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Study of p-(3-carboxymethyl-1-adamantyl)calix[4]arene and tetrapropoxy-p-(3-carboxymethyl-1-adamantyl)calix[4]arene by vibrational spectroscopy and DFT

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ABSTRACT

The IR and Raman spectra of p-(3-carboxymethyl-1-adamantyl)calix[4]arene (1) and tetrapropoxy-p-(3-carboxymethyl-1-adamantyl)calix[4]arene (2) were studied. In the IR spectra of crystals and solutions of calixarenes, there is no band of stretching vibrations of free OH groups. In the IR spectrum of compound 1 in the crystalline state, an intense wide band is observed at 3187 cm−1. In the IR spectrum of a dilute solution in CCl4, this band shifts to 3118 cm−1. The carboxyl groups form cyclic dimer or tetramer complexes.

The formation of dimers of carboxyl groups is more favorable than for cyclic tetramers. The energy difference is 33.8 and 53.0 kJ/mol in compounds 1 and 2, respectively. The calculation showed that molecules 1 and 2 of dimeric and tetrameric complexes assume the cone conformation. The molecules of compound 2 are in the cone conformation even in the absence of hydrogen bonds along the lower rim.

1. Introduction

Molecular receptors based on calixarenes can be obtained by functionalizing them with carboxyl groups [1–4]. Calixarenes carboxylated along the upper rim are receptors for different classes of compounds [2–4]. The adamantylcalixarenes carboxylated along the upper rim can be received using a convenient one-step procedure [5]. According to the data of various physical methods, a strong hydrogen bond is realized in the lower rim of calixarenes, and the molecules are in the cone conformation [6, 7].

Under the action of bulky adamantyl substituents in the para-position on the upper rim of calixarenes, the hydroxyl groups on the lower edge come closer together and strengthen the hydrogen bond [8]. Also, the volume of the cavity of calixarene molecules significantly increases, and their receptor properties change. Carboxyl groups form strong hydrogen bonds [9]. In the carboxylated adamantylcalixarenes, hydrogen bonds exist at the upper and lower edges. Adamantyl fragments can be used for the further modification of calixarenes [5].

Vibrational spectroscopy is one of the most convenient and widespread physical methods for studying molecular structure [10]. IR spectroscopy is used to study hydrogen bonds in calixarenes [11–14]. Raman spectra of calixarenes are insufficiently studied. Density functional theory (DFT) can predict the vibration frequencies of large organic molecules [15].

In this work, the H-bonds in p-(3-carboxymethyl-1-adamantyl)calix[4]arene (**1**) were investigated by vibrational spectroscopy. For comparison, the vibrational spectra of tetrapropoxy-p-(3-carboxymethyl-1-adamantyl)calix[4]arene (**2**) in which the phenolic hydroxyl groups are substituted by n-propyl were studied [5]. In the first compound, hydrogen bonds are formed at the upper and lower rims of the molecules.

Alkylation of hydroxyl groups leads to the breaking of hydrogen bonds at the lower rim. The carboxyl groups on the upper rim can form dimers and cyclic tetramers. It is interesting how additional hydrogen bonds along the upper rim of the calixarenes affect the

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conformation of the molecule and the hydrogen bonding system of the hydroxyl groups. We tried to establish how the hydrogen bonds affect the conformation and reactivity of calixarenes.

Adamantyl calixarenes are used for the extraction of radionuclides [8]. They are ionophores of compounds that play a significant role in biology [8]. Information on the structure and properties of calixarenes is necessary for their practical use.

2. Experimental

The p-(3-carboxymethyl-1-adamantyl)calix[4]arene (**1**) was synthesized using a one-step procedure from p-H-calix[4]arene and 3-carboxymethyl-1-adamantol (Fig. 1) [5]. Tetrapropoxy-p-(3-carboxymethyl-1-adamantyl)calix[4]arene (**2**) alkylated at the lower rim was obtained in three steps according to the procedure described earlier [5]. The proposed structures and purity of macrocyclic compounds 1 and 2 were confirmed by ^{1}H and ^{13}C NMR and elemental analysis data [5].

IR spectra of calixarenes in the range 4000–400 cm^{-1} were obtained on a Vector-22 Bruker FTIR spectrophotometer. The optical resolution of 4 cm^{-1} with the accumulation of 128 scanned images. Samples for recording IR spectra were KBr pellets (ground in a mortar and then pressed). Calixarenes typically contain water and solvent molecules in their cavity. Heating to a temperature of 180 °C makes it possible to get rid of the solvent molecules. The carbon tetrachloride solvent was passed through a molecular sieve to remove residual water. The solutions were placed in a glove box to avoid humidity. The thickness of the cell was 2 cm, and the concentration of the solutions in CCl_4 was $1 \cdot 10^{-4}$ mol l^{-1}.

Raman spectra were excited by a 1064-nm line of an Nd: YAG laser with a power of 50 mW on the sample. They were recorded in the 3500–100 cm^{-1} region on a Vertex 70 instrument (Bruker) equipped with a RAM II attachment with an optical resolution of 2 cm^{-1}.

3. Computational procedure

Molecular models for calix[4]arenes **1** and **2** have been constructed for the most energetically favorable cone conformation [1]. The geometry of the calix[4]arene in conical conformation has been optimized. Along the upper rim of the optimal calixarenes structure, adamantyl groups have been added in the para-position. Then, carboxyl groups were attached to the adamantane substituents. Calixarene **2** was constructed from calixarene **1** by replacing hydroxyl groups with n-propyl moieties. We consider structures with dimeric and tetrameric associates of carboxylate groups.

The DFT calculation of the spectra of molecules **1** and **2** was carried out using the Gaussian 09 program [16]. The molecules are composed of 176 (**1**) and 212 (**2**) atoms, respectively; therefore, for the optimum ratio of precision and computation time, the B3LYP functional and the 6–31G(d,p) (6D, 7F) basic set were chosen. Potential energy distribution (PED) was calculated using the SHRINK program to assign bands in vibrational spectra [17]. The natural bonding orbitals (NBO) [18] were calculated using Gaussian 09 software.

4. Results and discussion

Vibration bands of free hydroxyl groups are absent in the IR spectra of **1** in the crystalline state and dilute solutions in CCl_4 (Figs. 2 and 3, Table 1). Therefore, in molecules **1** and **2**, all hydroxyl groups participate in the formation of hydrogen bonds. Since these are very dilute solutions (concentrations of about $1 \cdot 10^{-5}$ mol/l) of compound **1**, it can be assumed that the hydrogen bonds between the carboxyl groups are intramolecular.

In the IR spectrum of compound **1** in the crystalline state in the νOH region, a strong band is observed at 3187 cm^{-1}. In the IR spectrum of the dilute solution, a band at 3118 cm^{-1} is ob-

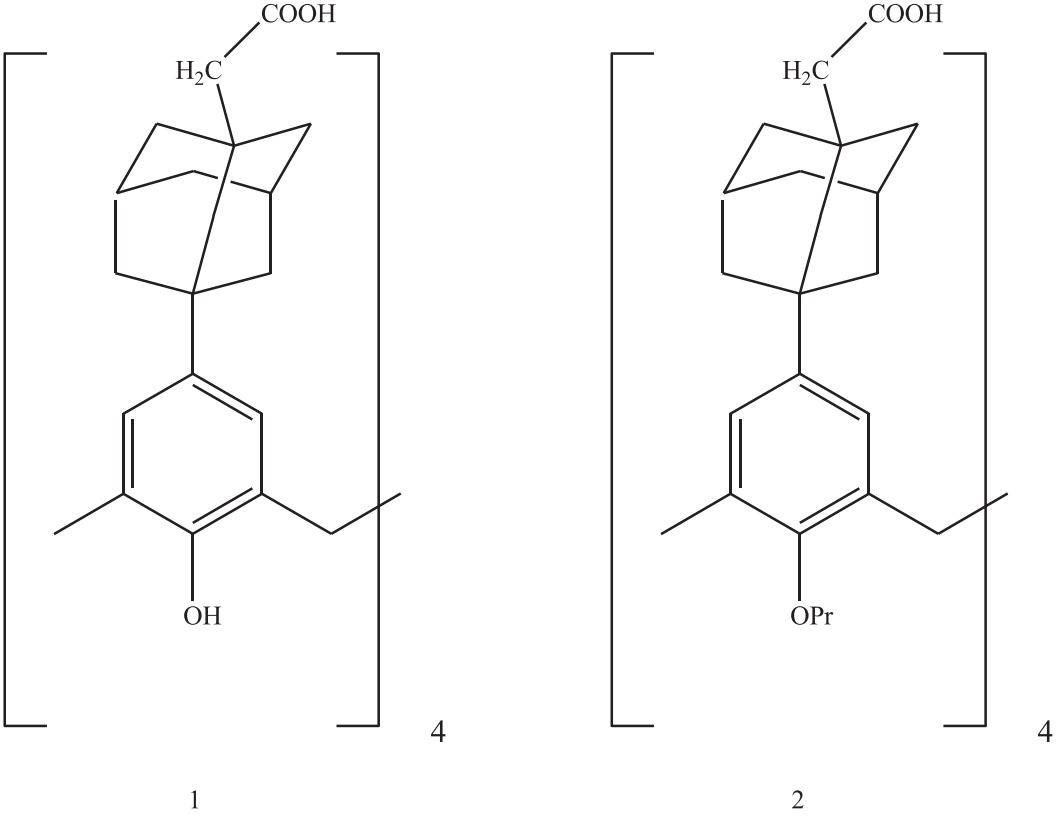


Fig. 1. Structure of compounds **1** (1) and **2** (2).

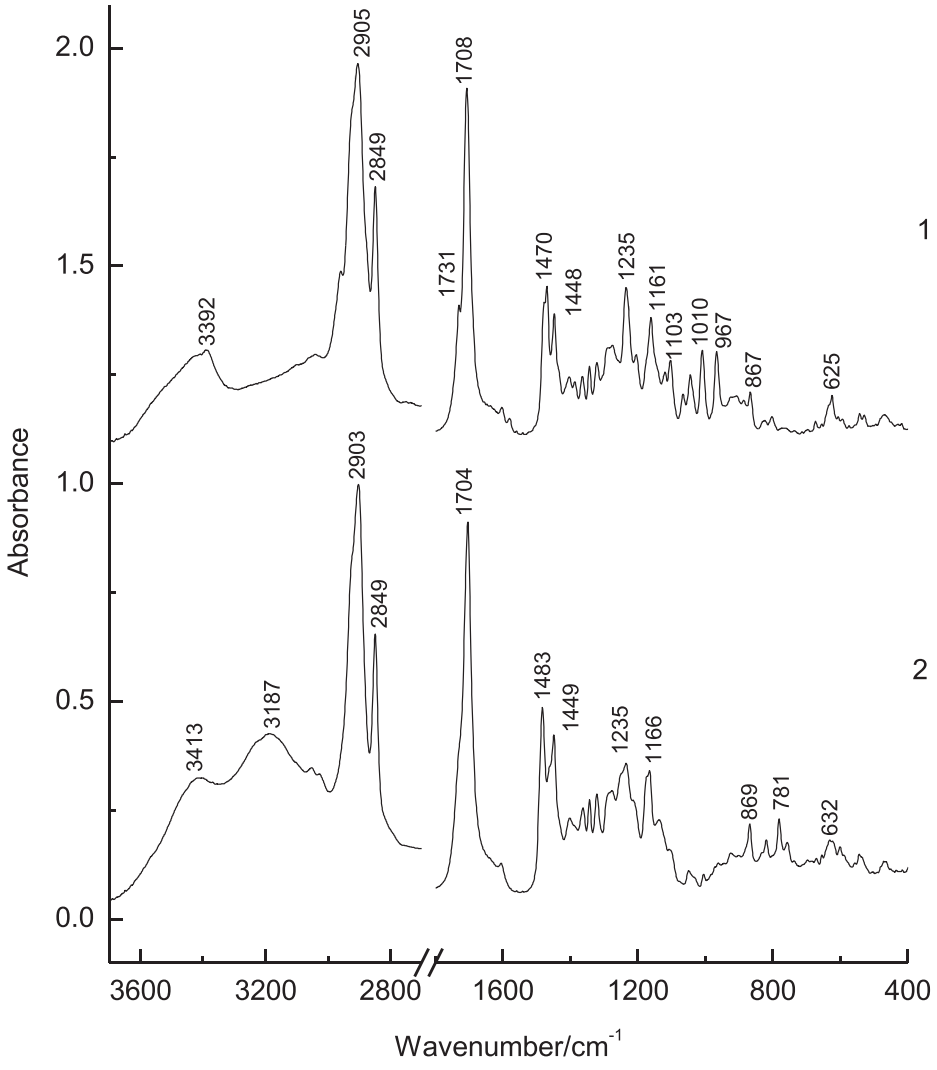


Fig. 2. Experimental IR spectra of crystalline compounds **2** (1) and **1** (2).

Table 1
Experimental frequencies of νOH (cm^{-1}) of crystals and dilute solutions in CCl_4 of **1** and **2**.

Compound	Original cryst., T_{room}	T=180 ^{0}C	Cooled cryst., T_{room}	Solution in CCl_4
1	3400, 3187	3528, 3242	3194	3118
2	3392			

served. It is absent from the IR spectrum of compound **2**. Therefore, this band can be attributed to the vibrations of alcoholic hydroxyl groups involved in the cyclic hydrogen bond along the lower rim of molecule **1**. Shifting this band to lower frequencies means that due to the removal of steric hindrances in dilute solutions, a stronger H-bond is achieved than in the crystalline state.

The νOH frequency at 3187 cm^{-1} in calixarene **1** is higher than 3137 cm^{-1} in p–tert-butylcalix[4]arene. But the cone conformation is preserved in these molecules. The frequency differences are due to steric hindrances for the larger adamantyl substituents of calix[4]arene. The hydrogen bond complexes on the lower and upper rims of calixarene molecules influence each other. In calixarene **1**, the lower macrocycle weakens hydrogen bonds between carboxyl groups. In turn, under the influence of hydrogen bonds on the upper rim of calixarene molecules, the cooperation of alcohol hydroxyl groups decreases, and the frequency of νOH increases.

The νOH vibrations of crystal lattice defects with frequencies 3400 and 3392 cm^{-1} appear in IR spectra of **1** and **2**, respectively. Upon heating to 180 °C and subsequent cooling of sample **1**, the band at 3400 cm^{-1} in the IR spectrum decreases.

The νOH band of carboxylic acids overlaps with stretching vibrations of CH bonds [9]. Therefore, they are hard to identify. This band lies in the region of 2700–2500 cm^{-1} due to the extraordinary strength of hydrogen bonds in carboxylic acids [9]. In the IR spectra of compounds **1** and **2**, there is a band at 2672 cm^{-1}, which can be carefully attributed to stretching vibrations of the hydroxyl bonds of the carboxyl groups. The νOH frequencies of dimers of carboxyl groups are the same in the IR spectra of compounds **1** and **2**.

The $\nu C{=}O$ band characterizes the hydrogen bonds of the carboxyl groups. For organic monocarboxylic acids, the cyclic dimer shows a $\nu C{=}O$ absorption band at about 1700 cm^{-1}. The chain of hydrogen bonds of carboxyl groups gives a band at about 1650 cm^{-1} [9].

In the IR spectrum of compound **1** contains a νC=O band at 1704 cm^{-1} with a shoulder at about 1730 cm^{-1} (Fig. 2). A dou-

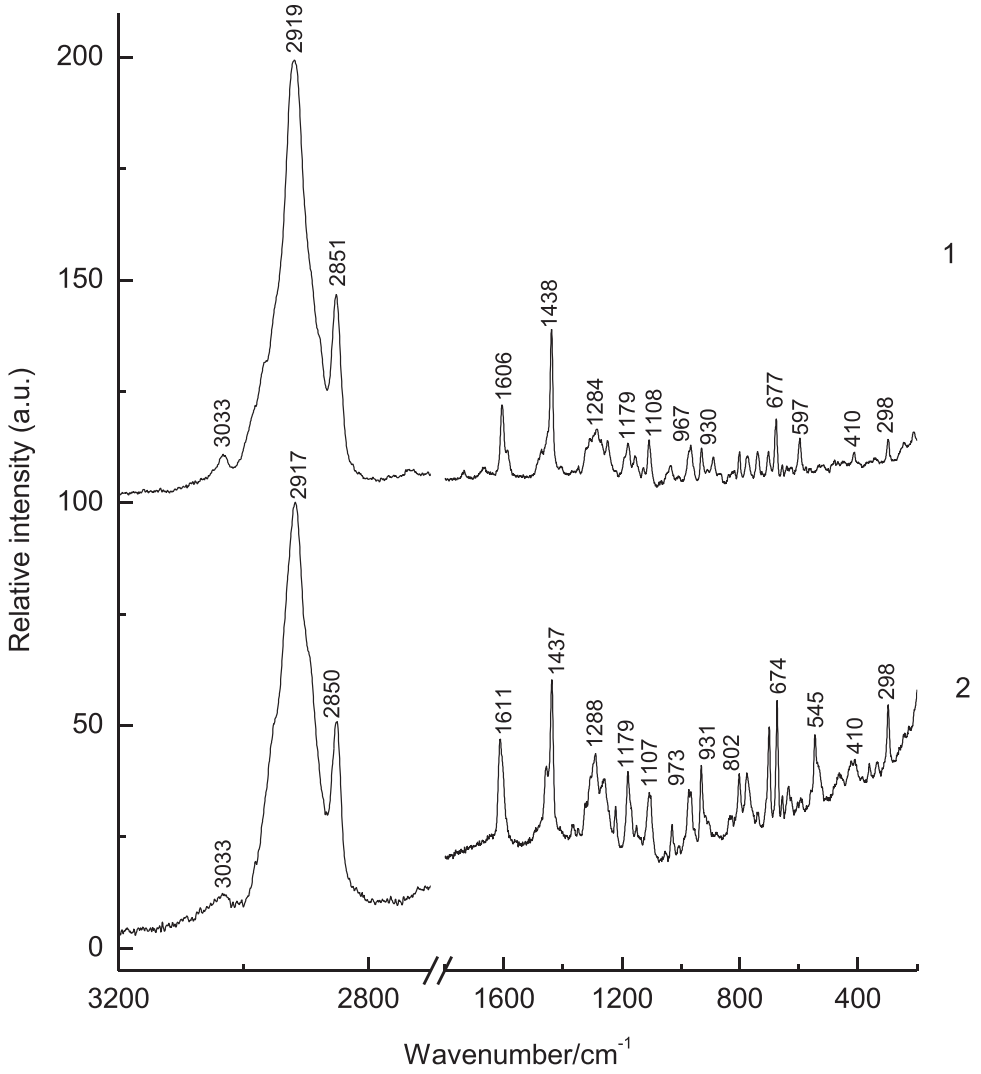


Fig. 3. Experimental Raman spectra of compounds **2** (1) and **1** (2).

blet of bands at 1731 and 1708 cm^{-1} is observed in this region of the IR spectra of calixarene **2**. Such frequencies are characteristic of carboxyl groups forming dimeric hydrogen-bonded complexes. Two frequencies $\nu C{=}O$ indicate the non-equivalence of the carbonyl groups in the complex.

We have considered two variants of hydrogen bond complexes of carboxyl groups in calixarenes **1, 2**, dimers, and cyclic tetramers (Figs. 4 and 5). The formation of dimers of carboxyl groups is more favorable than for cyclic tetramers. The energy difference is 33.8 and 53.0 kJ/mol in compounds **1** and **2**, respectively. The calculation showed that molecules **1** and **2** of dimeric and tetrameric complexes occupy the cone conformation (Figs. 4 and 5, Supplementary information S1, S2).

In dimers, the distance r(O•••O) is 2.64 Å equal for peripheral carboxyl groups and 2.63 Å for internal groups. In the tetrameric complex structure of carboxyl groups, the average distance r(O•••O) is 2.66 Å at the upper rim and 2.67 Å at the lower edge.

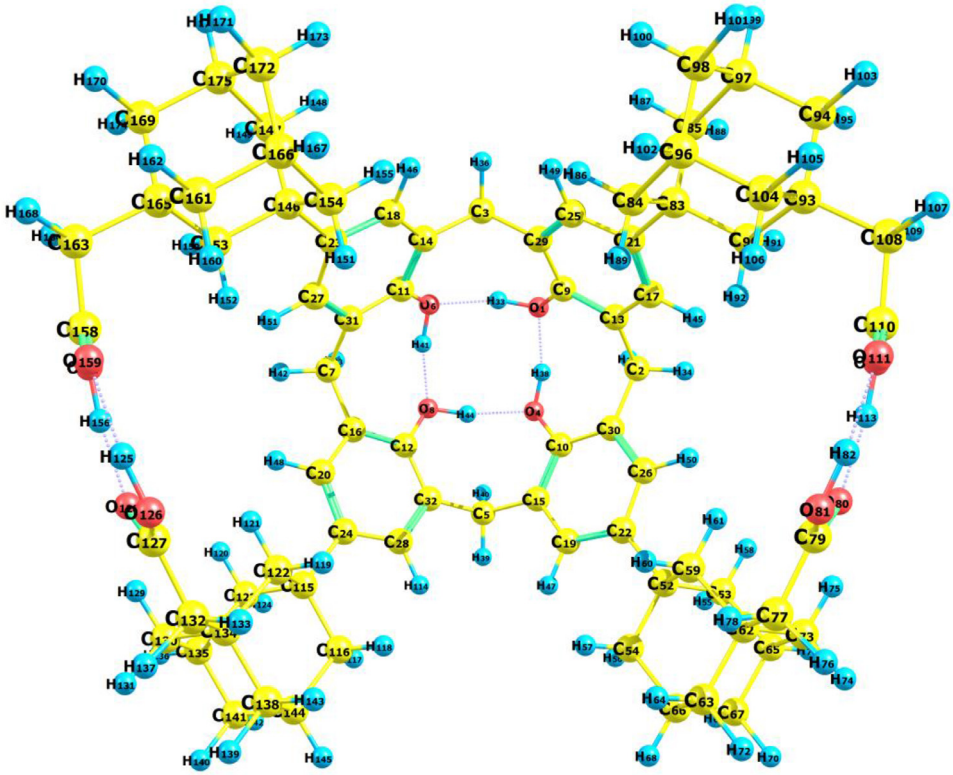
Molecule **2** has no hydrogen bonds on the lower rim. The average distance r(O•••O) is equal to 3.29 and 3.13Å, for dimeric and tetrameric complexes of carboxyl groups, at the upper rim, respectively. The mean distance r(O•••O) in dimeric complexes of carboxyl groups of molecule **2** is 2.64 Å, and in tetrameric complexes, it is 2.66 Å. The structure of dimeric complexes of carboxyl groups does not depend on the H-bonds of hydroxyl groups.

The angles of torsion φ(C26−C30−C2−C13) and χ(C30−C2−C13−C17) determine the conformation of calixarenes [19]. The mean absolute values of the torsion angles of molecule **1**, the dimeric associations of the carboxyl groups are equal to 94.6 and 95.0º, for the cyclic tetramer H-bonds, they are 90.5 and 90.9º (Supplementary information S3). In molecule **2**, the mean values of the angles of torsion are respectively equal to 95.2 and 89.0º (dimers) and 88.7 and 90.9º (tetramer) (Supplementary information S3).

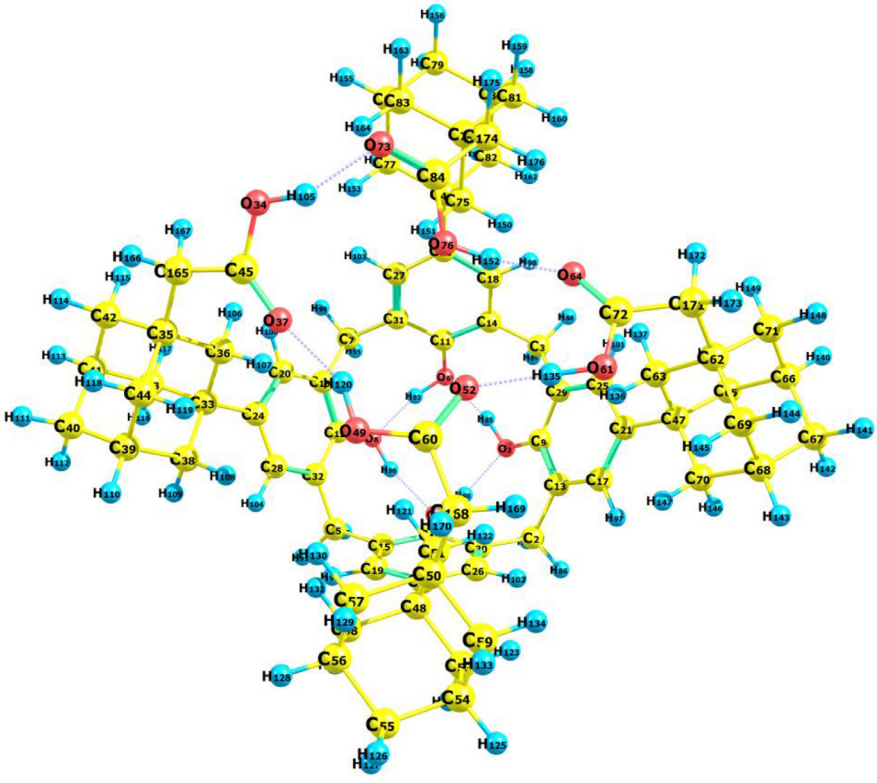
The association of carboxyl groups leads to a change in the orientation of the aromatic fragments of calixarenes. The other geometric parameters of molecules **1** and **2** change little upon association (Supplementary information S1 and S2). Thus, our calculations show that the molecules of compound **2** are in cone conformation even in the absence of hydrogen bonds along the lower rim.

We calculated the IR and Raman spectra of calixarenes **1** and **2** (Supplementary information S4, S5, Figs. 6–9). Such a calculation allows the assignment of bands in the experimental IR spectrum of calixarenes.

IR activity assumes a non-zero transition dipole moment, while Raman activity presupposes non-zero transition polarizability. For

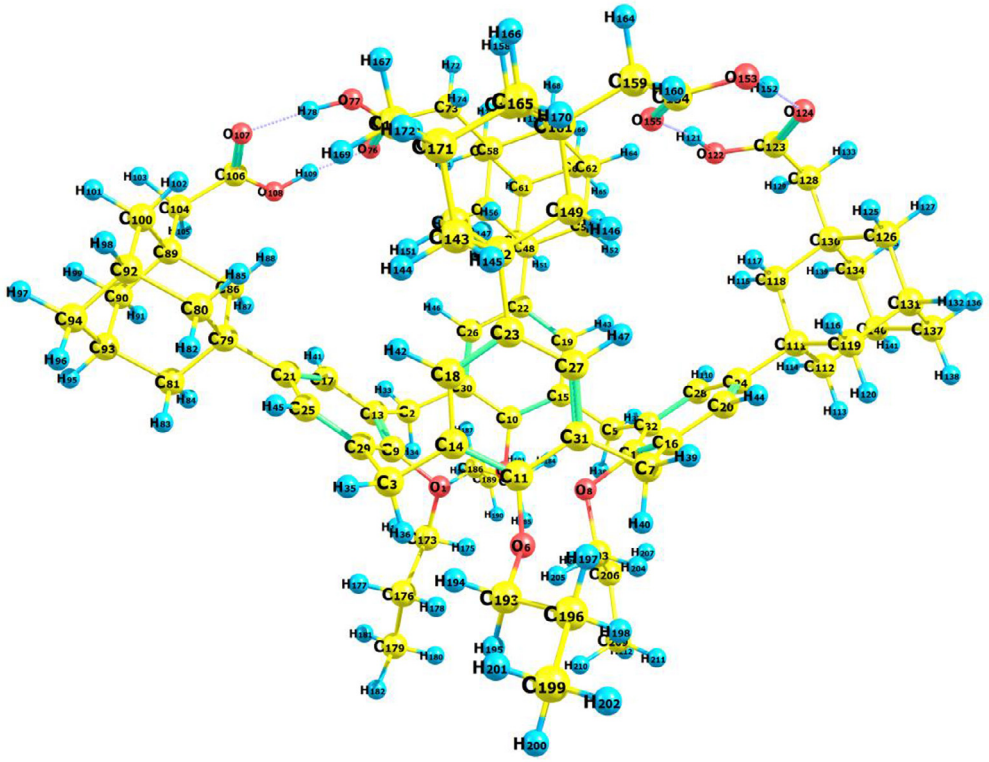


1



2

Fig. 4. Optimized geometry and atom numbering for compound **1** 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). Yellow, blue, and red colors correspond to carbon, hydrogen, and oxygen atoms.



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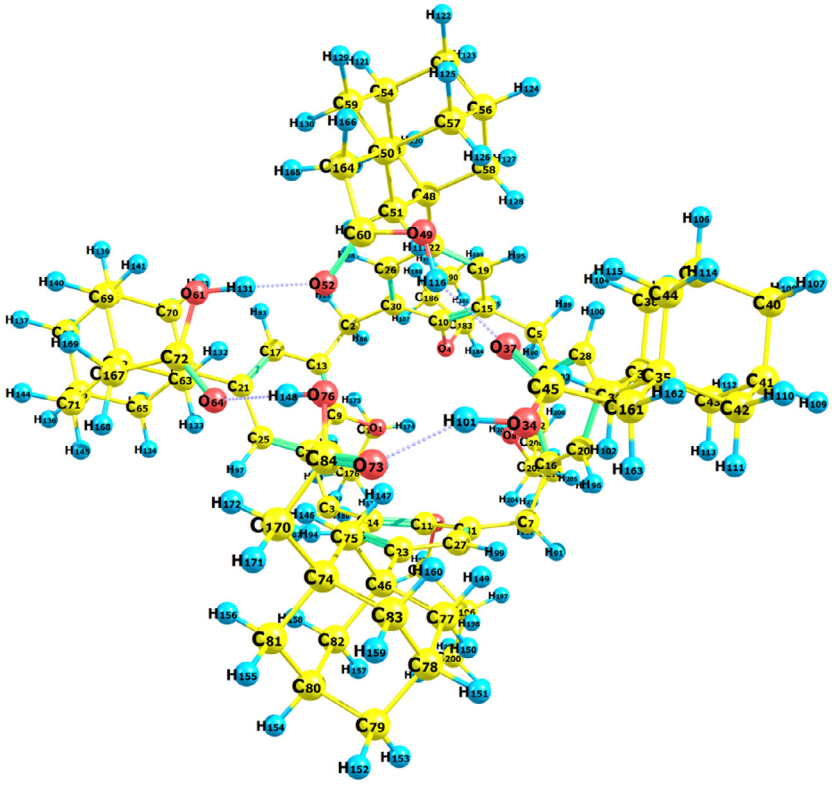

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Fig. 5. Optimized geometry and atom numbering for compound **2** in the conformation cone with dimers (1) and cyclic hydrogen bonds along the upper rim (2). Yellow, blue, and red colors correspond to carbon, hydrogen, and oxygen atoms.

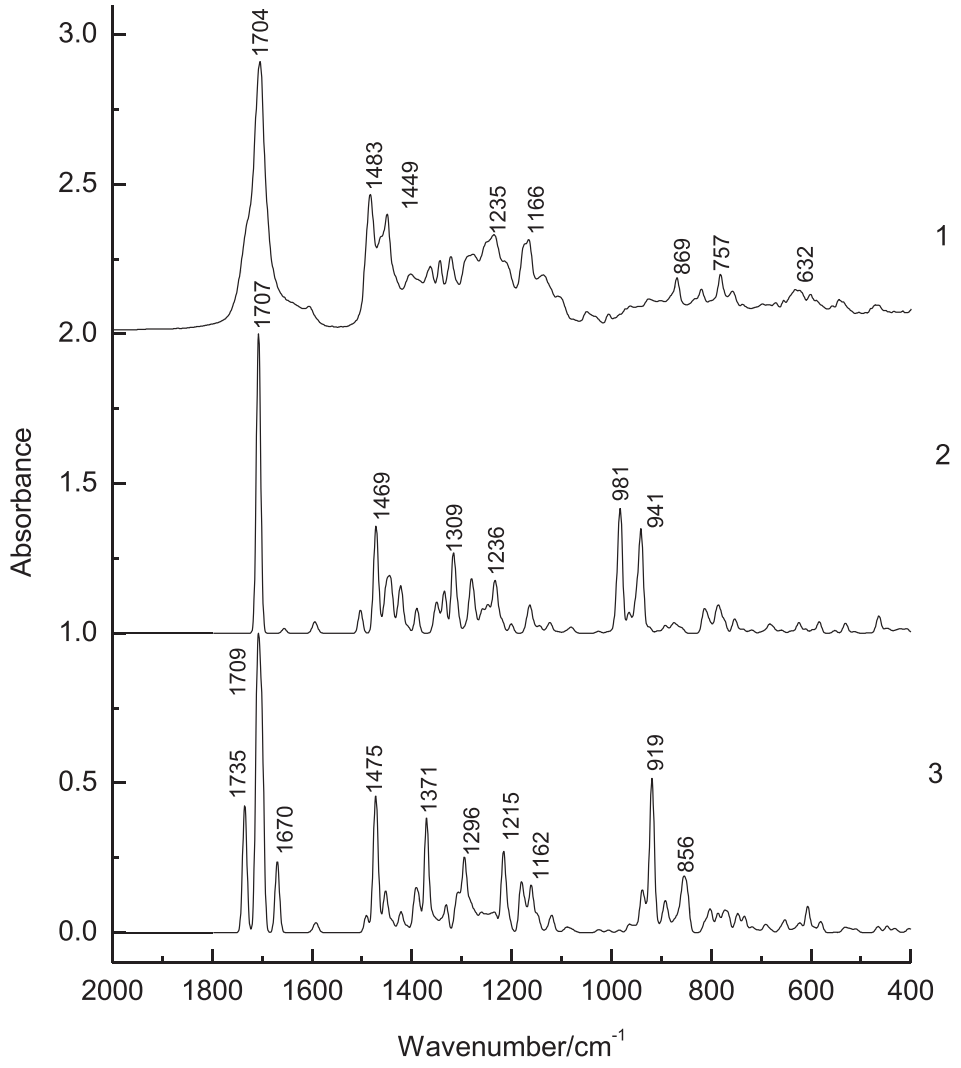

Fig. 6. Experimental (1) and theoretical IR spectra of compound **1** in the conformation cone with a cyclic system of hydrogen bonds along the lower rim and dimers (2) and cyclic hydrogen bonds (3) along the upper rim in the region 1800–400 cm^{-1}.

a complex asymmetric molecule, all normal modes are active in IR and Raman spectra. We see that some of the modes are inactive in both IR and Raman spectra (Supplementary information S4, S5). The ideal symmetry of calixarene molecules in the cone conformation belongs to the C_4 point group. In the crystalline state, the symmetry decreases to C_2. However, some local vibrations have higher symmetry and are inactive in the IR and Raman spectra.

The vibrational bands of CH bonds stretch are in the 2800–3000 cm^{-1} region of the experimental IR and Raman spectra of compounds **1** and **2** (Fig. 2). The IR spectra of the two compounds in this region are very similar and contain bands at 2903, 2849 cm^{-1}, and the shoulders at 3052, 3027 cm^{-1} due to the CH stretch vibrations. The lines at 3033, 2919, and 2851 cm^{-1} are observed in the Raman spectra of compounds **1** and **2**.

A band at 1611 cm^{-1} in the Raman spectrum of compound **1** is caused by stretching vibrations of aromatic groups. In this region of the Raman spectrum of compound **2**, two bands are visible at 1606, 1587 cm^{-1}, characteristic of para-substituted aromatic units.

Bending vibrations of the CH_2 groups cause a band at 1483 cm^{-1} in the IR spectrum of compound **1**. Bending vibrations of the methylene groups of the adamantyl substituent lead to the appearance of bands at 1449, 1402 cm^{-1} in the **1** IR spectrum (Fig. 6). Raman spectra of compound **1** in this region contain bands at 1455, 1437 cm^{-1} (Fig. 7). In the IR spectra of compound **2** in this region, there are bands at 1477, 1470, and 1404 cm^{-1} (Fig. 8). The first two bands are absent from the spectrum of compound **1** and belong to the bending vibrations of the CCH of the propylene groups (Supplementary information S5). The Raman spectrum of compound **2** contains the corresponding bands at 1472, 1438, and 1406 cm^{-1}.

The bands in the region 1365–1320 cm^{-1} of the IR spectra of calixarenes were attributed to the waging vibrations of CH_2 groups (Figs. 6, 8). The stretching vibrations of the CC and CO bonds cause bands in the 1290–1230 cm^{-1} region of the IR spectrum of compound **1**. The bands between 1175 and 800 cm^{-1} of the vibrational spectra of calixarenes were attributed to the twisting of the CH_2 groups.

The bands in the range 790–690 cm^{-1} in the vibrational spectra of calixarenes are due to the CC stretching. Bending vibrations of the CCC angles cause bands in the region 680–620 cm^{-1} in the IR and Raman spectra of compounds **1** and **2**. The bands in the range of 600–400 cm^{-1} were assigned to bending vibrations of the skeleton.

It is interesting to determine the differences in the IR spectra of the calixarene **1** for the dimer and tetramer associations of the carboxyl groups on the upper rim of the molecule (Fig. 6). A com-

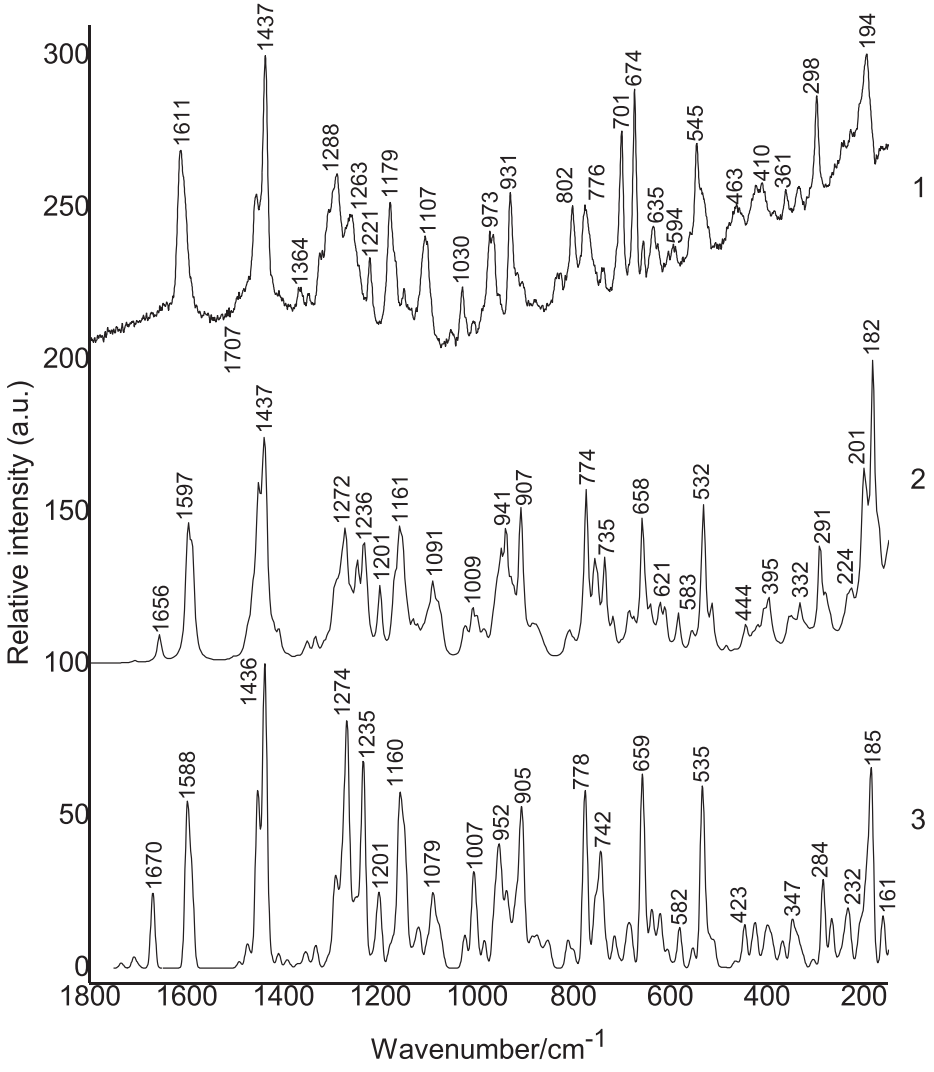

Fig. 7. Experimental (1) and theoretical Raman spectra of compound **1** in the conformation cone with a cyclic system of hydrogen bonds along the lower rim and dimers (2) and cyclic hydrogen bonds (3) along the upper rim in the region 1800–400 cm^{-1}.

parison of the theoretical IR spectra of molecule **1** shows the characteristic bands: 1423, 1245, 981 cm^{-1} (dimer), 1215, 1182, 919, 856 cm^{-1} (tetramer) (Fig. 6, Supplementary information S4). As the difference in energy between the two types of associates is not very large, both forms can exist in the crystalline state, and the distinct bands in the IR spectra allow them to be identified.

Comparison of the IR and Raman spectra of compounds **1** and **2** shows that they are very similar to each other, but there are some differences (Figs. 2 and 3). Analyzing these differences can be helpful for analytical purposes. In the IR spectra of compound **1**, there is a 3187 cm^{-1} band which is absent in the IR spectra of compound **2**. The contour and frequency of the band of stretching vibrations of the *C=O* bonds near 1700 cm^{-1} in the IR spectra of compounds **1** and **2** differ, indicating some difference in the dimeric complexes of carboxylate groups.

In the Raman spectrum of compound 2, two bands of stretching vibrations of the CC bonds of the aromatic fragments are observed at 1606 and 1587 cm^{-1}, characteristic of para-substituted benzene groups [9]. The Raman spectrum of compound 1 contains a band at 1611 cm^{-1}, generally observed for mono-substituted benzene [9]. The IR and Raman spectra of compound 2 show bands in the region of 1500–700 cm^{-1} associated with vibrations of CH_2 and CH_3 groups, which are not present in the spectra of compound 1.

In this article, we also attempted to describe the reactivity of calixarene using global and local descriptors (Tables 2 and 3). The ionization energy and electron affinity decrease in compound **2** compared to **1**. The chemical potential, calculated as $\mu \approx -(IE + EA)/2$, describes the ability of electrons to leave the system [20]. The value of the chemical potential is comparable in molecules **1** and **2**.

The chemical hardness $\eta \approx$ (IE - EA) describes the resistance to modification of the electronic distribution [20]. The inverse hardness is called softness $S = 1/2\eta$ [20]. The softness is the same for calixarene molecules **1** and **2**. The electrophilic index $\omega=\mu^2/2\eta$ describes the reduction in energy caused by the maximum transfer of electrons from the donor to the acceptor [20]. This indicator has the maximum value for the dimer of compound **1**. The reactivity of calixarenes **1** and **2** does not depend on the type of associates on the upper rim.

Fukui functions $f_k^+(r) = [q_k(N+1) - q_k(N)]$ for the nucleophilic attack, and $f_k^-(r) = [q_k(N) - q_k(N-1)]$ for the electrophilic attack, where q_k is the electron population of atom k in the molecule, N number of electrons were calculated. The local softness was obtained by projecting the global values for the atomic center k in the molecule by using the Fukui function: $s_k^+ = Sf_k^+, s_k^- = Sf_k^-$ The Fukui function and the local softness for each reactive atom were

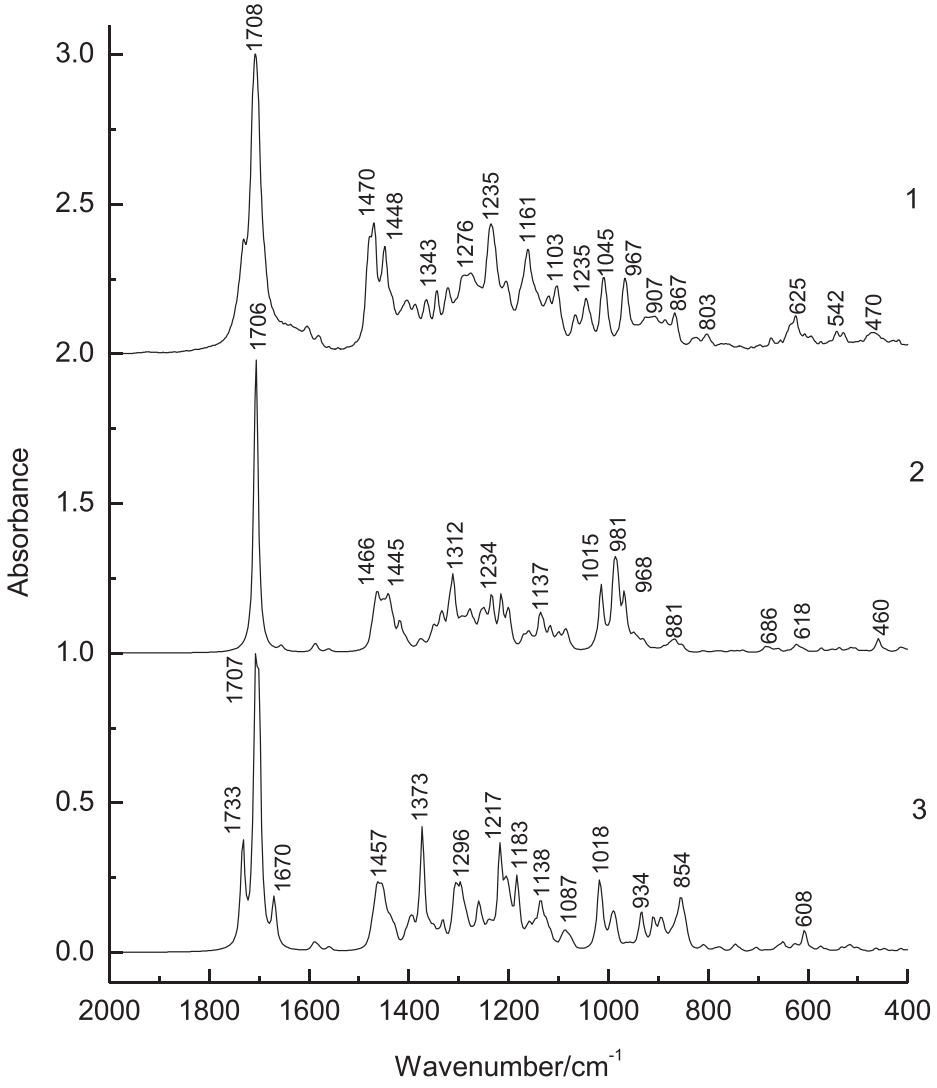

Fig. 8. Experimental (1) and theoretical IR spectra of compound **2** in the conformation cone with dimers (2) and cyclic hydrogen bonds (3) along the upper rim in the region 1800–400 cm^{-1}.

Table 2
Global reactivity descriptors of **1** and **2**.

System	Ionization energy, eV	Electron affinity, eV	Chemical potential, eV	Softness, eV	Electrophilicity index, eV
1, dimer	6.656	−0.591	−3.033	0.137	1.269
1, tetramer	6.670	−0.615	−3.028	0.137	1.258
2, dimer	6.528	−0.868	−2.830	0.135	1.083
2, tetramer	6.522	−0.854	−2.834	0.136	1.089

Table 3
The partial charges of the atoms determined by natural population analysis (NPA) and the local reactivity properties of compounds **1** and **2** calculated at DFT/ B3LYP/6–31G(d,p) level.

Atom	q_n	q_{n-1}	q_{n+1}	f_k^+	f_k^-	s_k^+	s_k^-	ω_k^+	ω_k^-
1, dimer									
O1	−0.760	−0.733	−0.766	0.006	0.027	0.001	0.004	0.008	0.034
H33	0.529	0.531	0.528	0.001	0.002	0.000	0.000	0.001	0.003
O80	−0.680	−0.682	−0.691	0.011	0.002	0.002	0.000	0.014	0.003
O81	−0.707	−0.703	−0.718	0.011	0.004	0.002	0.001	0.014	0.005
H82	0.521	0.522	0.520	0.001	0.001	0.000	0.000	0.001	0.001
2, dimer									
O1	−0.555	−0.532	−0.554	0.001	0.023	0.000	0.003	0.001	0.025
O76	−0.677	−0.676	−0.692	0.015	0.001	0.002	0.000	0.016	0.001
O77	−0.710	−0.709	−0.722	0.012	0.001	0.002	0.000	0.013	0.001
H78	0.521	0.522	0.520	0.001	0.001	0.000	0.000	0.001	0.001

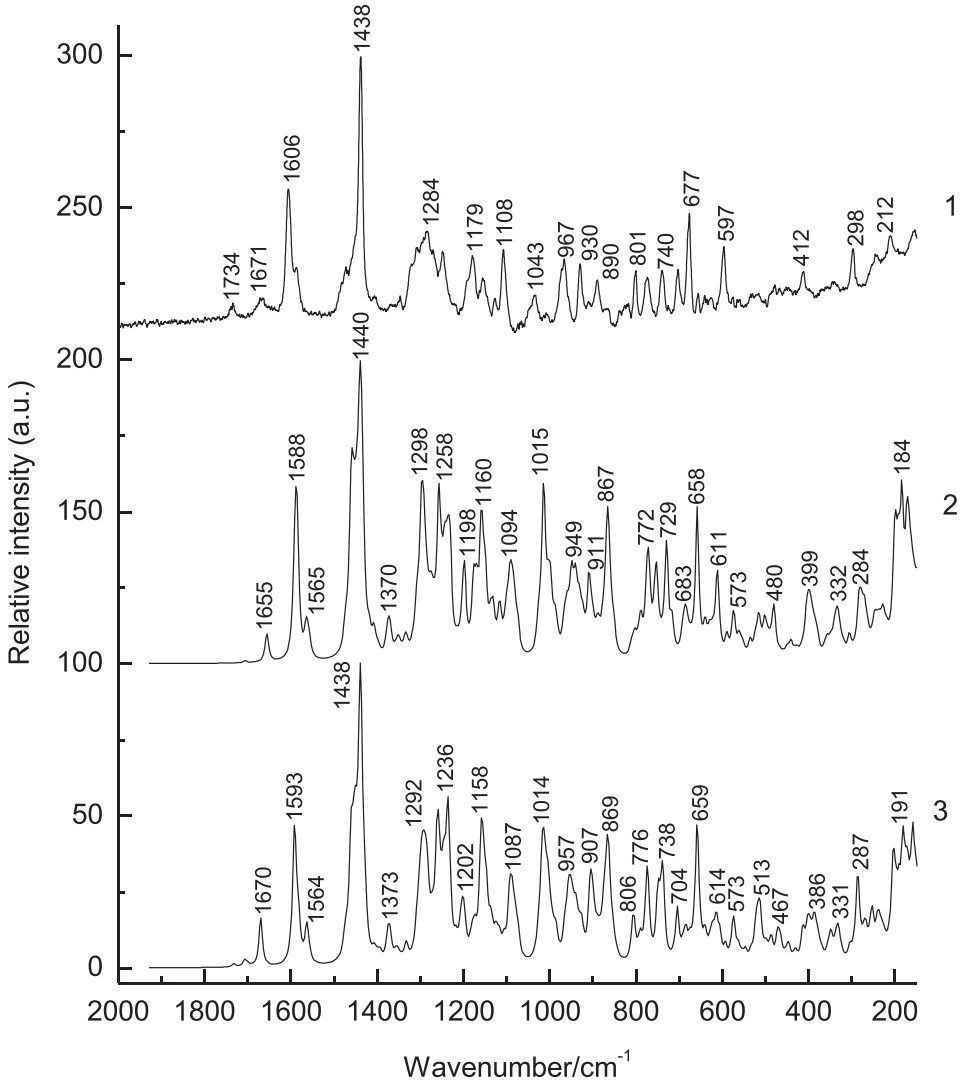

Fig. 9. Experimental (1) and theoretical Raman spectra of compound **2** in the conformation cone with dimers (2) and cyclic hydrogen bonds (3) along the upper rim in the region 1800–400 cm^{-1}.

calculated using the population analysis of natural atomic charges [20].

The local softness of compounds **1** and **2** is different (Table 3). For the oxygen atom O1 along the lower rim of calixarene molecules **1** and **2** $f_k^+(r)\cdot \leq \cdot f_k^-(r)$, it is subjected to nucleophilic attack. For the oxygen atoms O80, O81 of the carboxyl groups along the upper rim of calixarene molecules $f_k^+(r)\cdot \leq \cdot f_k^-(r)$, they are subjected to electrophilic attack. The softness values and the local electrophilicity index of the oxygen atoms confirm these conclusions. The hydrogen atoms of the alcohol and carboxyl groups of calixarene **1** have very low reactivity.

5. Summary

For 1 and 2 molecules in diluted solutions in CCl4, an intramolecular hydrogen bond between adjacent carboxyl groups occurs along the upper rim. They are hydrogen-bonded dimers of neighboring carboxyl groups. The structure of molecule 1 is determined by the mutual influence of two hydrogen-bonded macrocycles between the carboxyl (upper rim) and hydroxyl (lower rim) groups. The intramolecular hydrogen bond between the carboxyl groups weakens the cooperative cyclic intramolecular hydrogen bond.

CRediT author statement

Victor Furer: Conceptualization, Methodology, Software, Writing- Original draft preparation and Editing, **Ludmila Potapova**: Investigation of IR spectra, **Alexandr Vandyukov**: Investigation of IR and Raman spectra, **Denis Chachkov:** Computations of calixarenes, **Ivan Vatsouro:** Synthesis of calixarenes. **Elvira Shokova**: Synthesis of calixarenes, **Vladimir Kovalev:** Conceptualization, Methodology, Reviewing and Editing, **Valery Kovalenko:** Conceptualization, Methodology, Reviewing and Editing

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130508.

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