Intramolecular co-operative hydrogen bond in calix[*n*]arenes (*n* = 4, 6, 8) bearing bulky substituents

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Based on the Fourier transform IR spectroscopy together with the published NMR and X-ray data, it was shown that cyclic co-operative intramolecular hydrogen bond in calix[*n*]arene (*n* = 4, 6, 8) molecules is mainly responsible for their conformational state irrespective of the presence or absence of bulky substituents at the upper rim of the molecules. In accordance with the size of a macrocycle (*n* = 4, 6, 8), the stable conformation, secured by such a hydrogen bond, constitutes a *cone*, a *pinched cone,* and a *pleated loop*, respectively. The new, potentially competing system of hydrogen bonds in calix[6]arenes with 3-carboxymethyl-1-adamantyl substituents does not affect the conformational state of the macrocycle and its H-bonding. Six carboxy groups at the upper rim form in pairs three cyclic dimers, which does not disturb the hydrogen bonds of the hydroxy groups and the conformation of the macrocycle. In addition, the cavity of the molecule is considerably enlarged. The removal or rearrangement of the guest molecules in the solid calixarene by heating up to 180 °C only slightly affects the conformational state of macrocycles bearing bulky substituents, whereas in calixarenes devoid of such substituents, the similar procedure leads to somewhat of a distortion of the macrocycles (judging from the IR spectral indications of hydrogen bonding).

Key words: calix[*n*]arenes, Fourier transform IR spectroscopy, hydrogen bond, conformers.

Calix[*n*]arenes (*n* = 4, 6, 8)[1—4] are considered as prospective compounds for the creation of host molecules with pre-organized structure and with centers, capable of effective and selective bonding of neutral molecules and ions. By now, calix[4]arenes are studied the most.[1—4] On the basis of them, the highly effective receptors of metal ions, ammonium ions, anions, and neutral molecules were obtained. However, the size of the interior cavity of calix[4]arenes is small, which sets a limit on their application. The study of macrocycles with more than four phenol fragments as the host molecules assumes additional difficulties due to the higher conformational flexibility of the macrocycle.[4]

A comparative analysis of the X-ray crystallographic data (the Cambridge Crystallographic Data Center)[5] on the structures of calix[*n*]arenes (*n* = 4—8) with OH groups at the lower rim of the molecules and with or without *p*-*tert*-butyl substituent at the upper rim showed that, despite of possible conformational diversity, each calix[*n*]arene is represented in the crystal most often by a single conformer due to the cyclic co-operative intramolecular hydrogen bond (CCIHB).

Indeed, calix[4]arene and *p*-*tert*-butylcalix[4]arene in the solid state both exist in the *cone* conformation, while all oxygen atoms of the hydroxy groups are situated in one plane; the average distances between the neighboring oxygen atoms (r_a(O...O)) are equal to 2.66 and 2.71 Å for the unsubstituted and substituted calix[4]arenes, respectively.[5,6]

The *pinched cone* conformer[5,7] appears in the *p*-*tert*-butylcalix[6]arene molecule, the average distance r_a(O...O) is equal to 2.64 Å, being the shortest among calixarenes under consideration, whereas the oxygen atoms occupy the vertexes of the *boat* conformation

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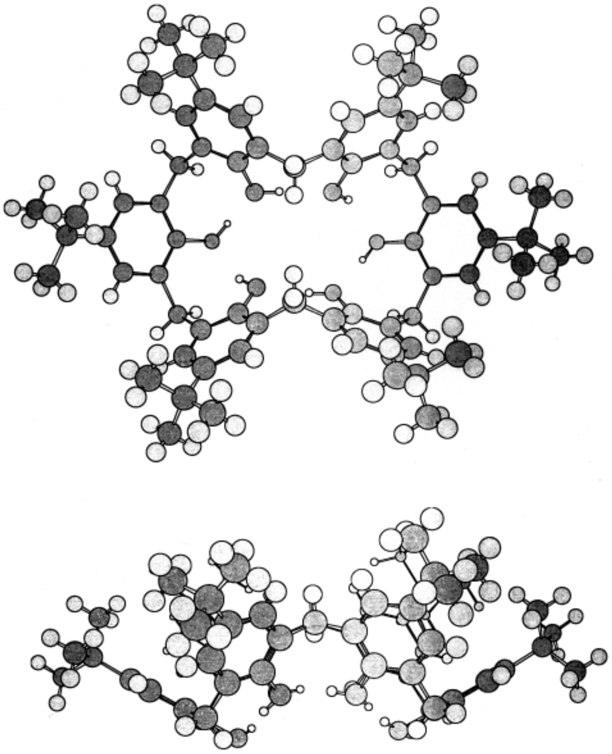


Fig. 1. The *pinched cone* conformer of calixarene **4** (two projections). The refcode of the structure (further, refcode) is VARGUR according to the Cambridge Databank data.[5]

(Fig. 1). A distinguishing feature of this molecule consists in the fact that two distal bridged CH_2 units, situated in the middle of the *boat*, are turned inside the macrocycle, in contrast to the other units, as well as to the methylene bridges in calix[4]arenes. As a result of this, the molecular cavity in *p*-*tert*-butylcalix[6]arene was found to be divided into two ones, each consisting of three phenol fragments, which considerably limits the possibility of the incorporation of guest molecules.

In the crystalline state *p*-*tert*-butylcalix[8]arene exists in the *pleated loop* conformation.[5,7–9] In this case, the oxygen atoms are virtually situated in one plane, forming a circle, and phenol rings, alternating the angle of slope, form the symmetrical pleats around this plane (Fig. 2). The distance r_a(O....O) is equal to 2.70 Å. Since the "pleats" made of phenol rings are evenly distributed upon both sides of the plane bearing the oxygen atoms, the "cavity of the molecule" notion for this conformer became meaningless.

Usually calixarenes contain molecules of a solvent, which they were crystallized from, inside the cavity of the molecule and in the crystal lattice (clathrates and/or solvates). If the solvent molecules are poor partners for hydrogen bonding, this only slightly affects the conformational state of the compound; the solvents, capable of forming hydrogen bonds, significantly influence the conformational behavior of the macrocycle. Thus the study of the structures of *p*-*tert*-butylcalix[6]arene and its complexes with chloroform, benzene, and dichloroethane showed that all of them exist in the *pinched cone* conformation.[10] In its complex with DMSO, the macrocycle is fixed as the 1,2,3-*alternate* conformer, which is caused by disturbance of the cyclic system of hydrogen bonding by the presence of included molecules of the solvent.[11] Upon crystallization of *p*-*tert*-butylcalix[8]arene from pyridine, at least three pseudo-polymorphs[9,12,13] (refcodes are DOVHIF, LAYKUR, XUNLEX) were obtained, one of which does not contain and the other two do contain pyridine molecules in the crystal lattice. The cyclic regularity and co-operativity of hydrogen bonding in the latter two are broken due to the formation of H-bonds between the OH groups of the macrocycle and pyridine molecules. These two polymorphs exist only in pyridine, the crystals undergo decomposition in the air.

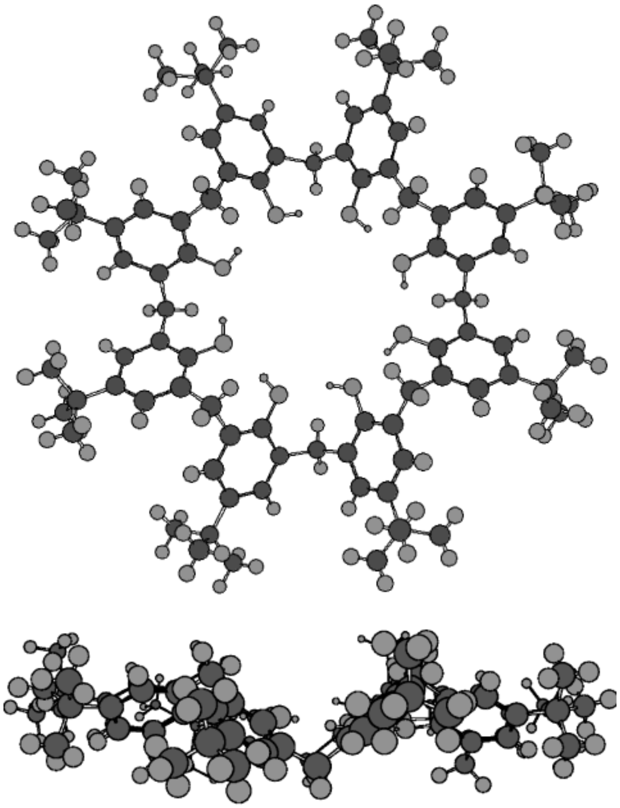


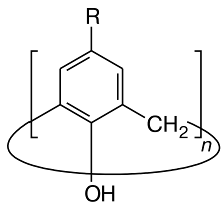
Fig. 2. The *pleated loop* conformer of calixarene **7** (two projections). Refcode is VARHAY.[5]

Together with investigation of geometry of the molecules in the crystal, their conformational state in solutions normally is studied by NMR. Thus the role of the intracyclic hydrogen bonds in conformational behavior of calixarenes in solutions was shown by this method.[14] It turned out that in diluted solutions of a neutral solvent, they exist in the same conformation as in the solid state:

for *p-tert*-butylcalix[4]arene, the *cone*, for *p-tert*-butylcalix[6]arene, the *pinched cone*, and for *p-tert*-butylcalix[8]arene, the *pleated loop*.

Due to a possibility to record IR spectra both for crystals and solutions, IR spectroscopy provides the opportunity to objectively compare the X-ray and NMR data. A systematic research of hydrogen bonding in calix[*n*]arenes by IR spectroscopy has not been undertaken. There is information about influence of a cooperativity of hydrogen bond on the ν(OH) frequencies in the spectra of *p-tert*-butylcalix[4]arene and its analogs,[13,15,16] about interpretation of the IR spectra of calix[4]arenes on the basis of quantum chemical calculations,[17—19] there are also separate pieces of information on the temperature dependence of the ν(OH)[15,20] frequencies.

The present work is aimed at the investigation of hydrogen bonding influence on conformational behavior of calix[*n*]arenes (*n* = 4, 6, 8) with respect to the macrocycle size, the presence or absence of bulky substituents at the upper rim of the molecules, the nature of a substituent, and the temperature effects, as well as the presence or absence of potential H-bonding partners. Calix[4]arene, calix[6]arene, *p-tert*-butylcalix[*n*]arenes (*n* = 4, 6, 8), and *p*-(3-R-1-adamantyl)calix[6]arenes (R = H or CH_2COOH) have been chosen as the subjects of investigation (Table 1). The Fourier transform IR spectroscopy was a method of investigation.



1—7

The synthesis of calix[*n*]arenes of a new type, *viz.*, adamantylcalixarenes, has been accomplished by us for the first time.[24—26] The introduction of adamantyl fragments into a macrocycle molecule can significantly affect the size and shape of molecular cavity, as well as conformational properties of compounds. The influence of six carboxy groups of the upper rim on the hydrogen bonding system and conformation of calixarene earlier has not been studied.

Table 1. Some characteristics of calix[*n*]arenes **1—7**

Compound	*n*	R	M.p./°C	Reference
1	4	H	310	21
2	4	Bu^t	326	22
3	6	H	290	21
4	6	Bu^t	345	23
5	6	1-Adamantyl	340	24
6	6	3-Carboxymethyl-1-adamantyl	340	24
7	8	Bu^t	350	23

Experimental

Calix[4]arene (**1**),[21] *p-tert*-butylcalix[4]arene (**2**),[22] calix[6]arene (**3**),[21] *p-tert*-butylcalix[6]arene (**4**),[23] *p*-(1-adamantyl)calix[6]arene (**5**),[24] *p*-(3-carboxymethyl-1-adamantyl)calix[6]arene (**6**),[24] and *p-tert*-butylcalix[8]arene (**7**)[23] were obtained by the known procedures. For the final purification, all the compounds were recrystallized from $CHCl_3$—MeOH mixture and dried *in vacuo* at 140 °C (boiling xylene as the heating agent).

IR spectra were recorded on a Vector 22 Fourier spectrometer (Bruker) in the region 4000—400 cm^{-1}, the optical resolution being 4 cm^{-1}. The samples were prepared either in KBr pellets or in CCl_4 (purified and freshly distilled) solutions, concentration was 10^{-5}—10^{-4} mol L^{-1}. Before use, CCl_4 was twice re-distilled, the first time over P_2O_5, then as usual. Then the solvent was kept for 1 week over the pre-calcined (for 1 day at 350 °C) molecular sieves 4Å. The spectra of solutions were recorded in a hermetically-sealed 1 cm thick cell with fluorite windows. In some cases, for the better dissolution of the samples the solutions were slightly heated up.

The temperature experiments with the solid samples were carried out on a IR spectrometer with the help of a heating cuvette with the automatic temperature control (Graseby Specac) at 20 and 180 °C with the accuracy ±1 °C. Before running the IR spectrum, the sample was kept for 30 min at the set temperature.

Melting points of compounds under investigation were determined with the polarizing microscope MIN-8 (LOMO), equipped with the Boetius heating table. The error of measurement did not exceed ±3 °C.

Results and Discussion

The analysis of the IR spectra of the diluted solutions of calixarenes in the neutral solvent, carbon tetrachloride, suggested that in this case the conformational state of the molecules would be disturbed by the influence of the surroundings, at least in comparison with the one in the crystal lattice. It means that the IR spectra of all the calixarenes under consideration would be recorded in the equal conditions. As it was expected,[17—19] in the IR spectra of compounds **1—7** the absorption bands of stretching vibrations of free hydroxy groups at 3600—3650 cm^{-1} are absent (Fig. 3 and Table 2).

In all the cases, a broad ν(OH) absorption band with the maximum in the interval 3190—3125 cm^{-1}, characteristic of the CCIHB in calix[4]arenes,[17] was present. The band contour is virtually symmetrical, the observed low-frequency narrow bands were assigned to the ν(CH) stretching vibrations of the macrocycle fragments, the stretching vibrations of the CH-groups in aromatic rings having the highest frequencies among them.[17—19]

Calixarene **6** is of particular interest, since, apart from the OH groups at the lower rim of the molecule, it has six COOH groups at the upper one. In the IR spectrum of this derivative, the absorption bands in the region

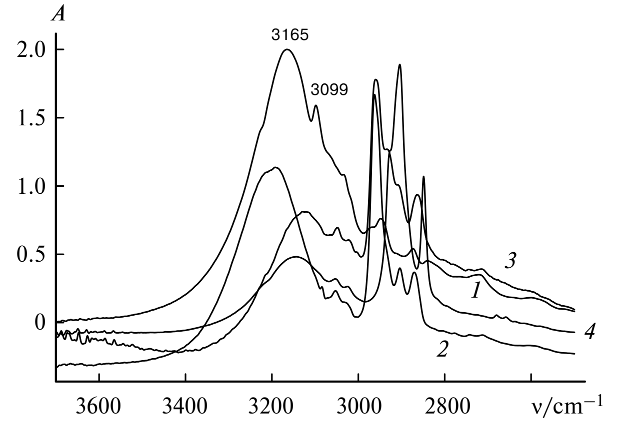


Fig. 3. The IR spectra of solutions of calixarenes **3** (*1*), **7** (*2*), **4** (*3*), and **5** (*4*) in CCl_4 ($1 \cdot 10^{-4}$ mol L^{-1}).

~3540 cm^{-1}, which are responsible for the non-bonding hydroxy fragments of the carboxy groups, are absent. This fact demonstrates the presence of hydrogen bonds between COOH fragments of the upper rim. Earlier,[24] we explained the unique decrease in flexibility of *p*-(3-carboxymethyl-1-adamantyl)calix[6]arenes and the formation of the *winged* or *the pinched cone* conformations by the intramolecular interaction of the upper rim functional groups. This conclusion was based on the analysis of the ^{1}H NMR spectra in the low-polar solvent, chloroform. The coalescence temperature of the NMR signals for hexacarboxylic acid was found to be close to 60 °C, which was 50 °C higher than for *p*-*tert*-butyl- or *p*-(1-adamantyl)calix[6]arenes, and was close to the coalescence temperature for *p*-*tert*-butylcalix[4]arene.

The IR spectral data (see Figs 3 and 4 and Table 2) reflect the system of hydrogen bonding for the more stable conformer of the macrocycle: for calix[4]arenes, the *cone*, for calix[6]arenes, the *pinched cone*, and for *p*-*tert*-butylcalix[8]arene, the *pleated loop.*[14]

Table 2. The ν(OH)/cm^{-1} frequencies in the IR spectra of the analyzed calixarenes **1—7**

Calix-arene	Solid sample			CCl_4 solution[b]
	20 °C	180 °C	20 °C[a]	
1	3154, 3237[c]	3193, 3265[c]	3146, 3246[c]	3173
2	3170	3231	3172	3137
3	3162	3329	3281	3165
4	3146	3163	3133	3125
5	3144, *3450 sh.*[d]	3161	3135	3143
6	3197, *3420 sh.*[d]	3173	3140	3124
7	3238, *3450 sh.*[d]	3242	3214	3192

[a] After heating of the sample at 180 °C.

[b] 10^{-4} mol L^{-1}.

[c] The duplication is caused by a deformation of the *cone* in a crystal.[17]

[d] In italic is given the absorption of absorbed moisture.

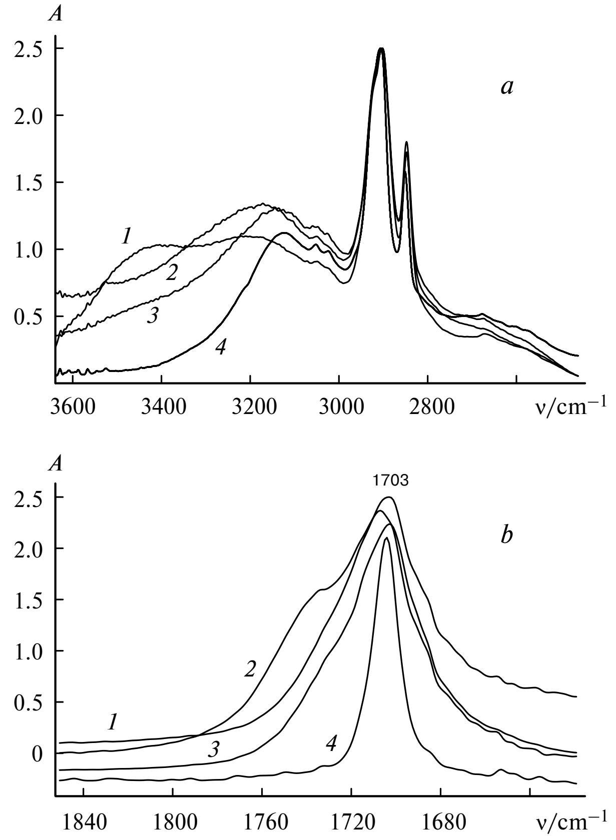


Fig. 4. The IR spectra of calixarene **6**, recorded at 20 (*1*) and 180 °C (*2*), as well as at 20 °C after cooling down of the sample, heated before at 180 °C (*3*), and for the CCl_4 solution (*4*) in the regions of the ν(OH) (*a*) and ν(C=O) (*b*) absorptions.

The maxima of the absorption bands of the hydroxy groups stretching vibrations for calix[4]- and calix[6]arenes with *p*-*tert*-butyl or adamantyl substituents at the upper rim of the molecules are within a narrow interval of frequencies, from 3124 to 3143 cm^{-1}. For the unsubstituted calixarenes **1** and **3**, the corresponding bands are positioned a little higher (3173 cm^{-1}). The lowest ν(OH) frequencies are characteristic of the calix[6]arene derivatives: 3124 and 3125 cm^{-1} for compounds **6** and **4**, respectively. For the series of *tert*-butylcalix[*n*]arenes (n = 4, 6, 8), a linear correlation is observed for the frequencies of the ν(OH) stretching vibrations in the IR spectra (3137, 3125, and 3192 cm^{-1}) and for the chemical shifts δ_{OH} of the protons in hydroxy groups in the ^{1}H NMR spectra (δ 10.35, 10.53, and 9.64),[14] respectively.

It is obvious that the strongest co-operative bond is formed in calix[6]arenes, but it is not very far from the H-bond strength in calix[4]arenes. In this series, the least strong CCIHB belongs to calixarene **7**.

In the IR spectra of the crystalline samples of the analyzed calixarenes, the frequencies of the hydroxy groups stretching vibrations are slightly higher than those in CCl_4 solution (see Table 2), though they tend to change along the same lines. This corroborate the strength of hydrogen bonds in the series calix[6]arenes ≥ ≥ calix[4]arenes > calix[8]arenes in both cases (also confirmed by the X-ray data).

The heating of calixarene samples for 30 min at 180 °C (far below m.p.) leads to the evaporation of absorbed moisture in compounds **5**—**7**, indicated by the disappearance of a shoulder at 3420—3450 cm^{-1} (see Fig. 4 and Table 2) and a weak δ(OH) band at about 1660 cm^{-1}. In calixarenes, first heated up to 180 °C and then cooled down to 20 °C, a slight drift is observed for the ν(OH) bands (about 20—40 cm^{-1}), with calixarenes **2** and **3** being the exception. For them, the high-frequency shift of the ν(OH) band is the most prominent in the IR spectra, amounting to ~170 and 60 cm^{-1}, respectively. However, a restoration of the ν(OH) band to the observed before heating frequency is typical of compound **2**, whereas for compound **3**, the similar restoration of the frequency does not take place. One can assume that the heating somewhat changes the conformational state of the molecule of this calixarene without bulky substituents, which is retained after the cooling down (see Table 2). Apparently the removal or rearrangement of the solvent molecules, typically held by a solid calixarene, plays a certain role in this. A room, left behind by them, allows a certain deformation of the macrocycle framework, which is retained after cooling down. The presence of bulky substituents, apparently, makes such a rearrangement difficult.

As to calixarene **6** with six CH_2COOH groups at the adamantane belt of the molecule, in the IR spectra of this compound (see Fig. 4), the ν(OH) bands of the hydroxy and carboxy groups, free of hydrogen bonds, are absent. The absorption of phenolic hydroxy groups from the high-frequency side overlaps with the absorption of carboxy groups, which has the maximum at about 3000 cm^{-1}; the ν(OH) band frequencies of phenolic hydroxyls in macrocycle **6**, both in the crystalline state and in solution, are very close to those of compound **4** (see Table 2). One can assume that similarly to the latter they also exist in the *pinched cone* conformation. The ν(OH) band of COOH groups can be visualized in the spectrum of the structural analog of calixarene **6**, 1-adamantylacetic acid (Fig. 5). In the IR spectrum of the crystalline sample, the ν(OH) absorption band is located in the interval 2400—3400 cm^{-1} with the maximum at about 2950 cm^{-1}, whereas its low-frequency wing serves as a pedestal for the absorption bands of the ν(CH) stretching vibrations. The absence of a band at about 3530 cm^{-1} in the IR spectra of calixarene **6** solution, characteristic of the free carboxy groups,[27] which can be seen in the spectrum of the starting acid (see Fig. 5), allows one to suggest that the carboxy fragments of the adamantane belt in solution form intramolecular H-bonds. They can either close a linear chain, similarly to the phenolic OH groups of the lower rim, or form in pairs three cyclic dimers (Fig. 6). In order to estimate the possibility of the formation of intramolecular hydrogen bond for carboxy groups in molecule **6**, it is necessary to have all the geometric parameters of this molecule. Since there is no the X-ray data, we "constructed" this molecule[1] from two, available from CSDS,[5] *viz.*, *p*-*tert*-butylcalix[6]arene[7] (refcode is VARGUR) and 1,3-adamantanediacetic acid[28] (refcode is HIHJIR). All the *tert*-butyl groups were removed from the former molecule and replaced by the fragments of adamantylacetic acid from the latter. It turned out that the geometric parameters of molecule **6**, considering the possibilities of the conformational rearrangements in the adamantyl fragment, allow one to form hydrogen bonds following the both variants (see Fig. 6).

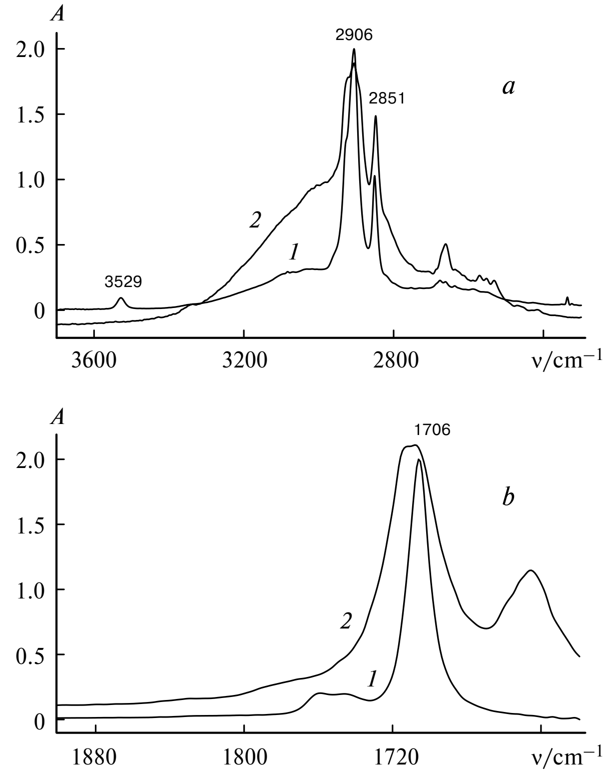


Fig. 5. The IR spectra of 1-adamantylacetic acid in the regions of ν(OH) (*a*) and ν(C=O) (*b*) absorptions for the CCl_4 solution (*1*) and for the crystal (*2*).

It is known[29] that for organic monocarboxylic acids, a linear chain of H-bonds and a cyclic dimer are characterized by the ν(C=O) absorption bands at about 1700 and 1650 cm^{-1}, respectively. For example, in the IR spectrum of 1-adamantylacetic acid solution, there is a single band (~1706 cm^{-1}), and in the spectrum of its crystalline sample, a pair of bands (1708 and 1645 cm^{-1}) is observed. This points to the fact that in the crystalline state of this acid, both kinds of H-bonding are present (see Fig. 5). In the IR spectra of calixarene **6**, there is a single band at 1704 cm^{-1}. This tells us about a dimeric H-bond, the probability of forming of which is much higher than of

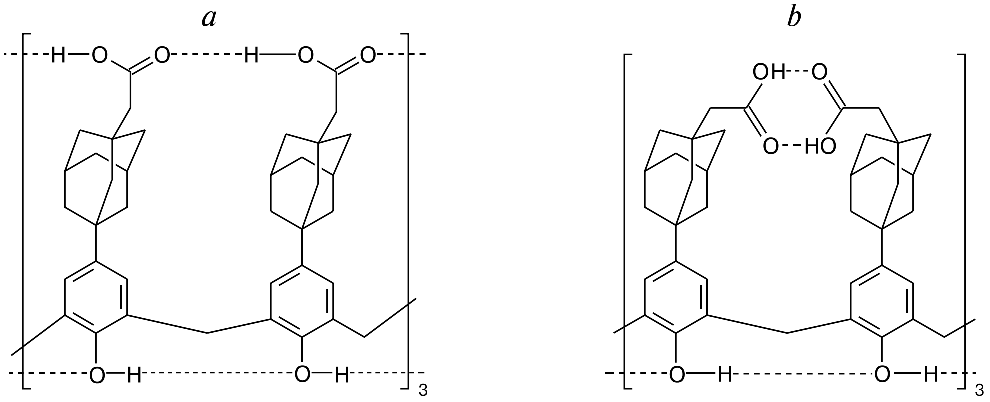


Fig. 6. The possibilities of the formation of cyclic (*a*) and dimeric (*b*) intramolecular hydrogen bond by carboxy groups in calixarene **6**.

a cyclic linear chain. Such a fixation of the adamantyl fragments considerably increases the size of the cavity in this molecule.

It is obvious that the potential of IR spectroscopy in the identification of a conformational state is limited, if it is not accompanied by a rearrangement of H-bonds. Nevertheless, this method, together with X-ray and NMR, provides a unique information, which allows one to follow the variations of hydrogen bonding together with conformational rearrangements. The changes in the frequency and shape of the ν(OH) absorption band, while varying amount of phenolic fragments, reflect the effect of mutual influence of two macrocycles in calixarene molecule, the covalent macrocycle and macrocycle, formed by CCIHB. The optimal conformation of the covalent macrocycle does not interfere with the formation of the hydrogen-bound macrocycle in calixarene molecule. In this conformation, the participating in CCIHB hydroxy groups have the lowest vibrational frequency, such as in calix[4]- and calix[6]arenes. If geometry of CCIHB and conformation of the covalent macrocycle are discoordinated, then the increase in the ν(OH) frequency reflects arisen tension in the molecule, as it can be seen in the IR spectra of substituted calixarene **7** and unsubstituted calixarenes **1** and **3**. The mentioned effect prominently reveals itself in the IR spectra of diluted solutions, whereas a crystal lattice can affect this sometimes very small shift of the ν(OH) frequency. Actually CCIHB serves as a sonde, allowing one to follow the changes in conformational state of calixarene molecules.

* * *

In the present work, a hydrogen bonding in the series of calix[*n*]arenes (*n* = 4, 6, 8), differing in a number of phenol units in the macrocycle, with free *para*-positions, as well as with *tert*-butyl or adamantyl substituents in the phenol fragments, has been studied by the Fourier transform IR spectroscopy. It was shown that all the analyzed compounds both in the crystalline form and in diluted CCl_4 solutions retain their conformation characteristics, defined by the strong cyclic co-operative intramolecular hydrogen bond. The conformers of the analyzed crystalline macrocycles with bulky substituents are retained upon heating up to 180 °C. The absence of a bulky substituent in calixarene **3**, apparently, leads to a conformational rearrangement under heating, accompanied by a change of the H-bonding system, which is fixed by a subsequent cooling down of the substance. The formation of hydrogen bonds between three pairs of the neighboring COOH groups in the molecule of calix[6]arene with six fragments of adamantylacetic acid does not affect the strength of the co-operative hydrogen bond of the phenolic hydroxy groups neither in the solid state nor in the neutral solvent and increases recepting potentialities of its molecular cavity.

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