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ORIGINAL PAPER

Experimental and DFT investigation of structure and IR spectra of H-bonded associates of *p*-(3-carboxy-1-adamantyl)thiacalix[4]arene

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Abstract

The IR spectra of *p*-(3-carboxy-1-adamantyl)thiacalix[4]arene (*1-AdCOOHTC4A*) have been studied. IR spectra of crystalline *1-AdCOOHTC4A* obtained at room temperature or upon heating to 250 °C or its dilute solutions lack bands of free hydroxyl groups. The frequency of hydroxyl groups at 3377 cm^{-1} indicates the formation of an intramolecular H-bond along the lower rim of the *1-AdCOOHTC4A* molecule. On the top edge of thiacalixarene, the carboxyl groups form dimeric or cyclic tetrameric complexes via intermolecular H-bonds. The conformation of the cone persists, but there is a mutual influence of H-bonds along the upper and lower rims of the thiacalix[4]arene molecule. The structure with dimer H-bonds between carboxyl groups is 31.9 KJ/mol less preferable than the conformation with tetramer cyclic H-bonds for *1-AdCOOHTC4A*. Comparison of the absorption band of νOH alcohol hydroxyl groups in the IR spectra of *1-AdCOOHTC4A* at 3377 cm^{-1}, with the corresponding band of *1-AdTC4A* at 3372 cm^{-1}, suggests that the presence of the second system of H-bonds of carboxyl groups in the first molecule does not affect the H-bond of alcohol hydroxyl groups.

Keywords Calixarenes · IR spectra · Hydrogen bonding · Normal vibrations · DFT

Introduction

Calixarenes are excellent building materials for the design of new host molecules for supramolecular chemistry [1, 2]. In thiacalixarenes, the introduction of a sulfur atom as a bridge offers additional opportunities to vary the ring size, conformation, and binding properties of the macrocycle [3]. In search of new receptors for the recognition of molecules and ions, adamantylated thiacalixarenes have been synthesized [4]. The adamantyl moiety was chosen as the *p*-substituent because, due to its high lipophilicity, adamantylated thiacalixarenes dissolve well in organic solvents. Also, it has several positions for adding substituents, which helps regulate the ability of molecules to form complexes. It has been shown that the carboxylated calixarenes are molecular receptors for amines, metal ions, and aromatic hydrocarbons [5, 6].

Earlier, we showed that thiacalix[4]arenes with large *p*-adamantyl substituents on the upper rim are in conical conformation [7]. According to X-ray, IR, and NMR spectroscopy data, a strong H-bond is formed in the macrocycles of adamantylated thiacalix[4]arenes along the lower rim [4, 7].

It is known that carboxylic acids form dimers via H-bonds [8]. IR spectroscopy is a traditional method for studying H-bonds in calixarenes [9–15]. In this work, the H-bonds and the conformation of previously synthesized [4] *p*-(3-carboxy-1-adamantyl)thiacalix[4]arene (*1-AdCOOHTC4A*) were studied by IR spectroscopy and DFT. It is important to know how the extra H-bonds along the upper rim of thiacalix[4]arenes affect

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the molecular structure. We calculated the structure and IR spectra of *1-AdCOOHTC4A* for dimeric and tetrameric complexes formed by carboxyl groups. These studies are important for the synthesis of therapeutic drugs and tubes based on adamantyl thiacalix[4]arenes and to study their ionophoric and extraction properties [16–19].

Experimental

The synthesis of *p*-(3-carboxy-1-adamantyl)thiacalix[4]arene (*1-AdCOOHTC4A*) (**1**) has been previously described [4]. This compound was obtained from *p*-H-thiacalix[4]arene and 3-carboxy-1-adamantanol [2] (Fig. 1). For comparison, *p*-(3-carboxy-1-adamantyl)calix[4]arene (*1-AdCOOHC4A*) (**2**) and adamantylthiacalix[4]arene (*1-AdTC4A)* (3) have also been studied (Fig. 1).

The melting and destruction temperatures of this compound are quite high (350 °C and above) [4]. To remove residual water and solvent from the thiacalix[4]arene cavity and to determine changes in conformation and H-bonds, IR spectrum temperature studies were performed. Gradually, the samples were heated up to 180 °C.

IR spectra of thiacalix[4]arene samples in KBr pellets were recorded on a Vector-22 Bruker FTIR spectrophotometer in the range 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Solvent CCl_4 was passed through molecular sieves, 3 or 4 Å, before being used to remove residual water. All solutions have been designed in a glove box to avoid humidity.

Computational procedure

The DFT optimization of the geometry and the calculation of the IR spectra of *1-AdCOOHTC4A* were carried out using the B3LYP functional [21, 22], a 6-31G(d,p) basis set, and Gaussian 09 software [20]. We also calculated the energy difference between the dimeric and tetrameric structures using the Moller-Plesset second-order perturbation theory (MP2) [23] with the basis set 6-311++G(d,p) [20]. The SHRINK software [24] was used to calculate the potential energy distribution. The chemical potential, hardness, softness, and global electrophilicity index were calculated [25, 26].

Results and discussion

The IR spectra of *1-AdCOOHTC4A*, in the crystalline state and dilute CCl_4 solution, do not contain free absorption bands of νOH, neither about 3650 cm^{-1} for alcoholic hydroxyl groups nor about 3540 cm^{-1} for acidic hydroxyl groups (Fig. 2, Table 1). Therefore, we can conclude that in this molecule, all hydroxyl groups participate in the formation of intramolecular H-bonds.

Besides, alcoholic hydroxyl groups form cyclic intramolecular H-bonds with an νOH frequency of 3377 cm^{-1}, while the position of the νOH band of acidic hydroxyl groups, unfortunately, cannot be determined because it is below the outline of the bands of the stretching vibrations of the CH groups and is masked by these bands (Fig. 2). Therefore, the control of the mutual influence of two H-bonding systems, alcohol and acid in the *1-AdCOOHTC4A* molecule, is possible only through the νOH bands of hydroxyl groups and partially through the νC = O bands.

Comparison of the absorption band of νOH alcohol hydroxyl groups in the IR spectra of *1-AdCOOHTC4A* at 3377 cm^{-1}, with the corresponding band of *1-AdTC4A* at 3372 cm^{-1}, suggests that the presence of the second system of H-bonds in the first molecule of carboxyl groups does not affect the H-bond of alcohol hydroxyl groups (Fig. 2). Of course, the conical conformation of these molecules is also preserved.

The νC=O band shifts to lower frequencies when an H-bond is formed, although this shift is much less than that of hydroxyl groups. A doublet of bands at 1777 and 1697 cm^{-1} is observed in this region of the IR spectra of *1-AdCOOHTC4A*

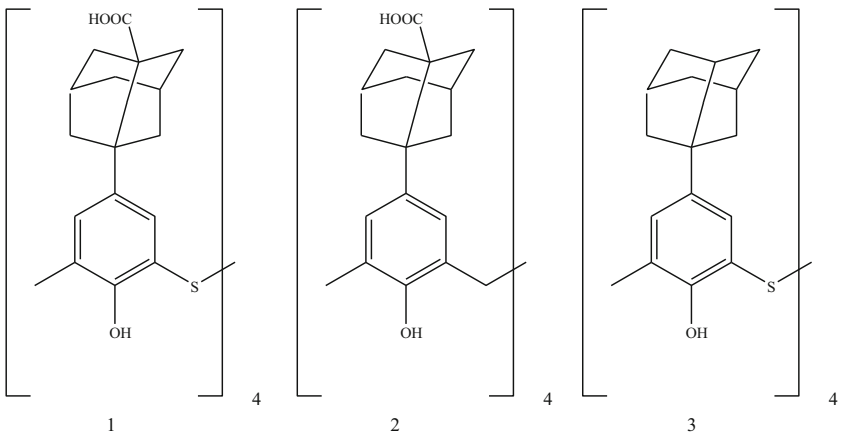


Fig. 1 Structure of *1-AdCOOHTC4A* (**1**), *1-AdCOOHC4A* (**2**), and *1-AdTC4A* (**3**)

Table 1 Experimental frequencies of νOH (cm^{-1}) of crystals and dilute solutions in CCl_4 of *1-AdCOOHTC4A*, *1-AdCOOHC4A*, and *1-AdTC4A*

Compound	Original cryst., T_{room}	T=250 °C	Cooled cryst., T_{room}	Solution in CCl_4
1-AdCOOHTC4A	3377	3372	3391	3379
1-AdCOOHC4A	3226, 3418	3251, 3534	3228	3152
1-AdTC4A	3372	3375	3372	3254

in the crystalline state (Fig. 2). The first band can be attributed to the vibrations of free carboxyl groups and the second frequency to the corresponding vibrations of the groups involved in the formation of H-bonds. Analysis of band intensities shows that the majority of carboxyl groups are involved in the formation of H-bonds. It is likely that the thiacalix[4]arene macrocycle somewhat spatially limits the possibility of H-bonding and results in a significant asymmetry in the dimers of the carboxyl group. Unfortunately, the limited solubility of thiacalixarene *1-AdCOOHTC4A* does not allow the observation of the free stretching vibrations bands νOH between 3700 and 3500 cm^{-1}.

Thiacalixarene molecules differ from classical calixarenes in the large size of the macrocycle and the electronic effect of sulfur atoms; therefore, the H-bond is weaker in the thiacalixarenes. In the IR spectrum of the *1-AdCOOHTC4A* molecule in the νOH region, there is a 3372 cm^{-1} band with a 3395 cm^{-1} shoulder. The IR spectrum of the corresponding *1-AdCOOHC4A* classical calixarene contains the 3226 and 3418 cm^{-1} bands. Thus, the weakening of the cyclic H-bond in thiacalixarene compared to classical calixarene is manifested by an increase in the νOH frequency.

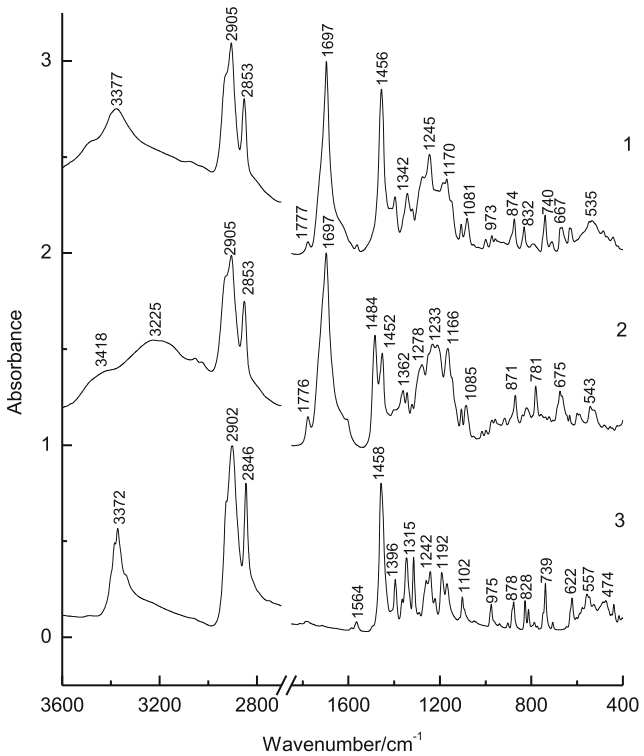
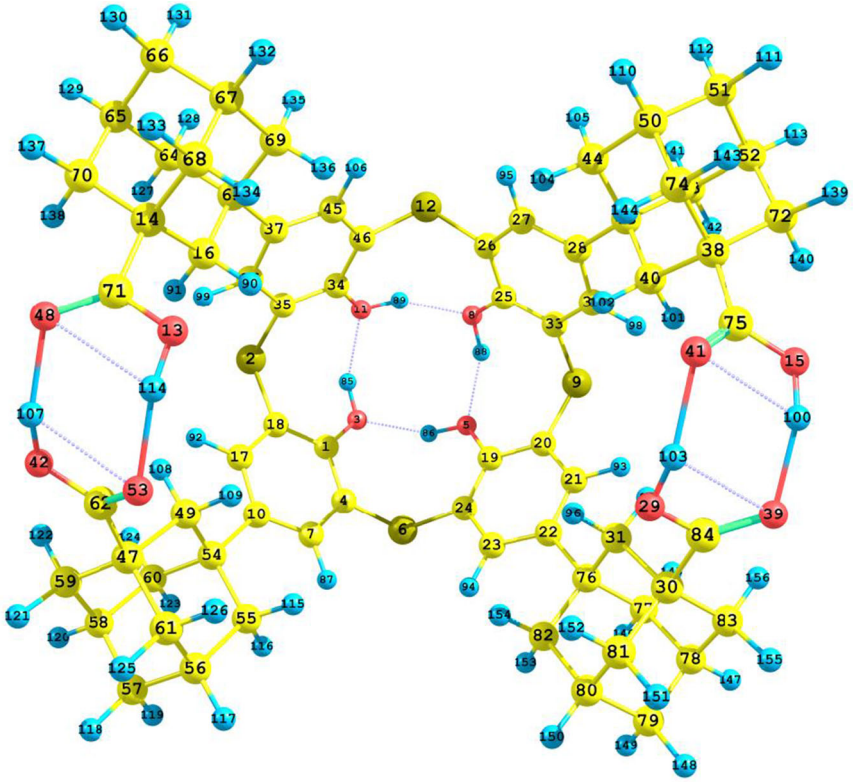


Fig. 2 Experimental IR spectra of crystalline *1-AdCOOHTC4A* (**1**), *1-AdCOOHC4A* (**2**), and *1-AdTC4A* (**3**)

The carboxyl groups of *1-AdCOOHTC4A* can be expected to form H-bonding dimers in pairs. The DFT calculations of the *1-AdCOOHTC4A* molecules were carried out, taking into account the possibility of formation of carboxyl group dimers or H-bonding rings (Fig. 3, Supplementary information S1). Both variants of the formation of H-bonds of carboxyl groups have been considered—H-bonded dimers and cyclic chains. It was found that the pattern of formation of two H-bonded dimers between adjacent carboxyl groups in the *1-AdCOOHTC4A* molecule was less energetically favorable; the energy difference calculated at the DFT B3LYP/6-31G(d,p) level was small—about 1.5 KJ/mol. It is known that DFT cannot correctly reproduce the relative energy of conformers. We calculated the energy difference between dimeric and tetrameric structures using the MP2 theory with the 6-311++G(d,p) basis set and get 31.9 KJ/mol. It is interesting to note that in classical calixarene *1-AdCOOHC4A*, the formation of dimeric complexes of carboxyl groups is more favorable [15]. The larger size of the macrocycle in thiacalixarene reduces steric hindrances to the formation of a cyclic system of H-bonds on the upper rim. Besides, due to the action of steric stress, the carboxyl groups in dimers become non-equivalent.

Thus, the distance r(O···O) is 2.65 Å for an H-bond located at the periphery of the macrocycle (external H-bond), while the second H-bond of the dimer, which is closer to the center of the macrocycle (internal H-bond), at a distance r(O···O) equal to 2.68 Å. This difference may explain the presence of a pair of νC=O bands in the spectrum of *1-AdCOOHTC4A*. It is important to emphasize that these parameters of the H-bonds of the dimers of the carboxyl groups do not change on switching to the classical calixarene *1-AdCOOHC4A* [15]. The dimers have a closed localized structure that changes little on going from molecule *1-AdCOOHTC4A* to molecule *1-AdCOOHC4A*. As follows from Fig. 2, the frequencies of carboxyl groups in the IR spectra of compounds *AdCOOHTC4A* and *1-AdCOOHC4A* remain unchanged.

For a scheme with a cyclic intramolecular H-bond between the four carboxyl groups of molecule *1-AdCOOHTC4A*, the mean distance r(O···O) is 2.68 Å on the upper rim and 2.85 Å on the lower rim (Fig. 3). The corresponding parameters for classical calixarene *1-AdCOOHC4A* are 2.67 and 2.69 Å [15].



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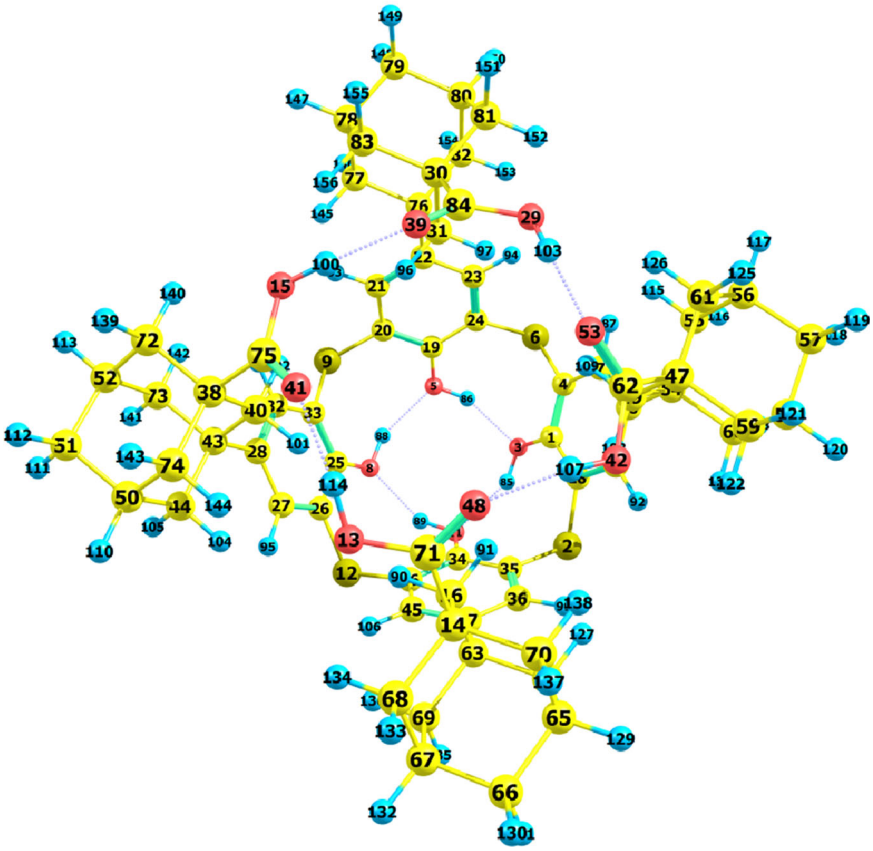

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Fig. 3 Optimized geometry and atom numbering for *1-AdCOOHTC4A* in the conformation cone with a cyclic system of hydrogen bonds along the lower rim and dimers (**1**) and cyclic hydrogen bonds along the upper rim (**2**)

For this type of complex, the parameters of the H-bonds along the upper rim of the molecules change very little, while the sizes of the lower macrocycles in *1-AdCOOHTC4A* and *1-AdCOOHC4A* differ markedly.

Hydrogen bonding strength can be described using Wiberg bond indices [27]. For the molecule *1-AdCOOHTC4A*, the average order of the cycle H-bonds on the lower rim is 0.057, which is noticeably less than the corresponding parameter 0.097 in molecule *1-AdCOOHC4A* [15]. These values of the Wiberg indices are consistent with the fact that thiacalixarenes have less strong H-bonds on the lower rim of the molecules in comparison with classical calixarenes.

For the H-bonds of dimeric associates of carboxyl groups on the upper rim of molecule *1-AdCOOHTC4A*, the Wiberg indices are 0.093 and 0.087. These values show that the external H-bonds of dimeric complexes are slightly stronger than internal, and the corresponding parameters in molecules *AdCOOHTC4A* and *AdCOOHC4A* change insignificantly.

The orders of the H-bonds for the cyclic associates on the upper and lower edges of the molecule *1-AdCOOHTC4A* are, respectively, 0.079 and 0.043. From these data, it follows that the H-bonds on the upper and lower rims of the molecules influence each other and that in thiacalixarene, there is a weakening of H-bonds.

The torsional angles φ(C17−C18−S2−C35) and χ(C18−S2−C35−C36) determine the conformation of the calixarenes [28]. The mean absolute values of the torsion angles of the molecule *1-AdCOOHTC4A* for the dimeric associations of carboxyl groups are equal to 95.0 and 94.9°, and for cyclic tetrameric H-bonds, they are 89.3 and 89.4° (Supplementary information S2). In molecule *1-AdTC4A*, these angles are 97.2 and 97.4°, respectively. We see that the association of carboxyl groups on the upper rim of calixarenes affects the orientation of aromatic fragments, while other geometric parameters of the molecules remain unchanged (Supplementary information S2).

We calculated the IR spectra of *1-AdCOOHTC4A* with dimeric and tetrameric associations on the upper rim (Supplementary information S3). Even the calculation of the harmonic DFT cannot correctly reproduce the experimental values of νOH alcohol hydroxyl groups (due to the anharmonic effect), it is interesting to compare the DFT frequencies for *1-AdCOOHTC4A* at 3378 cm^{-1} (dimer), 3426 cm^{-1} (tetramer) with the corresponding frequency of *1-AdTC4A* at 3360 cm^{-1}. Thus, the presence of the second system of H-bonds in the first molecule of carboxyl groups does not strongly affect the H-bond of alcohol hydroxyl groups.

The stretching vibration bands of the CH bonds are in the region 2800–3000 cm^{-1} of the experimental IR spectra of the *1-AdCOOHTC4A, 1-AdCOOHC4A*, and *1-AdTC4A* (Fig. 2). In this region, the IR spectra of the three compounds are very similar and contain bands of about 2930, 2905, 2853 cm^{-1} due to the CH stretching vibrations.

The intense band at 1697 cm^{-1} and a weak band at 1777 cm^{-1} are caused by stretching vibrations of the C=O bonds of carboxyl groups in the IR spectrum of *1-AdCOOHTC4A*. Bending vibrations of the methylene groups of the adamantyl substituent give rise to the 1456 cm^{-1} band. The IR spectrum shows 1417, 1396, 1342, and 1321 cm^{-1} bands caused by the CH bond deformation vibrations and the methylene groups waging vibrations (Fig. 2).

Stretching vibrations of CC and CO bonds and bending vibrations of CH bonds appear as bands 1276, 1245, and 1210 cm^{-1} in the IR spectrum. The bands 1185, 1170, 1149, and1107 cm^{-1} of the IR spectrum are attributed to the torsion of the methylene groups and the deformation of the CH bonds. Stretching vibrations of CC bonds and twisting vibrations of methylene groups give bands at 1081, 1053, and 1033 cm^{-1} in the IR spectrum. The 999, 973, 958, and 924 cm^{-1} bands in the IR spectrum have been attributed to the stretching of the CC bond vibrations, the rocking vibrations of the methylene groups, and the bending vibrations of the CCC angles.

The stretching vibrations of the CC bonds and the rocking vibrations of the methylene groups lead to the appearance of 891, 874, and 832 cm^{-1} bands in the infrared spectrum. The stretching vibrations of the CC bonds determine the frequencies at 795, 740, and 710 cm^{-1} in the IR spectrum.

The bands at 674, 667, 633, and 626 cm^{-1} in the IR spectrum were identified as deformation vibrations of skeletal angles. The bands at 547, 535, 486, 469, 443, and 425 cm^{-1} in the IR spectrum are caused by deformation and torsion vibrations of the macrocycle and molecular skeleton.

It is interesting to determine the differences in the IR spectra of the thiacalix[4]arene *1-AdCOOHTC4A* for the dimeric and tetrameric associations of the carboxyl groups on the upper rim of the molecules (Fig. 4, Supplementary information S3). For analytical purposes, the characteristic bands of the molecule *1-AdCOOHTC4A* bands 1264, 1238, and 724 cm^{-1} (dimer) and 1223, 1192, and 652 cm^{-1} (tetramer) were selected. These bands are caused by stretching and bending vibrations of the cyclic dimeric and tetrameric associates.

In this article, we have also attempted to describe the reactivity of calixarenes using global descriptors (Table 2). Due to the carboxyl substituents, the ionization energy increases in *1-AdCOOHTC4A* compared to *1-AdTC4A*, but electron affinity decreases. The chemical potential increases from *1-AdTC4A* to *1-AdCOOHTC4A*. The softness of the molecules of thiacalix[4]arenes decreases with the transition to *1-AdCOOHTC4A* from *1-AdTC4A*. The global electrophilic index is higher for *1-AdCOOHTC4A*. The reactivity of the thiacalix[4]arenes *1-AdCOOHTC4A* and *1-AdTC4A* is higher than for the classical calix[4]arene *AdCOOHC4A*.

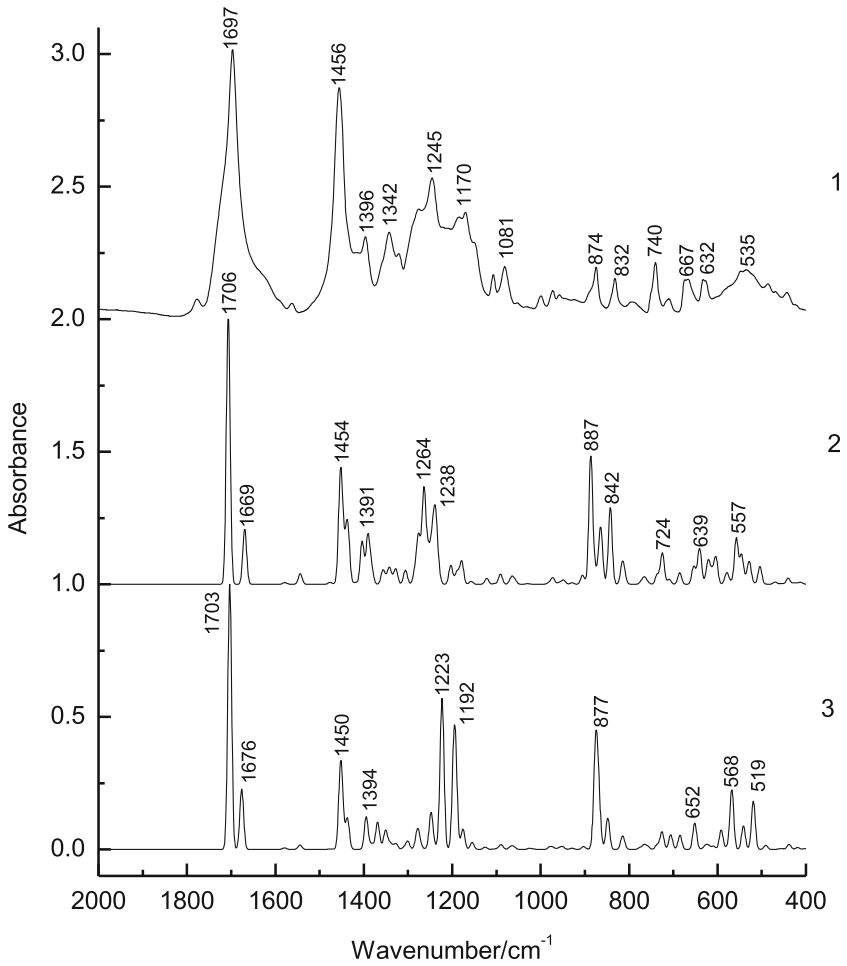

Fig. 4 Experimental (**1**) and theoretical IR spectra of *1-AdCOOHTC4A* in the conformation cone with a cyclic system of hydrogen bonds along the lower rim and dimers (**2**) and cyclic hydrogen bonds (**3**) along the upper rim in the region 1800–400 cm^{-1}

Summary

We studied the IR spectra of *1-AdCOOHTC4A* and *1-AdCOOHC4A* in a crystalline state, in solution, and at different temperatures. The formation of an intramolecular H-bonds between the carboxyl groups on the top rim of the calixarene molecules *1-AdCOOHTC4A* and *1-AdCOOHC4A* does not weaken the cooperative cyclic intramolecular H-bonding on the lower rim of the molecules. Theoretical infrared spectra are presented, and the characteristic bands for each type of associates are identified.

For *1-AdCOOHTC4A* molecules in diluted solutions in CCl4, intramolecular H-bonding between adjacent carboxyl groups is performed along the top rim. These are either H-bonded dimers of neighboring carboxyl groups or a cooperative cyclic intramolecular H-bond with the participation of the four carboxyl groups along the top rim.

The structure of the molecules is determined by the mutual influence of two H-bonded macrocycles between the carboxyl (upper rim) and hydroxyl (lower rim) groups. In the thiacalix[4]arene *1-AdCOOHTC4A*, it causes a slight weakening of the cooperative cyclic intramolecular H-bond to the calix[4]arene molecule *1-AdCOOHC4A*.

Table 2 Global reactivity descriptors of *1-AdCOOHTC4A*, *1-AdCOOHC4A*, and *1-AdTC4A*

System	Ionization energy, eV	Electron affinity, eV	Chemical potential, eV	Softness, eV	Electrophilicity index, eV
1-AdCOOHTC4A, dimer	7.184	−0.091	−3.547	0.275	1.729
1-AdCOOHTC4A, tetramer	7.193	−0.161	−3.677	0.284	1.923
1-AdCOOHC4A, dimer	6.822	−0.452	−3.185	0.137	1.395
1-AdCOOHC4A, tetramer	6.821	−0.423	−3.199	0.138	1.413
1-AdTC4A	7.038	−0.163	−3.438	0.278	1.641

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Author's contributions Victor Furer: Conceptualization, methodology, software, writing—original draft preparation and editing.
Ludmila Potapova: Investigation of IR spectra.
Denis Chachkov**:** Computations of calixarenes.
Ivan Vatsouro**:** Synthesis of calixarenes.
Vladimir Kovalev: Conceptualization, methodology, reviewing, and editing.
Elvira Shokova**:** Synthesis of calixarenes.
Valery Kovalenko**:** Conceptualization, methodology, reviewing, and editing.

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Data availability We allow the journal to review all the data, and we confirm the validity of results.

Code availability NA.

Declarations

Ethics approval The authors agree with ethical standards. This work was not published previously and is not submitted to more than one journal. No data have been fabricated or manipulated.

Consent to participate The authors agree to participate in the article.

Consent for publication The authors agree to participate in the publication of the article.

Conflict of interest The authors declare that they have no conflicts of interest.

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