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Investigation of H-bonding of *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene by IR spectroscopy

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ABSTRACT

The IR spectra of calix[6]arenes with adamantylacetic acid (**1**) and adamantyl (**2**) substituents along the upper rim of the molecule were studied. It was shown that the formation of an intramolecular H-bond between carboxyl groups on the upper rim of the calix[6]arene molecules with adamantylacetic acid fragments does not weaken the cyclic cooperative H-bond at the lower rim of the macrocycle, which is confirmed by DFT calculations. The calculation has shown that molecules **1** and **2** take on the conformation of a *compressed cone*.

The reactivity of adamantylcalix[6]arenes changes due to the association of carboxyl groups. The formation of dimeric complexes due to H-bonds of carboxyl groups along the upper rim of molecule **1** does not lead to a noticeable redistribution of the charges of hydroxyl groups on the lower rim.

Heating a sample of **1** to a temperature of 180 °C destroys a small part of the H-bonds between neighboring carboxyl groups, as evidenced by the appearance of a weak band at 3535 cm^{-1}. However, after cooling to room temperature, the H-bonds between the carboxyl groups are restored.

Heating up to 355° C-leads to irreversible changes in the H-bonding system, but even at this temperature, structure destruction has not been observed.

1. Introduction

Calixarenes are used in supramolecular chemistry as host molecules and molecular receptors [1–4]. The study of the conformational behavior of calixarenes is one of the most important problems in supramolecular chemistry [1–4]. The conformation of the host molecule is a major factor in the creation of new synthetic receptors [1–4].

The successful use of calixarenes for the recognition of molecules is conditioned by the hydrophobic cavity formed by aromatic fragments in a certain conformation [1–4]. Calix[4]arenes can be obtained in a given macrocyclic conformation and are widely used as molecular receptors [1–4]. However, the size of the cavity in calix[4]arenes is small, and many interesting classes of compounds require the use of calix[6]arenes as host molecules. The main problem with the use of these compounds is their high conformational lability. Therefore, the conformational organization of such calixarenes is important.

A possible way to reduce the conformational mobility of calixarenes is to modify the upper rim with functional groups capable of participating in non-bonded interactions, for example, in H-bonds [5]. Systematic studies on this topic have not been conducted. Although the ability, for example, of carboxyl groups to form intra- and intermolecular H-bonds should affect the conformational behavior of the macrocycle [5].

A decrease in the conformational mobility in calix[5]arene was reported due to the formation of intramolecular H-bonds between two benzoic acid fragments on the upper rim [6]. The realization of dimeric associates due to the formation of intermolecular hydrogen bonds between the carboxyl groups of calix[4]arene and calix[6]arene derivatives has been described [7].

The influence of adamantyl substituents on the conformational properties of cyclic hexamers was studied by 1H NMR spectroscopy [5]. Analysis of ^{1}H NMR spectra at various temperatures showed that the replacement of tert–butyl groups on the upper rim in calix[6]arene by adamantyl groups insignificantly affects the con-

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formational mobility of the macrocycle [5]. According to ^{1}H NMR data, adamantylcalix[6]arenes with carboxymethyl groups exhibit reduced conformational mobility [5].

Calix[6]arenes (**1, 2**) with adamantyl substituents can be obtained in a one-step reaction of p-H-calix[6]arene with 3-R–hydroxy-adamantanes (R = H, CH2COOH) in trifluoroacetic acid medium [5]. In these compounds, the size of the cavity increases, H-bonds of hydroxyl groups are formed along the lower edge of molecules and carboxyl groups on the upper edge. Two systems of H-bonds in the carboxylated adamantylcalix[6]arenes significantly limit the lability of molecules and fix them in one conformation.

X-ray structural analysis is the optimal method for studying the conformational state and structure of crystalline substances. The strength of an H-bond can also be estimated from the value of the distance between oxygen atoms, for example, adjacent hydroxyl groups involved in H-bonding.

The disadvantage is that the method of X-ray structural analysis allows one to obtain information about the structure if it is possible to obtain a single crystal for the compound. However, it is not always possible for calixarenes. Most often, calixarene samples are crystalline powder, and it is necessary to obtain information about their structure using X-ray diffraction analysis. An X-ray diffraction pattern from a polycrystal is more difficult to decipher and often contains insufficient data to establish the atomic structure. However, there are numerous polycrystalline objects for which other important structural characteristics can be determined by X-ray diffraction, which has a significant effect on the properties and are therefore used for applied purposes.

IR spectroscopy is used successfully to study the conformation and H-bonds of calixarene molecules [8–13]. However, in contrast to calix[4]arenes, the structure, conformational properties, and H-bonds in calix[6]arenes have been studied to a much lesser extent. Earlier, in the study of IR spectra, it was found that in all molecules of calix[4]arenes with fragments of adamantyl formic acid, the intramolecular H-bond between adjacent carboxyl groups is realized along the upper edge [8].

This article is devoted to the study of the influence of H-bonds on the structure of the *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**1**) and *p*-1-(adamantyl)calix[6]arene (2) and their thermostability by IR spectroscopy and quantum-chemistry. The presence of a bulky lipophilic group increases the size of the hydrophobic cavity, and the functional groups present in the adamantane fragment open up the possibility of further modification and conformational organization of the molecule. Considering that the substitutes, conformational parameters and cavity size in calixarene derivatives are decisive factors responsible for their behavior as host molecules it is important to study the structure of these compounds by IR spectroscopy and quantum chemistry.

H-bonds define the structure of calixarenes. In compound **1**, H-bonds are made on the upper and lower rims of the molecules, and in compound **2**, only cyclic H-bonds of the hydroxyl groups on the lower edge are observed. It seemed important to us to answer the question of whether the formation of H-bonds between carboxyl groups occurs (and the type of such H-bond is inter- or intramolecular). How does the appearance of new partners in the H-bonds affect the structure of the molecules studied. It was interesting to discover how the H-bonds of hydroxyl and carboxylate groups manifest in IR spectra and how they affect the conformation and reactivity of calixarenes. We were the first to study adamantylcalix[6]arenes by IR spectroscopy DSC and TGA, which made it possible to characterize the thermal stability of these compounds.

Adamantyl calixarenes are used for extracting lanthanides and actinides [14]. Information on the structure and properties of the calixarenes under study will lead to a significant improvement in the ability to extract radionuclides.

2. Material and method

2.1. Experimental

The *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**1**) and *p*-(1-adamantyl)calix[6]arene (**2**) were synthesized by us earlier [5] (Fig. 1). At the last stage of purification, all compounds were precipitated from a mixture of chloroform with methanol and dried in a vacuum at 140 °C (boiling xylene). Samples for recording IR spectra were prepared as solutions in freshly distilled purified CCl4 with concentrations in the range of 10^{-5}–10^{-4} mol/l, the thickness of the cuvette was 1 cm, and in the form of pellets with KBr. In some cases, to increase the solubility of the samples, they were resorted to gentle heating of the solutions.

Calixarenes can contain water or solvent molecules in their cavity. Heating to a temperature of 180 °C makes it possible to get rid of the solvent molecules and to appreciate the nature of the destruction of H-bonds. Temperature experiments with solid samples were performed in a heating tank with an automatic temperature controller at temperatures from 20 to 250° C.

The IR spectra of the compounds were recorded on a Vector 22 Fourier spectrometer (Bruker) in the mid-IR range (4000−400 cm^{-1}), with an optical resolution of 4 cm^{-1}, an accumulation of 64 scans, a recording time of 16 s.

TGA and DSC measurements were performed on the NETZSCH STA 449C Jupiter device in an argon atmosphere in a temperature range of 30 °C–600 °C. The heating rate was 10 deg/min. The samples were placed in unsealed aluminum crucibles (to remove the released products and reduce the overpressure effect).

X-ray diffraction analysis of substances was carried out on a D8 ADVANCE powder diffractometer. Shooting conditions: Bregg-Brentano geometry, CuKα radiation, tube voltage 40 kV, current 40 mA, monochromated with Ni-filter. Shooting interval from 3 to 40°, discrete scanning step 0.02°, exposure time at point 5 s. Slit system - fixed 0.1 mm, using a Vantec coordinate detector. The sample was applied to glass substrates or pressed into standard cuvettes.

2.2. Computational details

Molecular models for compounds **1** and **2** have been constructed for the most energetically favorable *compressed cone* conformation [1]. The geometry optimization was conducted for the *compressed cone* conformation. Then, adamantyl substituents were attached to aromatic moieties of calixarene. After that, complete adamantylation of the macrocycle was performed. Carboxylate groups form the associated dimers. DFT quantum-chemical analysis of calixarenes was performed using Gaussian09 [15]. The calculation was performed using the B3LYP functional and the 6–31G(d,p) basic set. To assign the bands in the IR spectra, the total energy distribution was calculated using the VEDA program [16]. Natural bond orbitals (NBO) [17] were calculated using Gaussian 09 software.

3. Results and discussion

3.1. Structural analysis

The *compressed cone* conformer manifests itself in molecule *p–tert*-butylcalix[6]arene, oxygen atoms occupy the tops of the boat conformation [18]. In this molecule, two distal bridging CH2 blocks located in the middle of the boat are turned inward of the macrocycle. As a result, the cavity in the *p–tert*-butylcalix[6]arene molecule is divided into two parts, which significantly limits the possibility of including guest molecules.

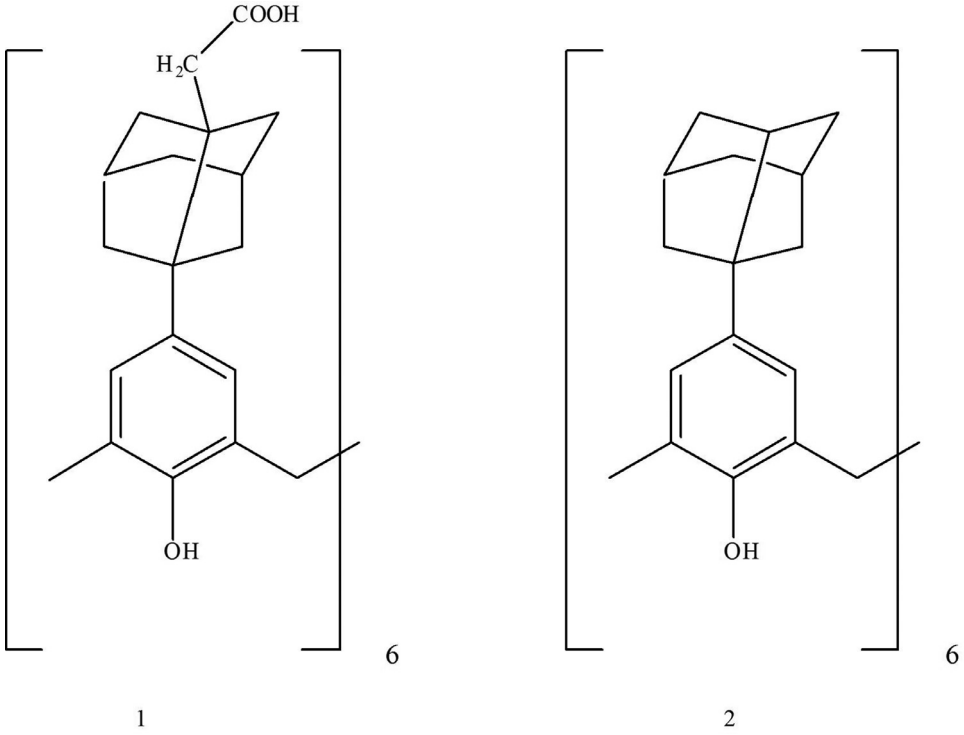

Fig. 1. Structure of compounds **1** (1) and **2** (2).

Compound **1** is an amorphous powder. The conformational changes in system **1** are not observed on heating, as evidenced by the data from the X-ray powder diffraction analysis (Supplementary information S1).

According to quantum-chemical calculations, molecules **1** and **2** exist in the conformation of the *compressed cone*. While oxygen atoms on the inner rim are located at vertices of the bath conformation (Fig. 2, Supplementary information S2, S3).

In molecule **1** with dimeric complexes of carboxyl groups, the average distance r(O···O) is 2.63 Å, and for a cyclic system of H-bonds along the lower rim, it is 2.62 Å. In dimers, the distance r(O···O) is 2.64 Å for peripheral and 2.62 Å for internal carboxyl groups. Molecule **2** has no H-bonds on the upper edge, and the average distance r(O···O) is 2.64 Å. Thus, the H-bonds of the hydroxyl and carboxyl groups of calixarene do not significantly affect each other.

The angles of torsion φ(C6−C4−C48−C47) and χ(C4−C48−C47−C46) determine the conformation of calixarenes [19]. The mean absolute values of the angles φ and χ of molecule **1** are equal to 95.1 and 94.1° (Supplementary information S3). The mean values of these angles are equal to 89.6 and 99.2° for molecule **2** (Supplementary information S3). Thus, the association of carboxyl groups of calixarene **1** affects the orientation of the aromatic fragments. The rest of the geometric parameters of molecules **1** and **2** do not change (Supplementary information S2). Thus, H-bonds of hydroxyl and carboxyl groups fix the molecules in *compressed cone* conformation.

3.2. Frontier orbitals and descriptors

In this article, we also attempted to describe the reactivity of calixarene using global descriptors (Table 1). The ionization energy is higher in compound **1** and the electron affinity in compound **2**. The chemical potential, calculated as $\mu \approx$ - *(IE + EA)/2,* describes the ability of electrons to leave the system [20]. In compound **1**, the chemical potential is higher than in compound **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]. This parameter is higher in compound **2**. The electrophilicity index $\omega=\mu^2/2\eta$ is associated with the biological activity is higher for calixarene with adamantyl substituents [18]. The reactivity of adamantylcalix[6]arenes changes due to the association of carboxyl groups. The ability of molecules to form complexes in supramolecular systems also changes.

To estimate the electrical properties of the molecules, we calculated the charge distribution on the atoms of compound **1** and compared them to the corresponding amounts in compound **2** (Table 2). As expected, the distribution of natural atomic charges [17] on the oxygen and hydrogen atoms forming an H-bond along the lower rim of the **1** and **2** molecules is symmetrical and equal to (in e): O1 (−0.763) and H50 (0.534). This distribution of charges on oxygen and hydrogen atoms forming an H-bond along the lower rim is more symmetric in molecule **2**.

Oxygen and hydrogen atoms of carboxyl groups also carry a significant negative charge of O227 (−0.763), O228 (−0.677), and H229 (0.520). Electrostatic interactions of these atoms cause the formation of strong H-bonds in the calixarenes under study. Thus, the formation of dimeric complexes due to H-bonds of carboxyl groups along the upper rim of molecule 1 does not lead to a noticeable redistribution of the charges of hydroxyl groups on the lower rim.

3.3. NBO analysis

In the theory of NBO, electron density transfer from a donor to an acceptor is analyzed [17]. The **1** molecule has a complex pattern of interactions: $n(LP_1O5)\rightarrow\sigma^*_{12}$(C2–C12), $n(LP_1O5)\rightarrow\sigma^*_1$(O7–H53), $n(LP_1O5)\rightarrow\sigma^*_1$(O7–H53), $n(LP_2O5)\rightarrow\sigma^*_1$(O7–H53), $n(LP_2O5)\rightarrow\sigma^*_2$(C21–C26) with stabilization energy equal to 14.25, 23.86, 6.59, 10.08, 20.20 kcal/mol (Supplementary information S4).

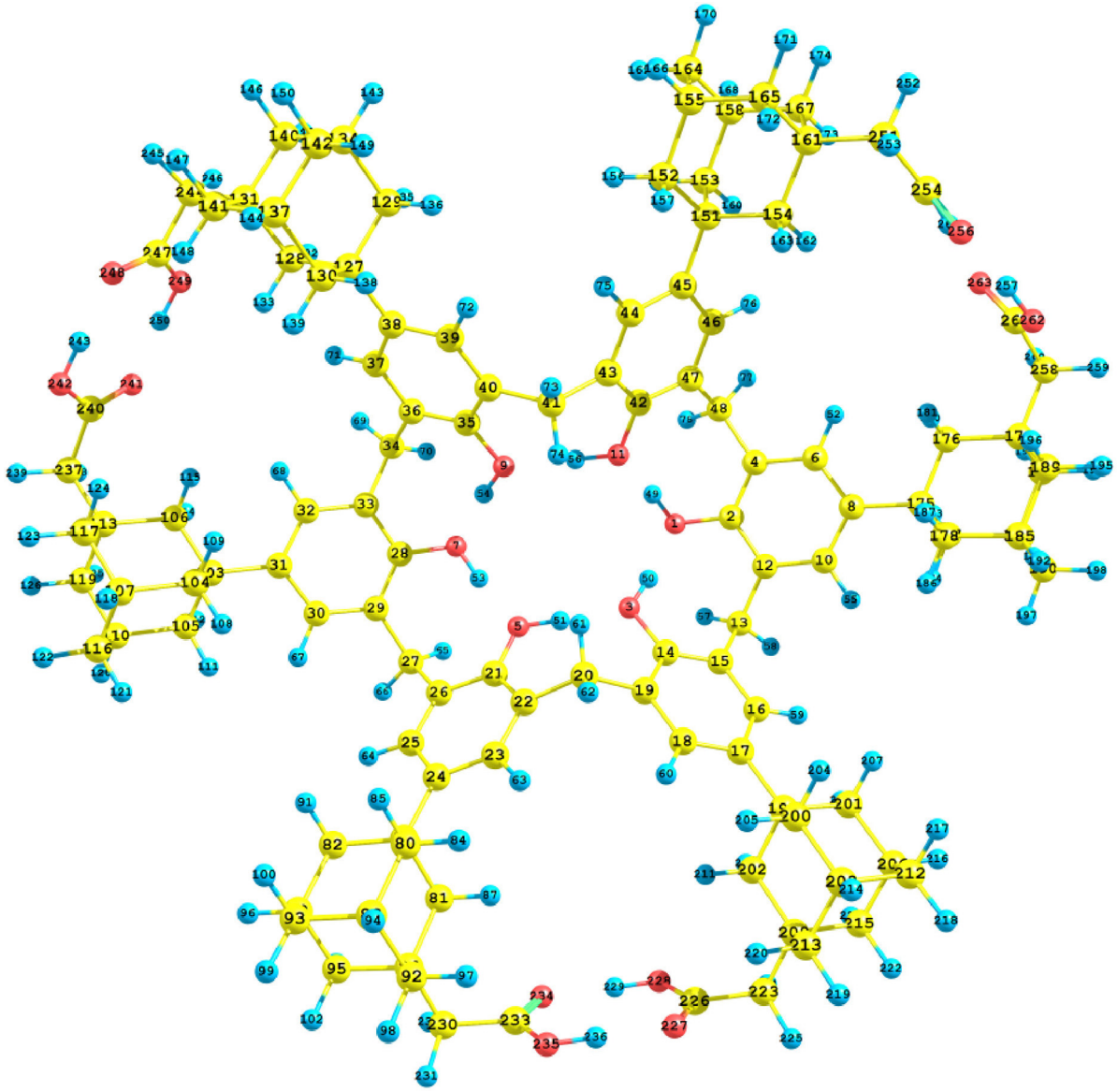

Fig. 2. Optimized geometry and atom numbering for compound **1** in the conformation *compressed cone* with a cyclic system of H-bonds along the lower rim and dimers along the upper rim (1) and compound **2** in the same conformation (2). Yellow, blue and red colors correspond to carbon, hydrogen, and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

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

System	Ionization energy, eV	Electron affinity, eV	Chemical potential, eV	Softness, eV	Electrophilicity index, eV
Compound **1**	6.479	0.468	−3.474	0.167	2.011
Compound **2**	6.414	0.580	−2.917	0.171	2.096

In aromatic moieties, conjugation bonds participate in interactions σ_2(C2–C12)→σ^*_2(C4–C6), σ_2(C2–C12)→σ^*_2(C8–C10), σ_2(C4–C6)→σ^*_2(C2–C12) with energies equal to 20.17, 20.82, and 21.32 kcal/mol. Strong are the interactions with the account of the lone electron pairs of oxygen atoms: n(LP$_2$O228)→σ^*_2(C226–O227), n(LP$_2$O227)→σ^*_1(C223–C226), n(LP$_2$O227)→ σ^*_1(C226–O228), n(LP$_1$O228)→σ^*_1(C226–O227) with energies 64.42, 16.72, 16.83, 10.04 kcal/mol.

3.4. IR spectra and H-bonds

The IR spectra of compounds **1** and **2** are shown in Fig. 3. The band of free OH groups for compounds 1 and 2 is observed neither in the spectra of the solid-state nor in dilute solution in CCl_4 (Table 3). Unfortunately, it is impossible to determine the position of the νOH band of acidic hydroxyl groups since it is located under the contour of the stretching vibration bands of CH groups and is masked by these bands. The νOH bands in the spectra of dilute solutions of compounds **1** and **2** in CCl_4 lie at 3124 and 3143 cm^{-1}. Thus, all carboxyl groups on the upper edge of the molecule form an H-bond. Considering that these are dilute solutions (concentrations of the order of 10^{-5} mol/l), it can be assumed that the H-bonds between the carboxyl groups are intramolecular.

The νC=*O* band characterizes the behavior of the H-bonds of carboxyl groups, although it is less informative than the νOH band. For organic monocarboxylic acids, the cyclic dimer is known to be characterized by the νC=*O* absorption band at 1700 cm^{-1} and the H-bonded chain of carboxyl groups at 1650 cm^{-1} [21]. The νC=*O*

Table 2
The partial charges of the atoms determined by natural population analysis of compounds **1** and **2**.

Compound **1**		Compound **2**	
Atom	q_n	Atom	q_n
O1	−0.763	O1	−0.761
C2	0.320	C16	0.318
O3	−0.764	O3	−0.761
O5	−0.767	O5	−0.762
O7	−0.761	O8	−0.762
O9	−0.766	O10	−0.764
O11	−0.769	O24	−0.764
H49	0.493	H2	0.533
H50	0.534	H4	0.533
H51	0.539	H9	0.531
H53	0.534	H11	0.537
H54	0.532	H25	0.537
H56	0.539	H78	0.531
C226	0.865		
O227	−0.677		
O228	−0.706		
H229	0.520		

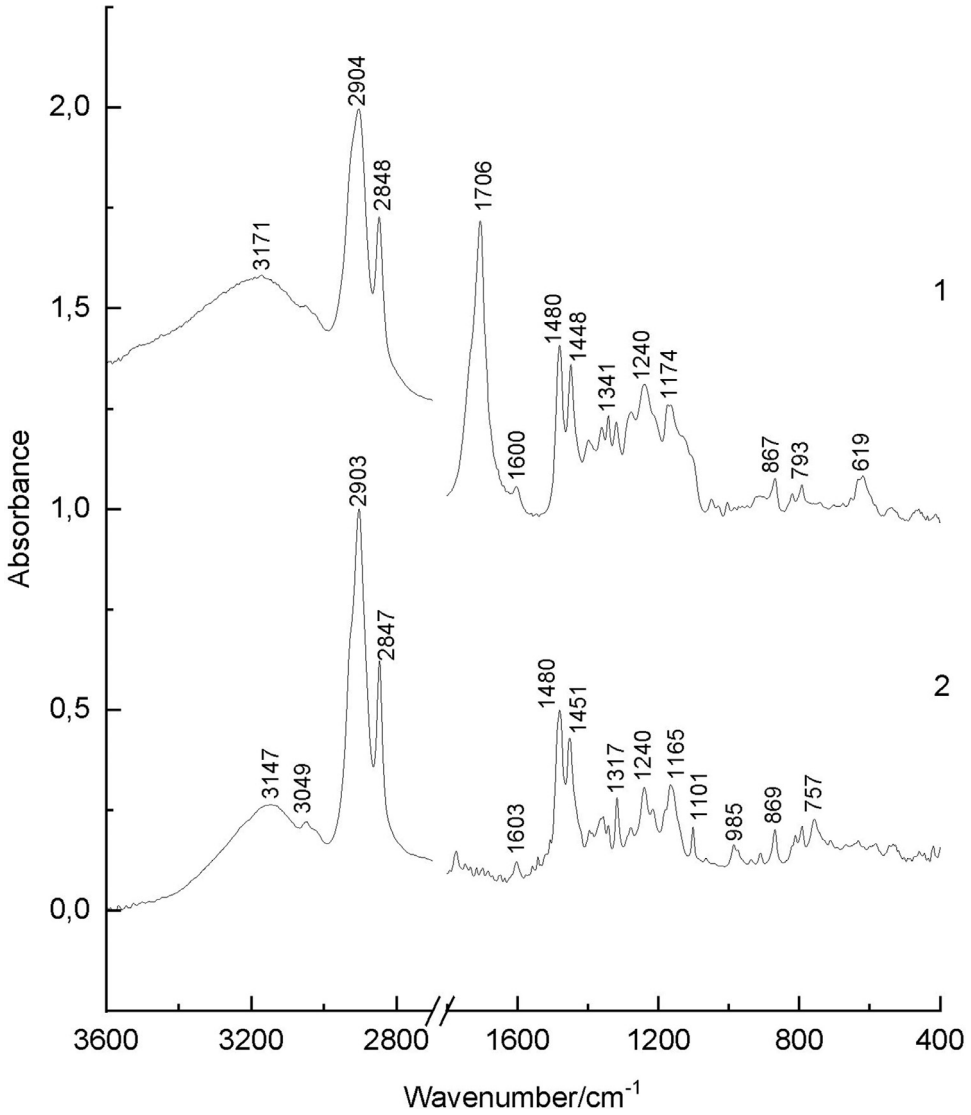

Fig. 3. Experimental IR spectra of amorphous solid samples of calixarenes **1** (1) and **2** (2).

Table 3
Experimental frequencies of νOH (cm^{-1}) of amorphous solid and dilute solutions in CCl_4 of compounds **1** and **2**.

Compound	Original amorphous solid, T_{room}	T=180 ^{0}C	Cooled amorphous solid, T_{room}	Solution in CCl_4
1	3171	3173	3140	3124
2	3147	3161	3135	3143

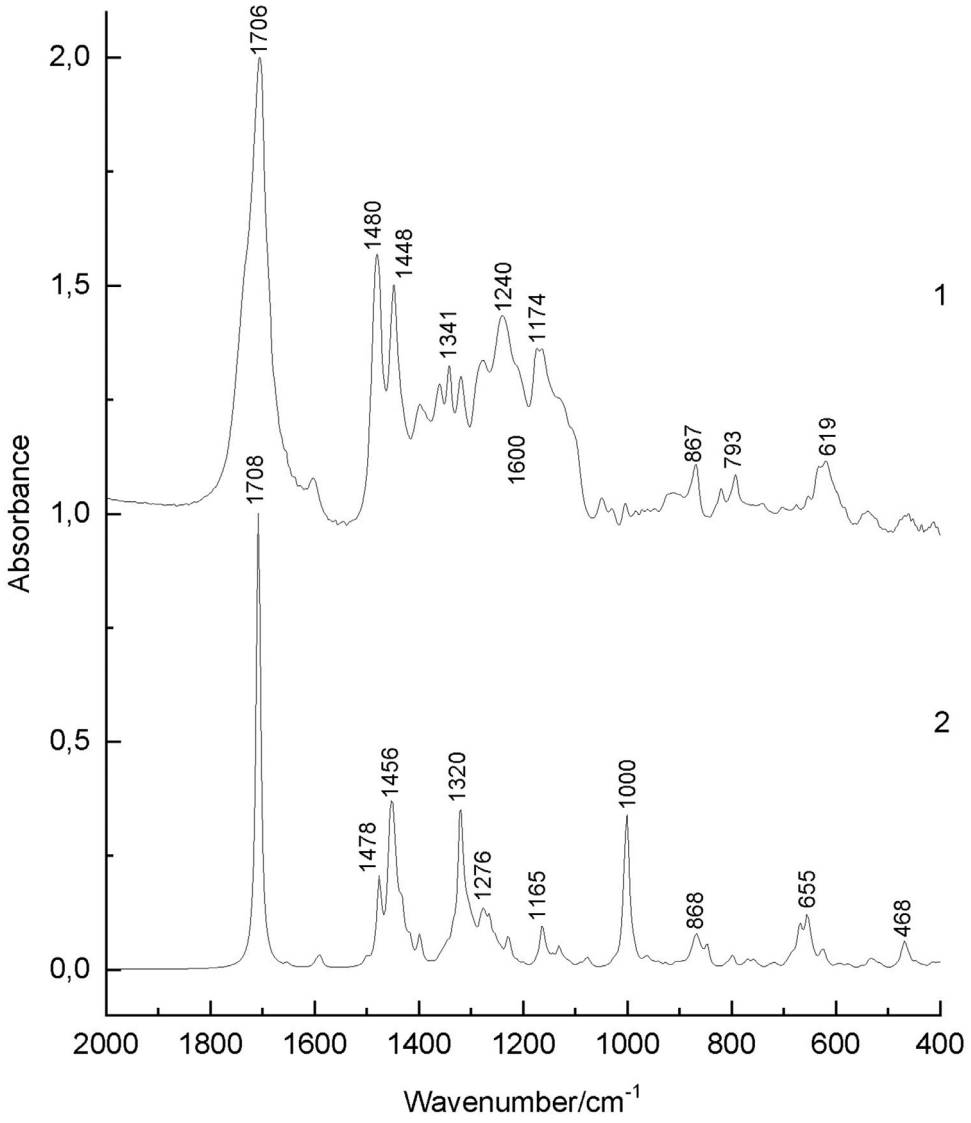

Fig. 4. Experimental (1) and theoretical IR spectra of compound **1** in the *compressed cone* conformation (2) in the region 1800–400 cm^{-1}.

band at 1706 cm^{-1} in the spectrum of crystalline compound **1** indicates the formation of cyclic dimers between adjacent carboxyl groups. In a solution of compound **1**, a single symmetrical band νC=O is observed at 1703 cm^{-1} with a width of about 20 cm^{-1}.

Heating a sample of **1** to a temperature of 180 °C leads to the destruction of a small part of the H-bonds between neighboring carboxyl groups, as evidenced by the appearance of a weak band at 3535 cm^{-1}. However, after cooling to room temperature, the H-bonds form again on the upper rim. For compound **1**, the νOH frequency is slightly higher.

To allow the formation of an intramolecular H-bond along the upper edge, dihedral angles in the macrocycle alter the O···H distances between hydroxyl groups forming a cyclic cooperative intramolecular H-bond along the lower edge of the molecule, and this H-bond slightly weakens. Despite the weakening of the H-bond along the lower rim of the molecule, the further formation of an intramolecular H-bond at the upper rim leads to an additional gain in the energy in the system. Two systems of H-bonds on the lower and upper rims of the molecules fix the structure of the covalent macrocycle in compound **1**.

A strong band is observed at 3197 cm^{-1} in the spectrum of compound 1 in the solid-state, which changes to 3124 cm^{-1} in the spectrum of a dilute solution in CCl_4 (Table 1). The corresponding bands at 3147 and 3143 cm^{-1} are observed in the spectra of the solid-state and the solution of compound **2** (Table 3). Consequently, these bands are due to vibrations of OH groups participating in the formation of a cyclic H-bond along the lower rim of molecules **1** and **2**. Shifting these bands to lower frequencies means that due to the elimination of steric hindrances in dilute solutions, stronger H-bonding is achieved than in the solid-state.

The νOH frequency at 3171 cm^{-1} in calixarene **1** is higher than 3144 cm^{-1} in **2**, but the *compressed cone* conformation is retained

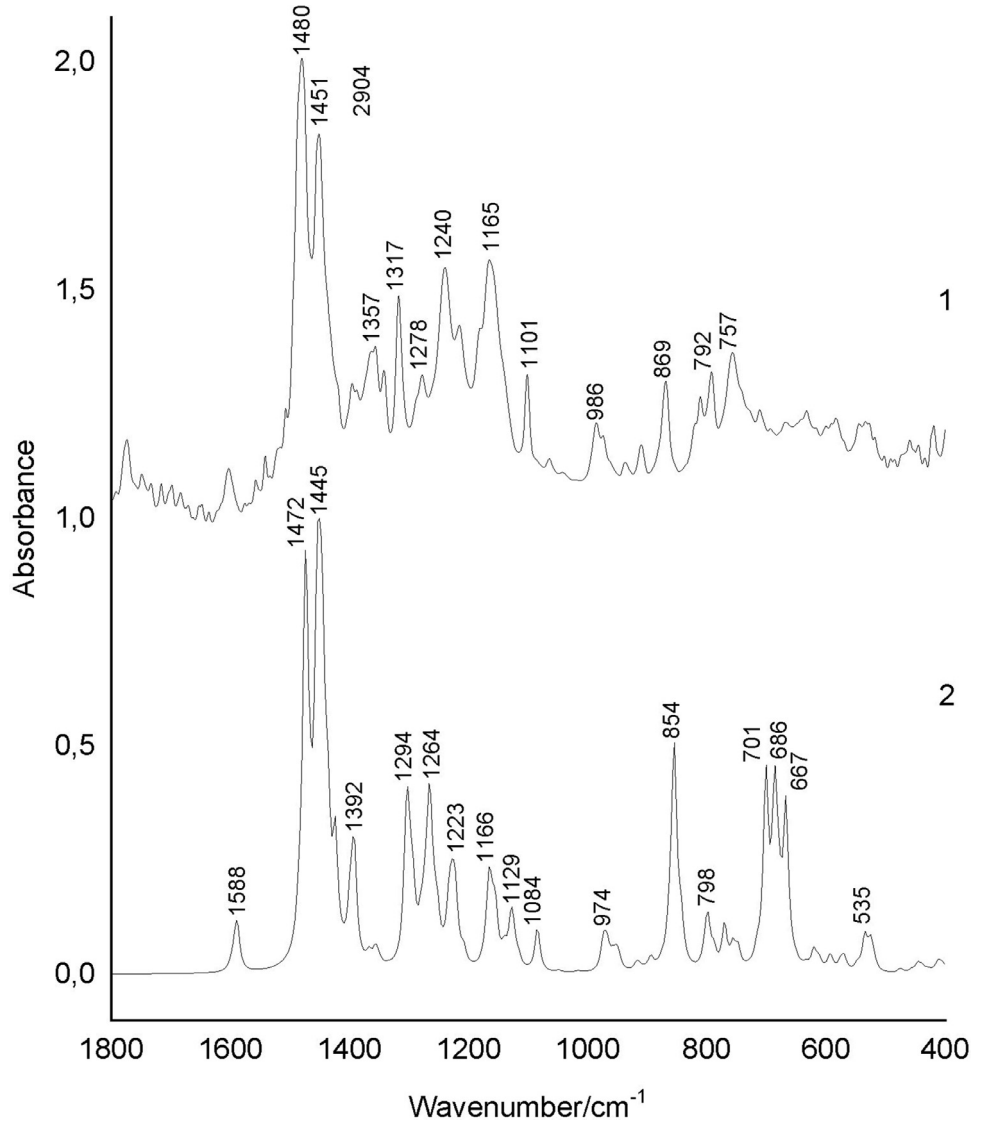

Fig. 5. Experimental (1) and theoretical IR spectra of compound **2** in the *compressed cone* conformation in the region 1800–400 cm^{-1}.

in these molecules. The frequency differences are due to steric barriers for the large adamantyl substituents of the calix[6]arene. The H-bonded complexes on the lower and upper rims of calixarene molecules affect each other. In calixarene **1**, the macrocycle hinders the formation of H-bonds between carboxyl groups along the upper rim of the molecule. The νOH vibrations with frequencies of 3420 and 3450 cm^{-1} appear in IR spectra of **1** and **2**, respectively. On heating to 180 °C and subsequent cooling of sample **1**, the intensity of these bands decreases.

Identification of the νOH band in carboxylic acids is complicated because it has low intensity and more intense bands of CH bond stretching vibrations that mask them [19]. This band lies in the region of 2700–2500 cm^{-1}, which is a further argument for the extraordinary strength of H-bonds in carboxylic acids [21]. The band at 2670 cm^{-1} refers to the νOH vibrations of carboxyl groups in the spectrum of compound **1** [22].

In the spectrum of compound 1 in the solid-state, there is a band of 1706 cm^{-1} νC=O with a shoulder at about 1735 cm^{-1} (Fig. 3). Such frequencies are characteristic of carboxyl groups forming H-bonded dimeric complexes. Two frequencies νC=O indicate the nonequivalence of the carbonyl groups in the complex.

3.4. Thermal analysis

For sample **1**, several endo-peaks are observed on the DSC curve (Supplementary information S5). Their attribution is not so easy. At a temperature of 276 °C, the decomposition of the substance begins since heating above this temperature is accompanied by a significant loss of mass of the sample on the TG curve (Supplementary information S6). The IR spectral study shows that heating to 312 °C does not yet lead to the destruction of the calixarene molecule; at this temperature, there is also no irreversible destruction of the H-bonds between the carboxyl groups (Supplementary information S7).

Heating up to 355° C - leads to irreversible changes in the H-bonding system, but even at this temperature, the destruction of the structure is not yet observed (Supplementary information S8). Heating to 355 °C resulted in the removal of intracavitary water and solvent molecules from the sample. Cooling and grinding the substance with potassium bromide (KBr) to prepare a spectral tablet causes the calixarene to reabsorb moisture from the atmosphere, which is reflected in its IR spectrum. Heating to 539 °C is accompanied by sample decomposition.

3.5. Vibrational analysis

The assignment of bands in the experimental IR spectra of compounds **1** and **2** was performed by calculating the potential energy distribution and comparison with related compounds [23]. The experimental IR spectra of calixarenes under study in the region 2800–3000 cm^{-1} are similar and contain bands at 2905, 2848 cm^{-1}, and the shoulder at 3050 cm^{-1} due to the CH_2 stretching vibrations of adamantyl groups (Fig. 3). In the IR spectra of adamantadine, bands at 2907 and 2853 cm^{-1} are observed, assigned to asymmetric and symmetric stretching vibrations of methylene groups [23].

Bands at 1600 and 1605 cm^{-1}, characteristic of para-substituted aromatic units, due to the stretching vibrations of the CC bonds of the aromatic moieties, are observed in spectra of compounds **1** and **2**, respectively (Supplementary information S9, Figs. 4 and 5).

Bending $\delta(CH_2)$ vibrations of the macrocycle and adamantyl substituent cause bands at 1478, 1448, 1395 cm^{-1} in the experimental IR spectra of calixarene **1** (Fig. 3). In the experimental IR spectra of compound **2** in this region, there are bands at 1480, 1451, and 1394 cm^{-1} (Fig. 3). Bending vibrations of methylene groups at 1454 and 1382 cm^{-1} were found in the experimental IR spectrum of adamantadine [23].

The bands between 1370 and 1310 cm^{-1} in the IR spectra of compounds **1** and **2** are attributed to rocking and waging vibrations of methylene groups (Fig. 3). The corresponding vibrations at 1368 and 1313 cm^{-1} were observed in the IR spectra of adamantadine [23]. The stretching vibrations of the CC and CO bonds lie in the 1300–1200 cm^{-1} region of the spectrum of compound **1**. In this region of the IR spectra of adamantadine, bands at 1288, 1265, 1209 cm^{-1} were observed, which were attributed to the torsion of the adamantane ring [23]. The bands between 1200 and 800 cm^{-1} of the IR spectra of compounds **1** and **2** were attributed to the rocking vibrations of the CH_2 groups. Bands in this region of the IR spectra of adamantadine were assigned to the corresponding vibrations of CH bonds [23].

The stretching vibrations of the CC bonds cause the bands in the 800–700 cm^{-1} region. Similar vibrations at 801, 779, and 724 cm^{-1} appear in the IR spectrum of adamantadine [23]. Bending vibrations of CCC angles cause bands in the 700–600 cm^{-1} region in the IR spectra of compounds **1** and **2**. The IR spectrum of adamantadine has a similar band at 644 cm^{-1} [23]. The bands in the 600–400 cm^{-1} region have been attributed to the deformation vibrations of the molecule's backbone and torsional vibrations around the CC bonds.

4. Conclusions

It was found by IR spectroscopy and quantum chemical calculations that in molecules of calix[6]arene with fragments of adamantylacetic acid at the upper rim, intramolecular H-bonded dimers of carboxyl groups are formed. H-bonds of hydroxyl and carboxyl groups fix the molecule in *compressed cone* conformation.

The association of carboxyl groups of calixarene affects the orientation of the aromatic fragments. In the spectrum of compound **1** in the crystalline state, there is a band of 1706 cm^{-1} νC=O with a shoulder at about 1735 cm^{-1}. Such frequencies are characteristic of carboxyl groups forming H-bonded dimeric complexes. Two frequencies νC=O indicate the nonequivalence of the carbonyl groups in the complex.

Heating induces changes in the H-bonds, but even at a temperature of 355° C, the destruction of the structure is not observed. Complete decomposition of the sample occurs at temperatures above 539 °C.

The reactivity of adamantylcalix[6]arenes changes due to the association of carboxyl groups. The formation of dimeric complexes due to H-bonds of carboxyl groups along the upper rim of molecule 1 does not lead to a noticeable redistribution of the charges of hydroxyl groups on the lower edge.

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.

CRediT authorship contribution statement

V.L. Furer: Conceptualization, Methodology, Software, Writing – original draft, Writing – review & editing. **L.I. Potapova:** Investigation. **D.V. Chachkov:** Software. **I.M. Vatsouro:** Conceptualization. **V.V. Kovalev:** Conceptualization, Methodology, Writing – review & editing. **E.A. Shokova:** Conceptualization. **V.I. Kovalenko:** Conceptualization, Methodology, Writing – review & editing.

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Supplementary materials

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