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DFT study of hydrogen bonding and IR spectra of calix[6]arene

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ABSTRACT

IR and far IR spectra of calix[6]arene were recorded at various temperatures, between 16 and 180 °C and spectra of solutions and crystalline solids were obtained. Density functional calculations (DFT) gave vibrational frequencies and infrared intensities for the compressed cone conformation. Complete assignments were made for experimental IR spectrum of the compressed cone conformer. DFT calculations, in conjunction with experimental data give a better understanding of the effect of hydrogen bonding on the typical bands of calixarenes. Method of FTIR spectroscopy shows that a cyclic cooperative intramolecular hydrogen bond is implemented in calix[6]arene. Weakening of the cooperative hydrogen bond in calixarenes is caused by the mutual influence of covalent and hydrogen-bonded macrocycles on each other. Analysis of IR spectra changes during heating showed that calix[6]arene remains in the compressed cone conformation. In a molecule of calix[6]arene six oxygen atoms form a “boat” conformation with three pairs of hydrogen bonds.

1. Introduction

Supramolecular chemistry since 30 years of its development, has made some important steps. Currently, the most promising direction of supramolecular chemistry can be considered creating hosts molecules capable of effectively and selectively bind neutral molecules and ions. Calixarenes are extremely useful for the realization of this goal [1]. Calixarene molecules constitute a macrocycles having a cavity of a noticeable size and hydroxyl groups capable of forming intramolecular and intermolecular hydrogen bonds (Fig. 1).

Generally molecules of calixarenes with unsubstituted hydroxyl groups on the lower rim are cup-shaped and therefore are able to include in its cavity and hold there a wide range of organic molecules and molecular ions [1–3]. Thanks to the hydroxyl groups of calixarenes they are readily amenable to chemical modification. Thus ensuring a high binding selectivity of guests through the optimal arrangement of functional groups on the rim of molecular bowls. This class of compounds may be successfully used as a highly selective platform in extraction processes [1,2].

IR spectroscopy is used mainly for characterization of hydrogen bonding and host-guest interactions in calixarenes [4–7]. Nevertheless, the full interpretation of IR spectrum based on the analysis of normal vibrations has been reported only for calix[4]arene [6,8]. We have studied and interpreted the IR spectra of calix[4]arene and thiacalix[4]arene [9–11]. Hydrogen bonding and conformations of *p*-*tert*-butyl-calix[4]arene were studied by IR spectroscopy and quantum chemistry density functional theory [12].

In this paper, our goal was to interpret the IR spectra and explore hydrogen bonding in calix[6]arene (6-*Cal*). Far IR spectrum of 6-*Cal* was obtained for the first time. The absorption curve for the conformation of the compressed cone of 6-*Cal* was calculated and compared with the experimental IR spectra over a wide frequency range. Bands characteristic of the compressed cone conformation was identified and classified. The data obtained allow us to interpret the IR spectrum of 6-*Cal*. Study of spectra at temperatures high enough in order to remove guest molecules, but not sufficient to destroy the 6-*Cal* itself, perhaps is the easiest way to observation of pure 6-*Cal*. At the same time, it is possible, that the heating (even within the crystalline phase) will cause conformational transitions and reconstruction of hydrogen bonds.

2. Experimental

Synthesis and main characteristics of 6-*Cal* were described in detail earlier [13,14] (Fig. 1). It is known that the melting and the destruction temperatures of these compounds are quite high

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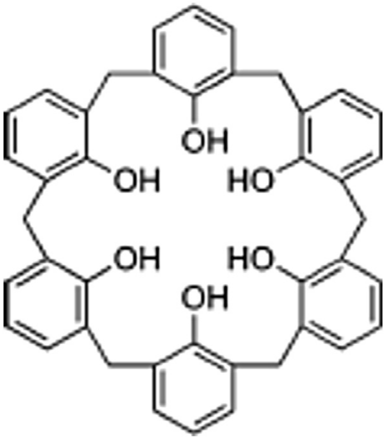

Fig. 1. Structure of 6-*Cal*.

(~350 °C and higher) [13,14]. In order to remove the remaining molecules of solute and water from the crystalline packing and to follow on the possible conformational transitions and changes in system of H-bonds, the temperature investigations were fulfilled, all the samples were step by step heated up to 180 °C.

The IR spectra in the region 4000-100 cm^{-1} were recorded using a Vector-22 and IFS66s Bruker FTIR-spectrophotometer with a resolution 4 cm^{-1}. The IR spectra of the crystalline samples were recorded in KBr pellets. The solvent CCl_4, was stored prior to use on molecular sieves, 3 or 4 Å, to remove traces of water. All solutions were carried out in a glove box with the exclusion of moisture. Concentration of solutions in CCl_4 was equal to ~$1 \cdot 10^{-4}$ mol l^{-1}, the thickness of the cell was equal to 2 cm. Far IR spectra were registered for the samples placed between CsI plates.

A powder diffraction analysis was made with D8 ADVANCE instrument (BRUKER, Germany). Bragg-Brentano geometry, CuKα radiation, 40 KV, 40 mA, Ni-monochromator. All measurements were conducted at room temperature. The samples were prepared as powder film onto a glass slide.

3. Computational procedure

Calculations of IR spectra of 6-*Cal* were performed at a DFT/B3LYP level with basis set 6-31G(d,p) using a GAUSSIAN 09 W program package [15]. All stationary points were characterized as minima by analysis of Hessian matrices. The software package SHRINK [16] was used for calculation of potential energy distribution. An assignment of bands was fulfilled by calculating the potential energy distribution (PED). The calculated vibrational wavenumbers were scaled as 0.953 for wavenumbers above 1700 cm^{-1}, and below 1700 cm^{-1} scaled as 0.967.

The natural bonding orbital (NBO) calculations [17] of 6-*Cal* were performed using the Gaussian 09 [15] package at the same level of theory in order to understand the nature of the various interactions of the second order between the filled orbitals of one subsystem and vacant orbitals of the other subsystem, which quantify the intermolecular delocalization or hyper conjugation. Analysis of the Fock matrix using perturbation theory of the second order in NBO basis of 6-*Cal* was performed to evaluate the donor-acceptor interactions. For each donor (i) and acceptor (j), stabilization energy E_2 associated with delocalization $i \rightarrow j$ is estimated as $E_2 = \Delta E_{ij} = \frac{q_i (F_{ij})^2}{\varepsilon_j - \varepsilon_i}$ where q_i is the donor orbital occupancy, ε_j and ε_i are diagonal elements and F_{ij} is the off diagonal NBO Fock matrix element [17].

Electronic chemical potential, chemical hardness, softness, and global electrophilicity index were obtained from expressions $\mu \approx -(\text{I}E + EA)/2$, $\eta \approx (IE - EA)/2$, $S = 1/\eta$, and $\omega = \mu^2/2\eta$ in terms of vertical first ionization energy *IE* and electron affinity *EA*, respectively [18]. Fukui functions $f_k^+(r) = [q_k(N+1) - q_k(N)]$ for nucleophilic attack, and $f_k^-(r) = [q_k(N) - q_k(N-1)]$ for electrophilic attack, where q_k is the electron population of atom k in the molecule, N number of electrons were calculated. Local softness was obtained by projecting the global values for the atomic center k in the molecule by using the Fukui function: $s_k^+ = Sf_k^+, s_k^- = Sf_k^-$. Fukui function and local softness for each reactive atom were calculated using Natural atomic charges population analysis [17].

4. Results and discussion

IR spectroscopy allows to track the small changes in strength and structure of H-bonds formed in calixarenes (Fig. 2). The band of free OH groups around 3600 cm^{-1} is not observed in the IR spectrum of 6-*Cal* in a solution of CCl_4 (Fig. 2). Maxima of the absorption band of hydroxyl groups in the IR spectrum of calixarenes in a solution of CCl_4 are observed at 3173 cm^{-1} - for 4-*Cal* and 3165 cm^{-1} - for 6-*Cal*. This is an indication that all six hydroxyl groups participate in hydrogen bonds and compressed cone conformation is retained in solution of 6-*Cal*.

For crystalline samples in the region of νOH stretching vibrations are observed bands at 3239 and 3152 cm^{-1} in the IR spectrum of 4-*Cal* and the band at 3162 cm^{-1} in the IR spectrum of 6-*Cal* (Fig. 3). In the IR spectrum of 6-*Cal* the νOH band is more intense

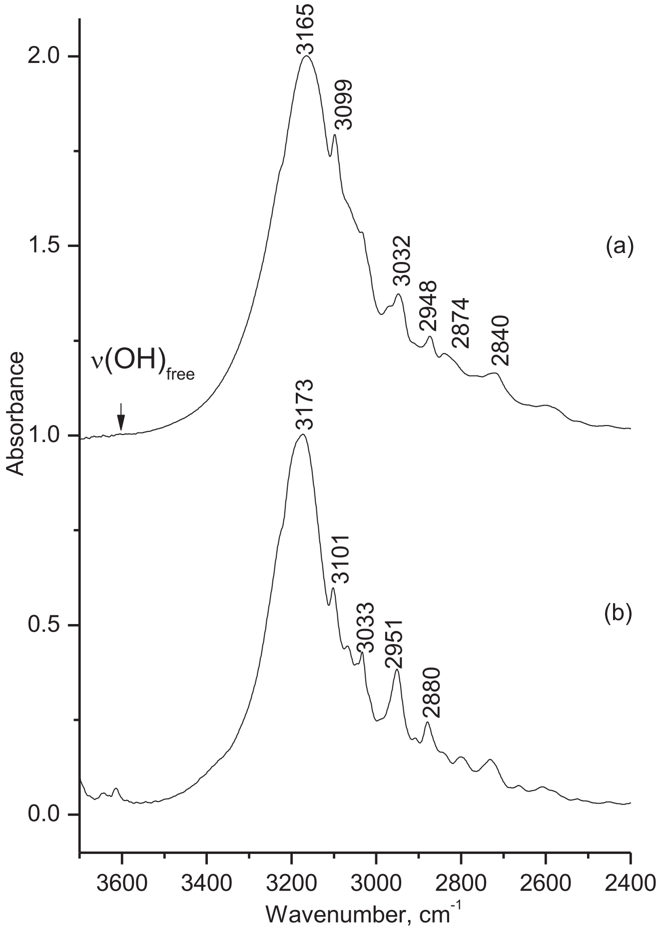

Fig. 2. Experimental IR spectra of calix[6]arene (a) and calix[4]arene (b) solutions in CCl_4 (1) in the region 3600–2400 cm^{-1}.