

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

Katsyuba S., Kovalenko V., Chernova A., Vandyukova E., Zverev V., Shagidullin R., Antipin I., Solovieva S., Stoikov I., Konovalov A.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

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>
