

# Investigation of the structure and hydrogen bonds in adamantylcalix[6]arene by IR spectroscopy and DFT



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## ABSTRACT

The IR spectra of p-tertbutylcalix[6]arene and adamantylcalix[6]arenes were investigated. The influence of heating and dissolution on the system of hydrogen bonds in calix[6]arenes was studied. The theoretical IR spectrum of adamantylcalix[6]arene in the conformation of a compressed cone agrees with experiment. Classification of bands in IR spectrum of adamantylcalix[6]arene was performed. Structure and strength of the H-bonding in calix[6]arenes depends on the type of substituent. In all calix[6]arenes studied, the cyclic H-bonds in the conformation of the compressed cone is realized. Under the action of adamantyl substituents, there is a convergence of oxygen atoms in the calix[6]arene molecules and the strengthening of H-bonds. Heating to a temperature of 180 °C and the dissolution of calix[6]arenes in neutral solvents does not lead to a change in their conformation.

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## 1. Introduction

To date, the most promising developed the direction of supramolecular chemistry can be considered the creation of “host molecules” with a pre-organized structure and with centers capable of efficiently and selectively binding neutral molecules and ions [1]. Calixarenes compounds whose chemistry has been intensively developed over the three decades are extremely useful for the realization of this goal [1–5]. Molecules of calixarenes are macrocycles with cavities of substantial dimensions and hydroxyl groups capable of forming intramolecular and intermolecular hydrogen bonds, which determines them as an object of supramolecular chemistry [1]. Calixarenes are often called the third generation of host molecules, macrocycles with almost unlimited possibilities; the ease of obtaining and modifying these compounds significantly distinguishes them from host molecules such as crown ethers and cyclodextrins [1]. As a rule, the calixarene molecules with unsubstituted hydroxyl groups on the lower rim, have a cup-like shape and therefore able to include in their cavity

and retain in it a wide range of organic ions and molecules [1]. Due to the presence of hydroxyl groups, calixarenes are easily subjected to chemical modification, which allows for high selectivity of binding of guests due to the optimal arrangement of functional groups on the rim of the molecular cup, i.e. this class of compounds can be successfully used as platforms of highly selective complexing agents in extraction processes [1].

Water-soluble modified, for example, -SO<sub>3</sub>Na groups in the upper rim, calixarenes are strong receptors for non-polar substrates in aqueous solutions [1]. To increase the selectivity of the extraction processes using calixarenes, attempts are being made to create cavities of certain dimensions in them, with the noncovalent binding being the leading role here, the cavity is fixed by a system of hydrogen bonds [1]. In connection with the rapidly deteriorating environmental situation, calixarenes are increasingly being used to solve serious problems. Calixarenes can be used as reliable sorbents of hazardous impurities. For example, calixarenes are used to purify acidic and alkaline media from technetium ions. In addition, calixarenes are able to selectively include carbon dioxide from their mixture of CO<sub>2</sub> and H<sub>2</sub> into their cavities, and also to adsorb methane molecules.

The study of hydrogen bonding in calixarenes is an integral part of modern studies that lead to the practical use of these compounds, for an example, to solve a number of environmental problems [1]. Calixarenes are currently used in various fields of

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human activity in medical practice and environmental protection [1]. The wide practical possibilities of calixarenes continue to attract research groups to their research [2–12]. Investigation of these objects continues to expand the scale of their use.

Various derivatives of calixarenes were studied by different physical methods [1–19]. These interesting data are scattered. Studies are usually conducted by authors using only one method. In calix[4]arenes a strong H-bond is realized. This is evidenced by data on the diffraction of X-rays. It can be expected that the introduction of adamantyl derivatives along the upper rim of calixarenes will significantly change the dimensions of their intramolecular cavity, and hence their ability to form complexes. But as far as we know the analysis of the summing up of these data to establish the structure-property relationship and the comparison of the strength of cooperative hydrogen bonds and the mutual influence of covalent and H-bonded macrocycles on each other have not been conducted before.

The purpose of our work was to establish the conformational state of adamantylcalix[6]arene (*AD6*) using the methods of IR spectroscopy and quantum chemistry. We tried to study the changes in the strength of hydrogen bonds in calix[6]arene molecules, depending on the type of substituent. The theoretical absorption curve of the molecule *AD6* is in good agreement with the experimental IR spectrum. The bands characteristic for conformation of the compressed cone were identified. Data obtained allowed us to interpret the IR spectra of *AD6*. Study of IR spectra at temperatures high enough to eliminate guest molecules but not high enough to destroy the *AD6* molecules themselves is perhaps the simplest way of observing pure *AD6*. At the same time, it is possible that even heating within the crystalline phase will cause conformational transitions and rearrangement of hydrogen bonds.

## 2. Experimental

Adamantylcalix[6]arene (*AD6*) was synthesized in [20] and is thermally stable. For comparison calix[6]arene (*C6*), and its *p*-*tert*-butyl derivative (*TB6*) have also been studied (Fig. 1). Synthesis and basic characteristics of *C6* and *TB6* have been described previously [1]. It is known that the melting and destruction temperatures of these compounds are rather high (350°C and higher) [1]. To remove the residues of water molecules and the solvent from the crystalline packaging, and to trace possible conformational transitions and changes in the hydrogen bond system, temperature studies of IR spectra were carried out. Gradually samples were heated up to 180°C.

The IR spectra in the 4000–400 cm<sup>-1</sup> region were recorded using a Vector-22 Bruker FTIR-spectrophotometer with a

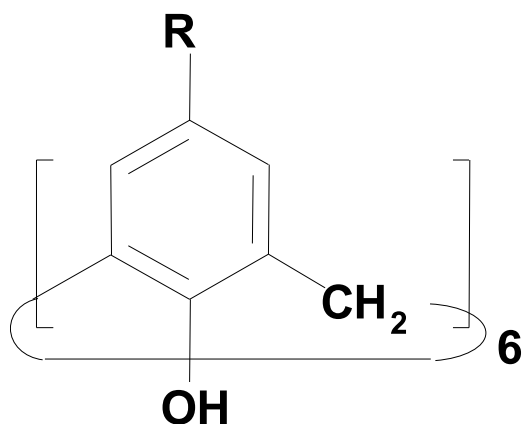


Fig. 1. Structure of calix[6]arenes; R = H, *t*-Bu, Ad.

resolution of 4 cm<sup>-1</sup>. The IR spectra of crystal samples were recorded in KBr tablets. Solvent CCl<sub>4</sub> was passed through molecular sieves, 3 or 4 Å, before being used to remove residual water. All solutions were prepared in a glove box to avoid moisture. The concentration of solutions in CCl<sub>4</sub> was 1·10<sup>-4</sup> mol l<sup>-1</sup>, the thickness of the cell was 2 cm.

## 3. Computational procedure

Optimization of the geometry and calculation of the IR spectrum of *AD6* was carried out in the framework of the density functional theory using the software package PRIRODA [21]. We used the PBE functional and the TZVP basis set. All stationary points were characterized as minima by analyzing the Hessian matrix. The software SHRINK [22] was used to calculate the distribution of potential energy. The assignment of bands in the IR spectrum was carried out by calculating the potential energy distribution (PED). Theoretical frequencies above 1700 cm<sup>-1</sup> were multiplied by 0.967. The calculations of natural bonding orbital (NBO) [23] were carried out using the Gaussian 09 software [24].

The electronic chemical potential, hardness, softness, and global electrophilicity index were calculated from the first vertical ionization energy *IE* and electron affinity *EA*:  $\mu \approx -(IE + EA)/2$ ,  $\eta \approx (IE - EA)$ ,  $S = 1/\eta$ , and  $\omega = \mu^2/2\eta$  [25].

## 4. Results and discussion

The IR spectra of *AD6*, *TB6*, and *C6* in the crystalline state and dilute solution in CCl<sub>4</sub> are shown in Figs. 2 and 3. OH groups show the frequencies: 3144 and 3143 cm<sup>-1</sup> for *AD6* in the crystal and solution. The degree of shift of  $\nu(\text{OH})$  band to low frequencies depends on the energy of the hydrogen bond. Band maximum of hydroxyl groups is characterized by the following frequency values: 3129 and 3165 cm<sup>-1</sup> for *TB6* and *C6* respectively. Consequently, the strongest H-bond is formed in a solution of

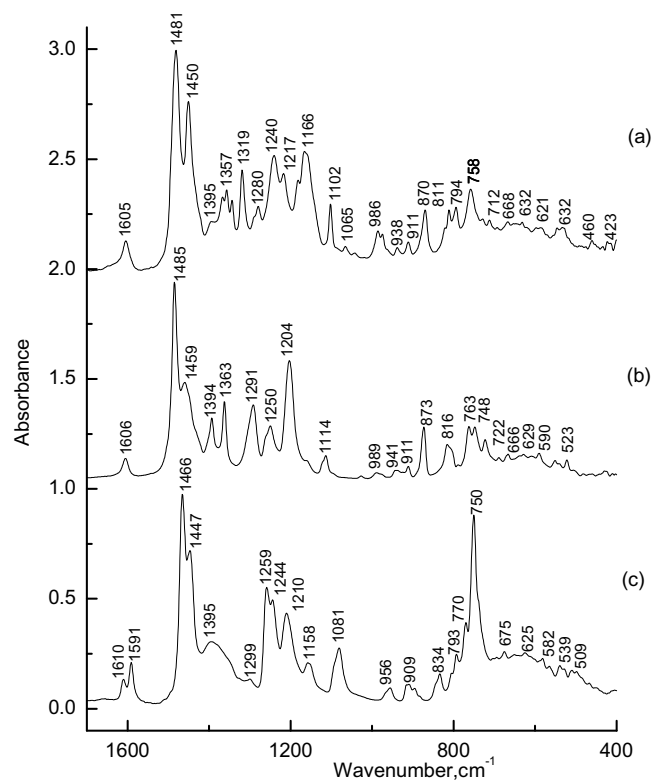


Fig. 2. Experimental IR spectra of crystalline *AD6* (a), *TB6* (b) and *C6* (c).

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