

Study of the
conformation and the
hydrogen bonds in p-
1-
adamantylcalix[8]aren
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Study of the conformation and the hydrogen bonds in *p*-1-adamantylcalix[8]arene by IR spectroscopy and DFT

Abstract

The hydrogen bonds and the conformations of calix[8]arene molecules with *p*-*tert*-butyl and *p*-1-adamantyl substituents were investigated by infrared spectroscopy in different states of aggregates. The conformations, reactivity, charge distribution and IR spectra of the calixarenes were calculated by the DFT method with the PBE functional and the TZVP basis set. The IR spectra of calix[8]arene molecules in the conformation of the pleated loop and the chair were compared. Optimized geometry of molecules reproduces experimental X-ray data. From our calculations, it follows that the conformation chair is less preferable than the pleated loop conformation of at least 20 Kcal/mol. It has been shown that the conformation of a pleated loop is the most stable in the solid state and solution. Hydrogen bonds determine the stability of this structure. In *p*-1-adamantylcalix[8]arene, hardening of hydrogen bonds occurs. The observed IR spectra were interpreted using the potential energy distribution computed with the quantum-chemical force constants. The absorption curves calculated for conformations of the pleated loop and the chair were compared with the experimental IR spectra of calix[8]arenes.

Keywords: Calixarenes, IR spectra, Hydrogen bonding, Normal vibrations, DFT

1. Introduction

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Calixarenes are a well-known class of organic substances whose molecules consist of a different number of substituted benzene moieties linked together by different groups or atoms [1]. The calixarene molecules are macrocycles with cavities of considerable size and hydroxyl groups capable of forming intramolecular and intermolecular hydrogen bonds. Hydrogen bonds affect the shape of molecules and their ability to retain and transport active agents [1]. Therefore, a study of the structure and hydrogen bonds in the calixarenes is of obvious interest [1-5]. Polycyclic- substituted calixarenes remain poorly known [1-5]. The adamantyl moiety has been chosen as a substituent because it has a lipophilic structure that provides solubility in organic solvents and several positions for the addition of substituents to modify the ability of calixarenes to form complexes. Spatial molecular models show that the introduction of 1-adamantyl substituents in calixarenes increases the size of the macrocycle [6]. We can therefore expect these calixarenes to be new beneficial hosts.

The vast practical possibilities of the calixarenes continue to involve scientific groups in their research [2-12]. The study of hydrogen bonds in calixarenes is an integral part of modern research that leads to the practical use of these compounds, for example, to solve environmental problems [1]. IR spectroscopy makes it possible to describe in detail the evolution of the hydrogen bonding system of compounds [9-13]. These changes, in turn, reflect the state and rearrangement of electron clouds of molecules [5, 7-10]. The hydrogen bond is therefore a probe through which it is very practical to study the structure of various systems, in particular complex architecture molecules. Like the hydroxylated calixarenes, which play an

important role in the formation of the spatial structure of compounds and determine their properties [1-19]. IR spectroscopy is one of the most common methods of studying hydrogen bonding and calixarene conformation [10-19]. Nevertheless, the interpretation of the IR spectra of calixarenes is generally performed only for the characteristic frequencies and has a limited value. To use all the possibilities of the method, it is necessary to carry out an interpretation of the experimental IR spectra using quantum computations.

For many practical applications, it is necessary to take into account the ability of the calixarenes to retain the solvent molecules, since in this case a reorganization of the hydrogen bonding system and a modification of the conformation of the host molecules occur [1]. The conformation of the pleated loop predominates for non-hydroxyl-substituted calix[8]arenes, but the interaction with pyridine molecules causes a modification of the hydrogen bonding system and the formation of a conformation chair [20]. As far as we know in the literature, there is no information on the cascade dissolution of these calix[8]arenes samples or the infrared spectra of the solutions.

The goal of our work was to establish conformations and to study the hydrogen bonds in the *p*-1-adamantylcalix[8]arene (AD8) by IR spectroscopy and quantum methods. It was interesting to follow the evolution of the strength of the hydrogen bond in the calix[8]arene molecules depending on the type of substituent. In experimental IR spectra, the substituent bands overlap the backbone bands of the molecule, making it difficult to identify bands of different conformers. We therefore calculated the absorption curves <https://assignbuster.com/study-of-the-conformation-and-the-hydrogen-bonds-in-p-1-adamantylcalix8arene/>

of the IR spectra for the two main conformers of calixarenes: pleated loop and chair and compared them to the experimental spectrum.

2. Experimental

The synthesis of *p*-1-adamantylcalix[8]arene (*AD8*) was performed for the first time by us earlier [21] (Fig. 1). For comparison, *p*-*tert*-butylcalix[8]arene (*TB8*) and calix[8]arene (*CA8*) were also studied (Fig. 1). Their synthesis and their main characteristics have been described previously [1]. In the purification process, these compounds were crystallized from the mixture with CHCl_3 -MeOH and dried under vacuum at 140 °C (boiling xylene). The melting and destruction temperatures of these compounds are rather high (350 °C and higher) [1]. To remove residual water and solvent from the crystalline package, the samples were gently heated to a temperature of 180 °C.

Infrared spectra of calix[8]arenes in KBr pellets were collected in the region of 4000- 400 cm^{-1} via Bruker Vector-22 FT-IR at a resolution of 2 cm^{-1} , recording 64 spectrum scans.

3. Computational procedure

Models of *AD8*, *TB8* and *CA8* were built with ChemCraft software [22]. The optimization of the geometry of the molecules was carried out by the DFT method in the PBE/TZVP approximation with application of the PRIRODA program [23]. When constructing theoretical infrared spectra, the Lorentz shape of bands with half-width 10 cm^{-1} was used. Potential energy distribution (PED) was computed by the SHRINK program [24]. The analysis <https://assignbuster.com/study-of-the-conformation-and-the-hydrogen-bonds-in-p-1-adamantylcalix8arene/>

of natural bonding orbitals (NBO) [25] was performed with Gaussian 09 software [26].

The electronic chemical potential, hardness, softness, and global electrophilicity index were calculated using the energy of the first vertical ionization IE and the electronic affinity EA : $\mu \approx -(IE + EA)/2$, $\eta \approx (IE - EA)$, $S = 1/\eta$, and $\omega = \mu^2 / 2 \eta$ [27].

4. Results and discussion

The IR spectra of crystalline *AD8* and *TB8* are shown in Fig 2, 3 and Table 1. By comparing IR spectra of crystalline samples of calix[8]arenes and their diluted solutions in carbon tetrachloride, we found only small differences in both frequency and relative intensity (Table 1).

As can be expected in the IR spectra of *AD8* and *TB8*, there are no absorption bands of stretching vibrations of the free hydroxyl groups at 3600 cm^{-1} (Fig. 3, Table 1). The IR spectral data indicate that in the calix[8]arenes, a cyclic system of hydrogen bonds characteristic of the conformation of a pleated loop is realized. The absorption bands of the hydroxyl stretching vibrations in dilute solutions of calix[8]arenes in CCl_4 with *tert*-butyl and *p*-1-adamantyl substitutions are in a narrow frequency range of 3185 cm^{-1} for *AD8* and at 3192 cm^{-1} for *TB8* (Table 1). In both cases, there are wide absorption νOH bands. The degree of shift of the $\nu(\text{OH})$ band towards the frequencies depends on the energy of the hydrogen bond. According to our data in a molecule of *AD8*, the less solid hydrogen bond is

implemented than in a molecule *TB8*. Our IR spectral data are therefore consistent with the results obtained by X-ray and NMR methods [1-18].

In the IR spectra of crystalline samples of calix[8]arenes, the stretching vibration frequencies of the hydroxyl groups are slightly higher than those of the solution in CCl_4 spectra (Table 1), 3241 cm^{-1} (*TB8*) and 3276 cm^{-1} (*AD8*). A stronger hydrogen bond in *TB8* over *AD8* may be caused by steric hindrance of adamantyl groups in the crystalline state.

Consider the evolution of the IR spectra of the calix[8]arenes with increasing temperature (Table 1, Fig. 2, 3). Gentle heating up to $100\text{-}180^\circ\text{C}$ is accompanied by a slight offset of the νOH band for all calix[8]arenes. But in different calixarenes, this happens in different ways. For example, at 180°C in the spectrum of *TB8*, the frequency of the νOH band increases by 4 cm^{-1} , while in the spectrum of *AD8* it decreases by the same amount. It is obvious that the preservation of the spectral pattern after heating at 180°C can be due to the preservation of the conformation of the pleated loop in all studied calix[8]arenes. The removal of the water and solvent molecules during heating can be accompanied by a decrease in the defects of the crystalline unit, which leads to a narrowing of the bands and to the appearance of a more resolved spectral pattern. Important information is contained in the values of νOH bands offsets when heated. They depend both on the degree of thermal movement of the arene fragments in the crystal and the differences in the packing of these calixarene fragments. *Tert*-butyl and adamantyl substituents play an important role. The study of the IR spectra of calixarenes at different temperatures makes it possible to follow the

modifications of the conformational state of the molecules and the restructuring of the hydrogen bond system, as well as the capacity to the complex formation and the properties of the receptors.

According to literature, for the calix[8]arenes with unsubstituted hydroxyl groups, the pleated loop conformation is formed [28-30] (Fig. 4). In this conformation, a circular system of eight hydrogen bonds is formed which ensures its stability [28-30]. According to our calculations, it follows that conformation chair is less preferred of at least 20 Kcal/mol (Table 2, Fig. 5). When volume substituents are introduced along the upper edge of the cycle, the energy difference between the conformations of a pleated loop and a chair increases (Table 2).

The bond length calculated for *AD8* and *TB8* corresponds to the experimental data obtained by the X-ray method for *TB8* (Table 3) [29, 30]. In the conformation, the pleated loop molecules *AD8* and *TB8* have eight hydrogen bonds, the distance between the oxygen atoms being equal to 2.68 Å. The theoretical angle O(9)–H(11)...O(22) in the molecule *AD8* is equal to 174.1° and 173.9° in the molecule *TB8*.

The rings formed on the lower and the upper edges of the calixarenes determine the structure of the molecules. Conformations that provide an optimal hydrogen bond and an acceptable covalent cycle without spatial tension are preferred. For the calix[8]arenes, the dimensions of the covalent and hydrogen-bonded macrocycles are comparable in size and the molecules are flat. As a general rule, in the crystalline state, the calix[8]arene molecules have the conformation of a pleated loop. In this case, the oxygen

atoms are in a plane forming a circle and the benzene rings form angles alternating with this plane and create symmetrical folds (Fig. 4). Therefore, for this conformer the concept of a molecular cavity loses its meaning.

The conformation of calixarenes can be represented as a set of pairs of torsion angles φ and χ around Ar-CH₂ bonds of a flexible part of molecules [32]. The calculated angular values for the calix[8]arene molecules are reasonably consistent with the experimental X-ray values (Table 4). The average absolute values of the torsion angles in the *TB8* molecule in the conformation of the pleated loop are 91.2 and 85.6° and correspond to the experimental data 85.4 and 91.4° (Table 4). In the conformation of the pleated loop of a molecule *AD8*, the mean values of the angles φ and χ are equal to 101.6 and 89.3°. Thus, the orientation of the benzene rings in calix[8]arenes depends on the type of substituent.

The theoretical absorption curve of an isolated molecule *AD8* is simpler than the experimental IR spectrum of a crystalline sample in which shifts and band splits are observed. The experimental IR spectrum of *AD8* corresponds to that calculated for the conformation of the pleated loop (Fig. 5, 6, Table 3). For the interpretation of the IR spectra of the calix[8]arenes, the potential energy distribution (PED) was calculated. The classification of the normal vibrations of the *TB8* and *AD8* molecules was performed by analyzing the displacements of atoms in Cartesian coordinates, the PED, and taking into account the intensity of the bands in the IR spectrum.

In the 2800 to 3400 cm⁻¹ region of the experimental IR spectrum *AD8*, OH and CH stretching bands were recorded (Fig. 3). A strong band at 3276 cm⁻¹

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is caused by the stretching of the OH groups involved in the formation of a strong hydrogen bond. The weak bands at 3050 and 3024 cm^{-1} belong to the stretching vibrations of the CH bonds of aromatic moieties. Frequencies at 2902 and 2847 cm^{-1} were attributed to symmetrical vibrations of methylene groups.

1603 and 1481 cm^{-1} bands in the experimental infrared spectrum of *AD8* were attributed to stretching vibrations of aromatic CC bonds (Fig. 2). The 1182, 1159 and 1103 cm^{-1} bands were caused by deformation vibrations of the CH bonds in the plane of the benzene ring. The 870 cm^{-1} band refers to out-of-plane vibrations of CH bonds from aromatic moieties. The medium intensity band at 1240 cm^{-1} in the observed infrared spectrum of *AD8* is due to the stretching vibrations of the CO, CC bonds and CCH bending.

The 939, 913 and 813 cm^{-1} bands were attributed to CC bonds stretching vibrations and CH bending vibrations. The 755 cm^{-1} band in the observed IR spectrum of *AD8* was caused by torsional vibrations of benzene rings.

It is interesting to clarify the changes in the IR spectra of calix[8]arenes during the passage of the pleated loop to the conformation of the chair. For this purpose, the calculation of the IR spectra of calix[8]arenes in these conformations has been carried out (Figs. 6, 7). A comparison of the theoretical IR spectra of the *TB8* and *AD8* molecules in the conformation, the pleated loop and the chair shows that when the aromatic units are reoriented, the frequencies and intensities of a number of bands are redistributed (Figs. 6, 7, Table 5). For analytical purposes, the characteristic

bands of each conformer of the *AD8* molecule were chosen: 1457, 1252, 1203, 1091, 720 cm^{-1} (pleated loop), 1235, 1123, 1087, 935 cm^{-1} (chair).

In this article, we have also attempted to describe the reactivity of calixarenes using global descriptors. The ionization energy, the chemical potential of the molecule *AD8* is lower than that of the molecule *TB8*, but the electron affinity, the global softness and the index of electrophilicity are higher in the *AD8* (Table 6).

In the hydrogen bond chains of calix[8]arenes, the cooperative effect is caused by the mutual polarization of these bonds. Natural population analysis (NPA) was used to determine the strength of the hydrogen bonds in the *AD8* and *TB8* molecules. The distribution of the charges on the atoms in the molecules *AD8* and *TB8* is almost identical (Table 7). In hydrogen bonding systems, the charge is transferred from oxygen atoms to hydrogen atoms. Our calculation shows that the charge distribution in the *AD8* and phenol molecules is different due to the charge transfer in the hydrogen bond system of the calixarene molecule. Higher charges on the oxygen and hydrogen atoms in the *AD8* molecule compared to a phenol show that in the cooperative hydrogen bonding system, electrostatic interactions are realized which stabilize the conformation of the pleated loop.

The nature of intramolecular hydrogen bonds can be determined by studying changes in electron density. The NBO approximation considers electron density transfer from the donor to the acceptor. The formation of the hydrogen bond is accompanied by the transfer of the electronic density of the lone electron pair of oxygen to the anti-binding orbital of the OH bond.

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This leads to hybridization of orbitals of electron lone pairs and bonds [25]. The second-order Fock matrix was calculated to establish a donor-acceptor interactions [25] (Table 8).

There is a hyperconjugated interaction between the lone electron pairs of oxygen as a donor and the anti-binding orbital of the OH bond as an acceptor, thus ensuring charge transfer from the first to the second system. Our data show that in the molecule *AD8*, a complex interaction pattern is achieved by hydrogen bonds: $n(\text{LP}_1 \text{O}9) \rightarrow \sigma^*_1 (\text{O}100\text{-H}101)$, $n(\text{LP}_2 \text{O}9) \rightarrow \sigma^*_1 (\text{O}100\text{-H}101)$, and $n(\text{LP}_1 \text{O}9) \rightarrow \sigma^*_2 (\text{C}12\text{-C}16)$ with stabilization energies of the second order 15.25, 10.16, and 15.66 kcal/mol.

5. Summary

The infrared spectra of *p*-*tert*-butylcalix[8]arene and *p*-1-adamantylcalix[8]arene in a crystalline state, a solution, and at different temperatures were studied. The experimental data obtained show that the conformation of the pleated loop with a cyclic system of intramolecular hydrogen bonds is realized for all the studied calix[8]arenes. The analysis of the results of the calculations by the DFT method shows that the pleated loop conformation is more stable than the conformation of the chair. Theoretical infrared spectra are presented and the characteristic bands for each conformation are identified.

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