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IR and NMR spectra, intramolecular hydrogen bonding and conformations of mercaptothiacalix[4]arene molecules and their para-tert-butyl-derivative

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Abstract

It is demonstrated that the introduction of p-tert-butyl groups dramatically influences the conformational behaviour of the mercaptothiacalix[4] arene molecules. Quantum-chemical computations in combination with IR and NMR spectroscopy prove that, in contrast to closely related calixarenes, the 1,3-alternate becomes a dominant conformer of p-tert-but-l-mercaptothiacalix[4] arene not only in crystal, but also in solutions and in vacuum. It is shown that the title molecules form essentially non-cooperative intramolecular hydrogen bonds: their SH groups are intramolecularly H-bonded solely to the sulfide groups bridging thiophenolic units. The enthalpy of this bonding, evaluated from logansen's rule, amounts to ca. 1.5 kcal mol-1 per one SH•••S bond, which about four times smaller than the enthalpies of cooperative intramolecular H-bonds formed by related calixarenes and thiacalixarenes. © 2007 Springer Science+Business Media B.V.

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Keywords

Conformations, DFT, Intramolecular hydrogen bonds, IR and NMR spectra, Mercaptothiacalix[4]arenes, P-tert-Butyl-substitution