

Organic and Biomolecular Chemistry 2005 vol.3 N14, pages 2558-2565

Vibrational spectra, co-operative intramolecular hydrogen bonding and conformations of calix[4]arene and thiacalix[4]arene molecules and their para-tert-butyl derivatives

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Abstract

The IR and Raman spectra and conformations of calix[4]arene, thiacalix[4]arene and their p-tert-butyl derivatives have been analysed within the framework of scaled quantum mechanics (SQM). It is shown that the introduction of four p-tert-Bu groups into the calixarene molecules influences the relative energies of their conformers and the enthalpy of the cooperative intramolecular H-bonding (ΔH_{intra}) almost negligibly. ΔH_{intra} , evaluated from logansen's rule, amounts to $\sim 26\text{-}28$ kcal mol⁻¹ for the calixarenes and $\sim 20\text{-}21$ kcal mol⁻¹ for the thiacalixarenes, which essentially exceeds the enthalpies of non-cooperative H-bonds formed by related phenols. As a result of this strong bonding, bands of stretching, bending and torsion vibrations of an eight-membered cyclic system (OH \cdots)₄ arise, e.g., two $\delta(\text{OH})_4$ bands are observed in the IR spectra of the most highly symmetric C₄ cone conformations of calix[4]arene and thiacalix[4]arene. The "duplication" of the number of OH infrared bands is a good new indicator of cooperativity of intramolecular H-bonding of the calixarenes. © The Royal Society of Chemistry 2005.

<http://dx.doi.org/10.1039/b504448k>
