

Modelling conformations and IR spectra of *p*-*tert*-butylthiacalix[4]arene tetraester using DFT method

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Abstract

The infrared spectra of the cone, partial cone and 1,3-alternate conformers of *p*-*tert*-butyltetrakis(ethoxycarbonyl)methoxytetra-thiacalix[4]arene (*TEMT*) have been recorded. The structural optimization and normal mode analysis were performed for this molecule on the basis of the density functional theory. These calculations gave the frequencies of vibrations and infrared intensities for the cone, partial cone (paco) and 1,3-alternate (1,3-alt) conformers. The energy difference between the paco and 1,3-alt conformers is 3.1 kcal/mol. The cone conformer is likely to be less stable compared to the paco and 1,3-alt conformers. The calculated in gas phase dipole moments 5.65, 3.33, and 0.02 D for the cone, paco and 1,3-alt conformers of the *TEMT* are in good accordance with theoretical values for the thiacalix[4]arene. Complete assignments were made for the experimental IR spectra of all conformers. The softness of sulphur atoms to nucleophilic and electrophilic attack is higher than softness of oxygen atoms of ester groups in the lower rim. The bands characteristic for each conformation were defined. IR spectroscopy combined with DFT computation provides unique detailed information about the structure of the technologically relevant materials, which could not be obtained before with any other technique.

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1. Introduction

The purpose of studying calixarene properties may be explained by their unusual complex structure and rich conformational possibilities governed by H-bonding of their molecules as well as by wide practical applications of these compounds [1,2]. Hydroxyl groups of calixarenes can be easily modified chemically. That enables one to provide high selectivity of “guest” binding due to optimal locality of functional groups on “calix” rim and may be successfully used as platforms of complexes during extraction processes [1–3]. In order to increase selectivity of extraction calixarenes with cavities of definite size fixed by system non-covalent hydrogen bonds are constructed [3,4].

Calixarenes reveal receptor properties to molecules of different nature. This is defined by an amphiphilic character of their molecules. Upper lipophilic rim forms an “entrance” to a cavity organized by the “cone” conformation on account of cooperative hydrogen bond of hydroxyl groups of lower rim. Polar molecules, for example, an alcohol, may, in principle, form a “guest–host” pair, oriented either into the cavity by aliphatic end, or connected with polar rim, most probably, out of the cavity. Investigation of molecular conformations in solution and solid state is important for understanding the problem of molecular recognition by interactions of a “guest–host” type [1–4]. Selectivity of molecular interactions in these supramolecular ensembles depends on cycle organization and conformations of calixarenes [1–3].

The “cone” conformation is dominating for parent calix[4]arene molecules, but corresponding ethers may exist in various conformers, such as partial cone (paco), 1,2- or 1,3-alternate (1,3-alt) [1–4]. The tetraacetates of

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p-*tert*-butylcalix[4]arene in the cone, paco and 1,3-alt conformations are produced by the alkylation of thiacalixarenes with ethyl bromoacetate [4,5]. Calixarene esters have exhibited unusual ionophoric properties toward the alkali metal ions such as sodium and cesium ion [4]. Binding studies have demonstrated a correlation between a calix[4]arenes conformation and its molecular recognition properties [1–5]. That is why physical methods for the identification of each conformer are highly desirable. Calix[4]arenes were studied by single crystal structure determination in the solid state and by NMR spectroscopy in solution [1–5].

FTIR spectroscopy is well known to be the most informative method of simultaneous control of H-bonding, conformational and phase transitions. It was used for characterization of hydrogen bonding, host–guest interactions, selectivity of the ion recognition process in calixarenes [6–9]. The full assignment of IR spectra of these molecules is rather complex. Normal coordinate analysis of the calixarenes is not widely applied due to the large size of molecules. FTIR spectra of calix[4]arene and thiacalix[4]arene were examined and interpreted [10–12]. The hydrogen bonding and conformation state of *p*-*tert*-butylcalix[4]arene and *p*-*tert*-butylthiacalix[4]arene were studied by FTIR spectroscopy and DFT calculations [13,14].

In this article we performed DFT study of the cone, paco and 1,3-alt conformers of *p*-*tert*-butyltetrakis(ethoxy-carbonyl)methoxytetrathiacalix[4]arene (*TEMT*). Frequencies and intensities of IR bands have been calculated and compared with experimental ones. FTIR spectra of different conformational states of *TEMT* were registered for the first time. The absorption curves for three conformations of *TEMT*: cone, paco, and 1,3-alt were calculated and compared with experimental IR spectra over a wide frequency range. The bands characteristic for each conformation are defined and assigned. The data obtained enable one to interpret IR spectra of thiacalix[4]arene esters.

2. Experimental

The synthesis and main characteristics of *TEMT* were described in detail earlier [1–5]. The IR spectra in the region 4000–400 cm⁻¹ were recorded using a Vector 22 spectrometer, with resolution 4 cm⁻¹, 64 scans were accumulated. Crystalline samples have been prepared as KBr pellets.

3. Computational procedure

Calculations of IR spectra were carried out using the gradient-correlated density functional theory with Perdew–Burke–Ernzerhof exchange-correlation functional (DFT/PBE) [15]. This functional is very satisfactory from the theoretical point of view, because it verifies many of the exact conditions for the exchange-correlation hole and it does not contain any fitting parameters [16]. The binding energies, geometries and dynamical properties of different molecules calculated with PBE functional show

the best agreement with experiment [17,18]. Calculations were performed using three exponential basis with two polarizing functions (TZ2P) [19]. This basis set was chosen in order to obtain the most advantageous relation of accuracy and computation time [19]. Its peculiarity is that the same set of exponents is used for all values of angle moment in atom [19]. The program PRIRODA was used to perform DFT calculations [19]. The minima of the potential surface were found by relaxing the geometric parameters with standard optimization methods. All stationary points were characterized as minima by analysis of Hessian matrices. The software package SHRINK [20] was used for transformation of quantum mechanical Cartesian force constants to the matrix in redundant internal coordinates and calculation of potential energy distribution. No scaling procedure of frequencies or force constant was applied. Recently, we checked the selected functional and basis set by calculation of geometry and IR spectra of *p*-*tert*-butylcalix[4]arene and *p*-*tert*-butylthiacalix[4]arene [13,14].

Spectra were generated from a list of frequencies and intensities using Gaussian band shape and half-width σ of 10 cm⁻¹ for each of N vibration modes calculated. The intensity of each band is A_k in km/mol.

$$I(\nu) = \sum_k^N \frac{A_k}{\sqrt{2\pi\sigma}} \exp \left\{ -\frac{(\nu - \nu_0)^2}{2\sigma^2} \right\}.$$

An assignment of bands was fulfilled on the basis of calculated potential energy distribution (PED).

The electronic chemical potential, the chemical hardness and softness were obtained from the expressions $\mu \approx -(IP + EA)/2$, $\eta \approx (IP - EA)$ and $S = 1/2\eta$, in terms of the first vertical ionization energy IP and electron affinity EA , respectively [21]. The 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 electronic population of atom k in the molecule, N the number of electrons, were calculated. The local softness is obtained by projecting the global quantity onto any atomic centre k in the molecule by using the Fukui function: $s_k^+ = S f_k^+$, $s_k^- = S f_k^-$. The Fukui function and local softness for each reactive atom were calculated using Hirshfeld population analysis [22].

4. Results and discussion

According to published data of thiacalix[4]arene [23,24] and to our own estimations of thiacalix[4]arene and *p*-*tert*-butylthiacalix[4]arene [12,14] the cone conformer is the most stable among them, its stability ensured by the cooperative effect of the intramolecular cyclic H-bonds in the lower rim. All other isomers, i.e., the paco, 1,2-alt, and 1,3-alt, are less favourable at least by 8 kcal/mol (Fig. 1).

The results of full optimization calculations for *TEMT*, where H-bonds are absent, are presented in Table 1. The overall order of conformations stability is

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