent to the chemical structure, crown ethers are remarkably flexible, adapting their conformation to the substrate to which they are bound. As such, it is valuable to study the conformational preferences of the isolated crown ethers in the absence of any substrate. Here, we present the electronic and infrared spectroscopy of jet-cooled, isolated dibenzo-15-crown-5 ether (DB15C). By incorporating two phenyl rings into the crown, we are afforded the opportunity to explore the ultraviolet spectroscopy of both groups and the coupling between them. One-color resonant two-photon ionization, laser induced fluorescence, UV-UV holeburning, and resonant ion-dip infrared spectroscopies are used to provide conformation-specific electronic and infrared spectra of the three conformers. Additionally, single vibronic level dispersed fluorescence spectra provide evidence for the existence of close lying S_2 states in the two major conformers, located about 527 cm^{-1} above their S_1 counterparts. Based on a comparison with benzo-15-crown-5 ether, we surmise that the local conformation of the ethoxy groups about the two phenyl rings are different. Electronic energy transfer appears to be slow between these phenyl rings on the timescale of the excited state fluorescence. Finally, DFT and MP2 calculations will be presented as a basis for tentative structural assignments and provide insight into the excitonic coupling of the two chromophores.