



# Comparative study of the vibrational spectra of carboxylate azocalix[4]arenes and azothiacalix[4]arenes

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## ABSTRACT

The vibrational spectra of calix[4]arene (*p*-CAC) and thiacalix[4]arenes with azobenzene units having carboxylate groups in the para (*p*-CATC) and meta position (*m*-CATC) were recorded and analyzed.

The calculated structures of molecules *p*-CAC, *p*-CATC, and *m*-CATC are consistent with experimental X-ray data. The most stable and polar is the *cone* conformation with four intramolecular cooperative hydrogen bonds. In classical calixarenes, the hydrogen bonds are shorter and, therefore, more durable than in thiacalixarenes. The cone conformation retains for all the studied calixarene molecules. The energy differences between *E*- and *Z*-forms of azobenzene groups in *p*-CAC, *p*-CATC, and *m*-CATC are 254.4, 260.2, and 249.4 kJ/mol, respectively. The shape of the molecules changes noticeably upon isomerization of azobenzene groups.

Upon passing from thiacalixarenes to classical calixarenes, the dipole moment of the molecule increases. The polarity of calixarene molecules changes upon isomerization of azobenzene units. Ionization energy electron affinity and electrophilicity are higher in classical calixarenes compared to thiacalixarenes. There are active sites of reaction and interaction in the narrow and wide rims of the calixarene molecules. Carboxylate groups are most active in the formation of complexes with metals.

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## 1. Introduction

Calixarene molecules are cup-shaped and used in supramolecular chemistry [1–6]. For biological experiments and drugs, solubility in water is especially important. The addition of carboxylate groups to calixarenes ensures their solubility in water [1–6]. Calixarenes with carboxylate groups interact with biological objects [7–11]. They are sensitive to bacteria and metal ions and purify water [7–11]. Calixarenes with azobenzene units are optical sensors for ions of various metals [12–17]. Calixarenes are used for analytical purposes because the formation of complexes of molecules with metal ions often changes the color of solutions [17]. Irradiation with a wavelength of 350 nm causes reversible isomerization of azobenzene units [18]. Earlier, we reported on the study of the IR spectra of calixarenes [19–30]. The study of IR spectra provides

information on the conformation and hydrogen bonds necessary for understanding the supramolecular properties of calixarenes.

In this article, we have studied for the first time the IR and Raman spectra of calixarenes and thiacalixarenes with azobenzene units and carboxylate groups. A comparative study of the vibrational spectra of calixarenes and thiacalixarenes makes it possible to highlight the characteristics of hydrogen bonds and the conformation of these compounds. Analysis of experimental vibrational spectra of calixarenes with different functional groups opens the possibility of separating bands of aromatic fragments, azobenzene units, and carboxylate groups. We have tried to establish changes in the spectra during the photoisomerization of azobenzene groups. The spectral characteristics of calixarenes will broaden the limits of their practical application.

## 2. Experimental

The synthesis of 5,11,17,23-tetrakis-[(4-carboxyphenyl)azo]-25,26,27,28-tetrahydrocalix[4]arene (*p*-CAC, Fig. 1) was performed

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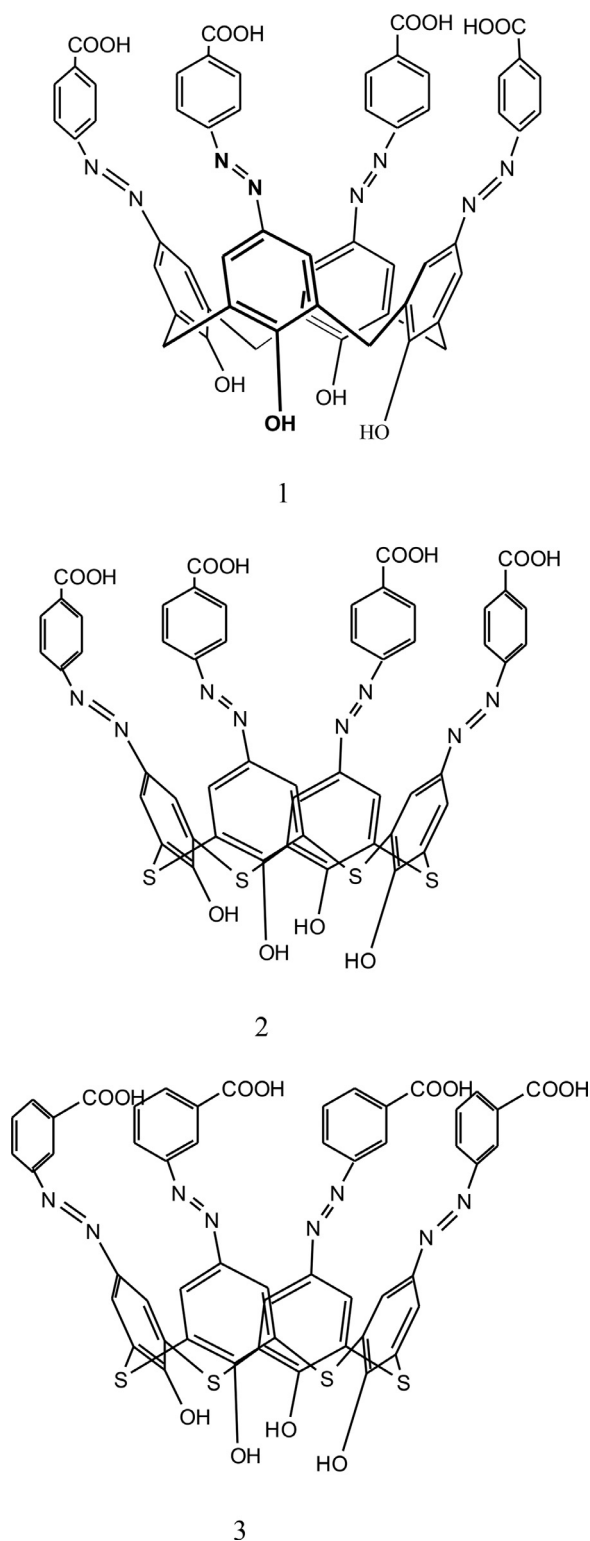


Fig. 1. Structure of *p*-CAC (1), *p*-CATC (2), and *m*-CATC (3).

according to [31], and all constants coincided with the literature data.

We synthesized the carboxyl azo derivatives of thiacalix[4]arene as follows (Scheme). In a 250 ml flask was placed a solution of the salt of methyl 4-aminobenzoate diazochloride (methyl 3-aminobenzoate) obtained by the reaction of methyl 4-

aminobenzoate (ethyl 3-aminobenzoate) (1.135 g), concentrated HCl (4.5 ml) in distilled water (7 ml) while stirring in an ice bath and adding dropwise a solution of sodium nitrite (0.69 g, 10 mmol) in distilled water (7 ml) (5°C). We added a cooled solution of thiacalix[4]arene (0.5 g, 1 mmol), NaOH (0.8 g) in MeOH-DMF (30 ml, 5: 8) to the obtained diazonium salt. The reaction mixture was stirred for 3 h in an ice bath, 24 h at room temperature, and 3–4 h at heating to 60°C (control of the pH of the reaction mixture to 7.5–8). Brick red crystals have been isolated.

5,11,17,23-tetrakis-[(4-methoxycarbonylphenyl)azo]-25,26,27,28-tetrahydroxythiacalix[4]arene **1**. 0.975 g (72%): <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, Ppm): 3.86 (12H, s, -OCH<sub>3</sub>); 7.87 (8H, d, Ar-H); 8.07 (8H, d, Ar-H); 8.17 (8H, s, Ar-H).

5,11,17,23-tetrakis-[(3-ethoxycarbonylphenyl)azo]-25,26,27,28-tetrahydroxythiacalix[4]arene **3**. 0.594g (52%): <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 1.32 (12H, t, -CH<sub>3</sub>); 4.33 (8H, q, -OCH<sub>2</sub>-); 7.67 (4H, t, Ar-H); 8.02 (4H, d, Ar-H); 8.07 (8H, d, Ar-H); 8.20 (4H, d, Ar-H); 8.29 (8H, s, Ar-H).

The synthesis of tetraacids **2** (**4**) was carried out as follows. We placed in a 250 ml flask 1.16 mmol of ether **1** (**3**), 16.3 mmol of NaOH, 50 ml of THF, and 10 ml of distilled water. We stirred the reaction mixture while heating at 500° C in an atmosphere of argon until the precipitate dissolved (42, 24 h, respectively). Then we added 80 ml of HCl (1: 4). Compound **2** (**4**) was precipitated (93%).

5,11,17,23-tetrakis-[(4-carboxyphenyl)azo]-25,26,27,28-tetrahydroxythiacalix[4]arene **2** or (*p*-CATC, Fig. 1) (93%): <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ ppm: 7.82 (8H, d, Ar-H); 8.02 (8H, d, Ar-H); 8.14 (8H, s, Ar-H). <sup>13</sup>C- {<sup>1</sup>H} NMR (100.9 MHz, DMSO-d<sub>6</sub>, 25°C) δC, ppm: 79.26, 122.43, 122.66, 123.09, 130.72, 131.93, 132.11, 154.67, 167.03. MALDI TOF (*m/z*): 1111.6 [*M* + *Na*]<sup>+</sup>. Tm > 350° C.

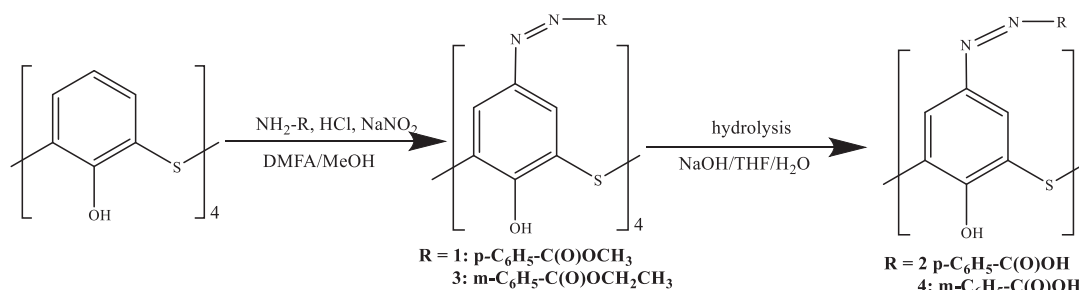
5,11,17,23-tetrakis-[(3-carboxyphenyl)azo]-25,26,27,28-tetrahydroxythiacalix[4]arene **4** or (*m*-CATC, Fig. 1) (91%): <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 7.64 (4H, t, Ar-H); δ-d<sub>g</sub>, 8.01 (4H, d, d, Ar-H); 8.06 (4H, d, Ar-H), 8.19 (4H, s, Ar-H), 8.29 (4H, s, Ar-H). <sup>13</sup>C- {<sup>1</sup>H} NMR (100.9 MHz, DMSO-d<sub>6</sub>, 25° C, δ, ppm): 120.91, 121.14, 121.85, 122.67, 126.79, 129.67, 131.95, 135.00, 143.07, 151.94, 166.71. MALDI TOF (*m/z*): 1089.7 [*M* + *H*]<sup>+</sup>. Tm > 350° C.

IR spectra of calixarene samples pressed into KBr tablets were recorded with a Bruker Vector 22 spectrometer. Raman spectra were obtained with an Nd: YAG laser and were recorded by the Bruker FT-Raman RAM II module.

### 3. Computational procedure

Due to the cyclic system of hydrogen bonds, the cone conformation of calix[4]arenes is the most stable [1]. Azobenzene units may take *E* and *Z* isomeric forms [18]. We have built molecular models of calixarenes for cone conformation and the *E* and *Z* isomers of azobenzene groups. At first, we optimized the geometry of calix[4]arenes and thiacalix[4]arenes in the cone conformation. Then we attached azobenzene units to aromatic fragments of calixarenes in the para position. Finally, we attached the carboxylate groups to the azobenzene substituents in the para and meta positions.

Calculation of the vibrational spectra of calixarenes was performed using the gradient-correlated DFT with a B3LYP functional [32,33] and a 6-31G(d,p) basis set and the Gaussian09 program [34]. As a first approximation of the geometry of *p*-CAC, *p*-CATC, and *m*-CATC, we used experimental data obtained by X-ray diffraction [35]. The assignment of oscillations was performed using the distribution of potential energy [36]. We evaluated the ability of calixarenes to form complexes using global chemical descriptors [37, 38].



Scheme 1.

#### 4. Results and discussion

Fig. 2 and Supplementary information S1-S3 show the results of the geometric optimization of calixarene molecules. The calculated structures of molecules *p*-CAC, *p*-CATC, and *m*-CATC are consistent with experimental X-ray data [39–41]. The mean values of the distances between neighboring oxygen atoms and the average values of the theoretical angles O–H...O in *p*-CAC, *p*-CATC, and *m*-CATC correspond to the experiment [41].

The most stable is the cone conformation with four intramolecular cooperative hydrogen bonds (Fig. 2). In molecules *p*-CAC, *p*-CATC, and *m*-CATC, the more stable is the *E*-form of azobenzene groups. The energy differences between *E*- and *Z*-forms of azobenzene groups in *p*-CAC, *p*-CATC, and *m*-CATC are 254.4, 260.2, and 249.4 kJ/mol, respectively (Table 1). The theoretical lengths of the N(70)–N(72) bond and dihedral angles C(51)–N(70)–N(52)–C(53) and N(50)–N(52)–C(53)–C(55) of the molecule *p*-CAC for *E* and *Z* forms are different, which corresponds to experiment [42]. The corresponding dihedral angles and length of the N–N bond in the molecules *p*-CATC and *m*-CATC in the *E*- and *Z*-forms has similar values. The shape of the molecules changes noticeably upon isomerization of azobenzene groups.

Torsion angles around CH<sub>2</sub>–Ar bonds determine the configuration of the calixarenes [39]. The average values of the calculated torsion angles show that the cone conformation retains for all the studied calixarene molecules (Supplementary information S1-S3). The orientation of aromatic units in calixarenes and thiacalixarenes changes during isomerization of azobenzene units.

The calixarene molecules in the cone conformation are bowl-shaped and can include guest molecules. Electrostatic interactions dominate in complexes of calixarenes with metals [43]. To evaluate these interactions, we calculated the charges on the atoms of the functional groups in the calixarenes (Table 2). It turned out that the molecules of calixarenes *p*-CAC, *p*-CATC, and *m*-CATC contain polar OH bonds along the lower rim. The carboxylate groups in molecules *p*-CAC, *p*-CATC, and *m*-CATC have high charges on oxygen atoms. The nitrogen atoms of the azobenzene unit in these calixarene molecules have sufficiently small charges. Thus, hydroxyl and carboxylate groups can participate in further reactions and actively interact with guest molecules.

Table 1

Energies *E* (a.u.) and relative energies  $\Delta E$  (kJ/mol) of conformers of calixarenes calculated at the DFT/B3LYP/6-31G(d,p) level.

Compound	Conformer	<i>E</i>	$\Delta E$
<i>p</i> -CAC	<i>E</i>	-3498.805538	0
	<i>Z</i>	-3498.708712	254.4
<i>p</i> -CATC	<i>E</i>	-4934.264810	0
	<i>Z</i>	-4934.165652	260.2
<i>m</i> -CATC	<i>E</i>	-4934.263883	0
	<i>Z</i>	-4934.168875	249.4

Table 2

The partial charges of the atoms determined by natural population analysis of *p*-CAC, *p*-CATC, and *m*-CATC.

	<i>E</i>	<i>Z</i>		<i>E</i>	<i>Z</i>
Atom	q <sub>n</sub>	q <sub>n</sub>	Atom	q <sub>n</sub>	q <sub>n</sub>
<i>p</i> -CAC					
O1	-0.752	-0.754	C53	0.120	0.090
C5	0.347	0.316	C101	0.814	0.814
H38	0.530	0.531	O102	-0.600	-0.599
N50	-0.188	-0.114	O103	-0.716	-0.719
C51	0.093	0.073	H104	0.508	0.516
N52	-0.207	-0.121			
<i>p</i> -CATC					
O1	-0.718	-0.723	C47	0.117	0.064
C5	0.355	0.343	N46	-0.202	-0.115
C8	0.081	0.049	C53	0.814	0.823
S13	0.290	0.292	O52	-0.598	-0.581
H41	0.535	0.535	O59	-0.716	-0.744
N45	-0.188	-0.131	H60	0.509	0.518
<i>m</i> -CATC					
O1	-0.719	-0.723	C47	0.094	0.064
C5	0.353	0.343	N46	-0.199	-0.115
C8	0.082	0.049	C91	0.818	0.823
S13	0.289	0.292	O92	-0.600	-0.581
H41	0.535	0.535	O93	-0.714	-0.744
N45	-0.192	-0.131			

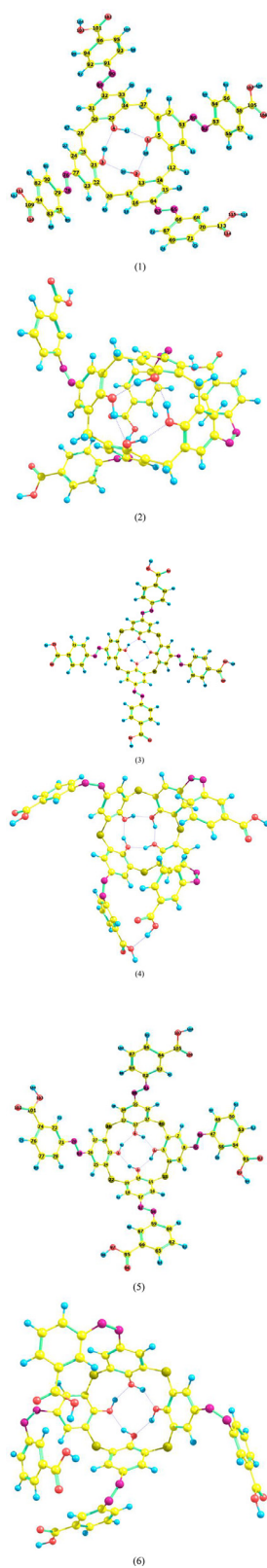
Classical calixarene molecules have a higher dipole moment than thiacalixarenes (Table 3). Besides, the polarity of calixarene molecules changes upon isomerization of azobenzene units (Table 3). Ionization energy electron affinity and electrophilicity are higher in classical calixarenes compared to thiacalixarenes.

Consideration of the molecular orbitals of molecules *p*-CAC, *p*-CATC, and *m*-CATC, shows that conjugation encompasses azobenzene fragments (Fig. 3). The formation of complexes of calixarenes with metal ions leads to a change in the length of the conjugated sections and the color.

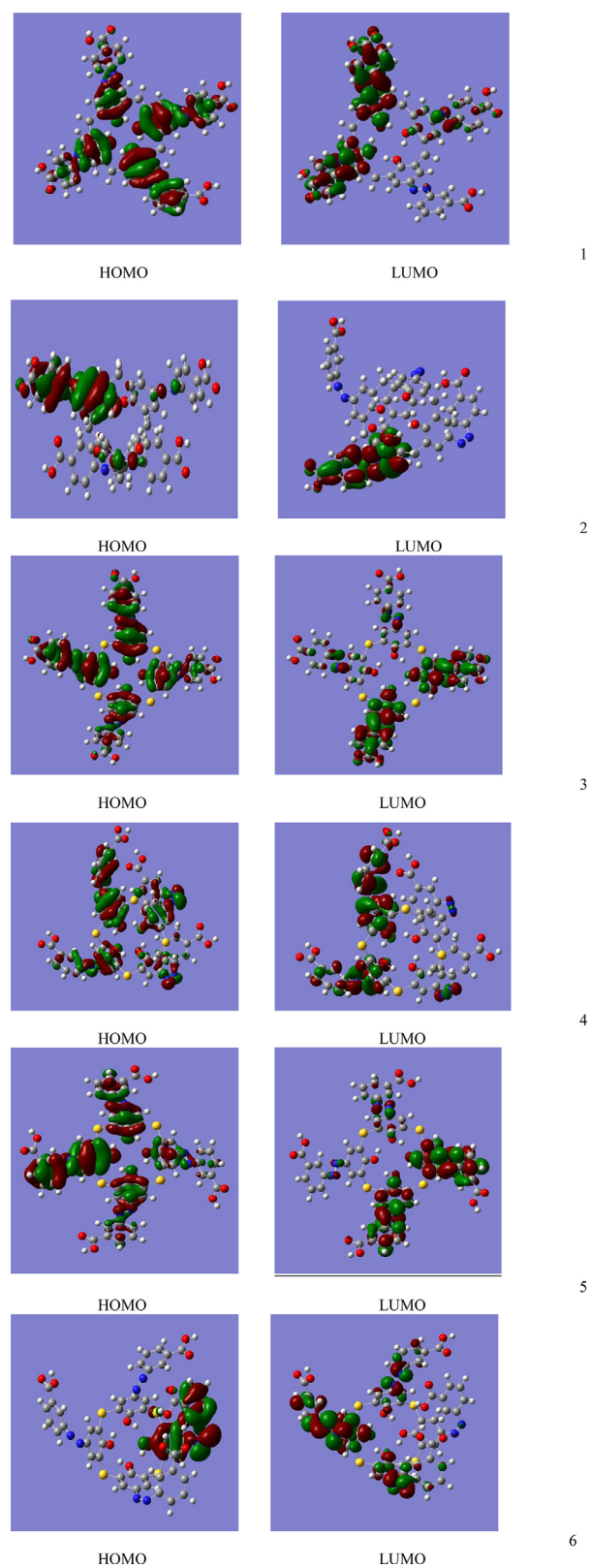
In the *p*-CAC molecule, hydrogen bonds are due to the interaction of non-bonded electron pairs of oxygen atoms and anti-bonding orbitals of OH groups (Supplementary information S4). The strong interactions of carbon-carbon, carbon-nitrogen, and nitrogen-nitrogen bonds describe the conjugation in aromatic and azobenzene fragments. Interactions of lone electron pairs of carboxylate groups with neighboring bonds occur with high energy. In the case of thiacalixarenes *p*-CATC and *m*-CATC, there are similar interactions.

Supplementary information S7-S9 and Figs. 6-11 show the vibrational spectra of *p*-CAC, *p*-CATC, and *m*-CATC. Our calculations reproduce the intensity of the most visible bands in the experimental spectra of *p*-CAC, *p*-CATC, and *m*-CATC (Figs. 6-11). The intensities of the bands in spectra of calixarenes change noticeably, while the frequencies remain constant.

The calixarenes studied have a complex system of hydrogen bonds. In the infrared spectra of *p*-CAC, *p*-CATC, and *m*-CATC, there



**Fig. 2.** Optimized geometry and atom numbering of *E*- and *Z*-forms for *p*-CAC (1,2), *p*-CATC (3,4), and *m*-CATC (5,6).

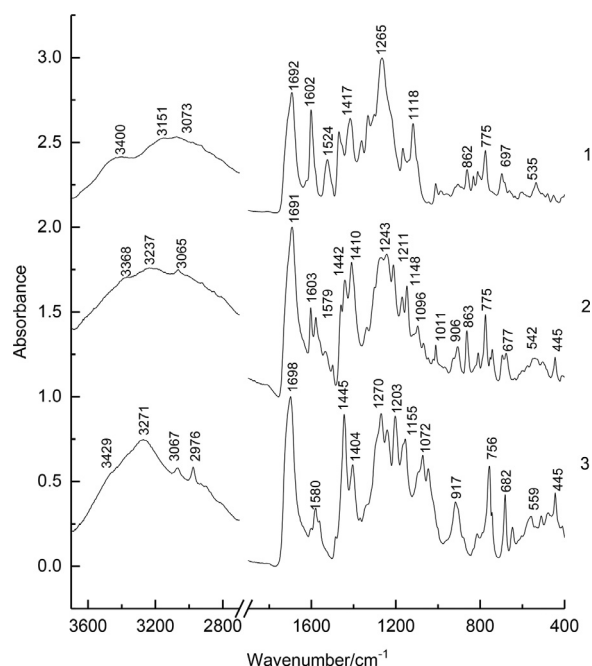
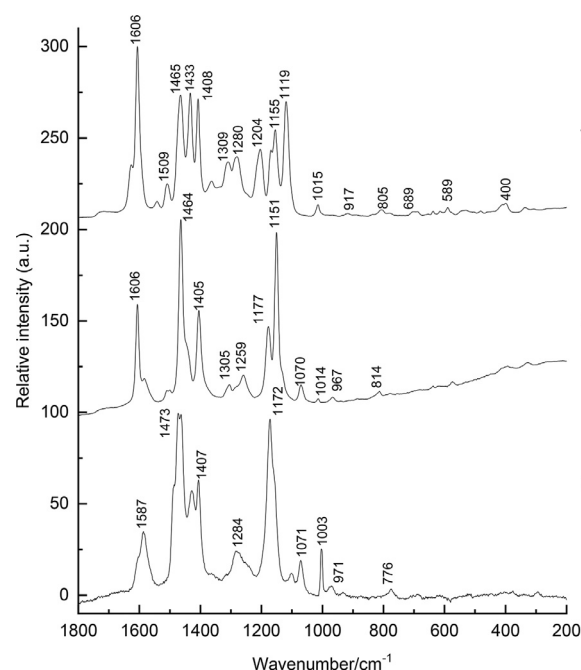


**Fig. 3.** Molecular orbital surfaces of *E*- and *Z*-forms for *p*-CAC (1,2), *p*-CATC (3,4), and *m*-CATC (5,6).



**Table 3**  
Global reactivity descriptors of *p*-CAC, *p*-CATC, and *m*-CATC.

Compound	Conformer	Ionization energy, eV	Electron affinity, eV	Chemical potential, eV	Softness, eV	Electro-philicity index, eV	Dipole moment, D
<i>p</i> -CAC	<i>E</i>	6.968	1.909	-4.439	0.198	3.894	2.490
	<i>Z</i>	6.933	1.564	-4.249	0.186	3.362	3.103
<i>p</i> -CATC	<i>E</i>	7.254	0.076	-3.665	0.139	1.871	1.480
	<i>Z</i>	7.068	1.620	-4.344	0.184	3.464	1.117
<i>m</i> -CATC	<i>E</i>	7.187	1.828	-4.508	0.183	3.814	0.941
	<i>Z</i>	6.974	1.542	-4.258	0.184	3.338	2.149

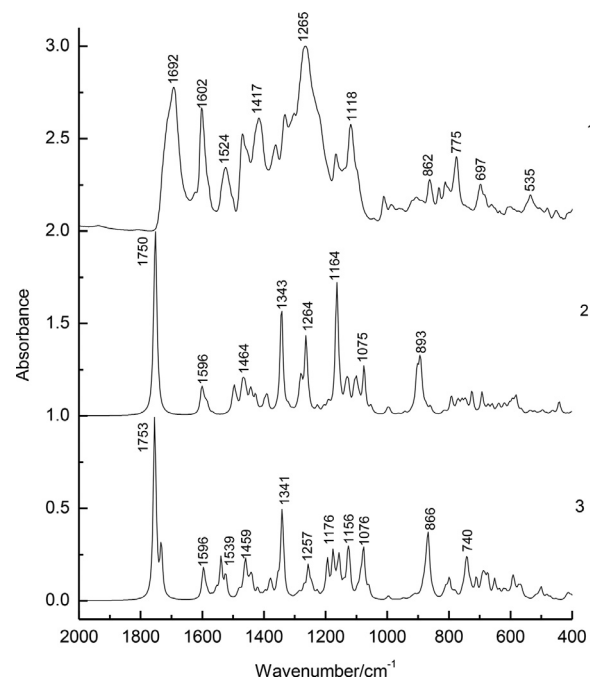
**Fig. 4.** Experimental IR spectra of *p*-CAC (1), *p*-CATC (2), and *m*-CATC (3).**Fig. 5.** Experimental Raman spectra of *p*-CAC (1), *p*-CATC (2), and *m*-CATC (3).

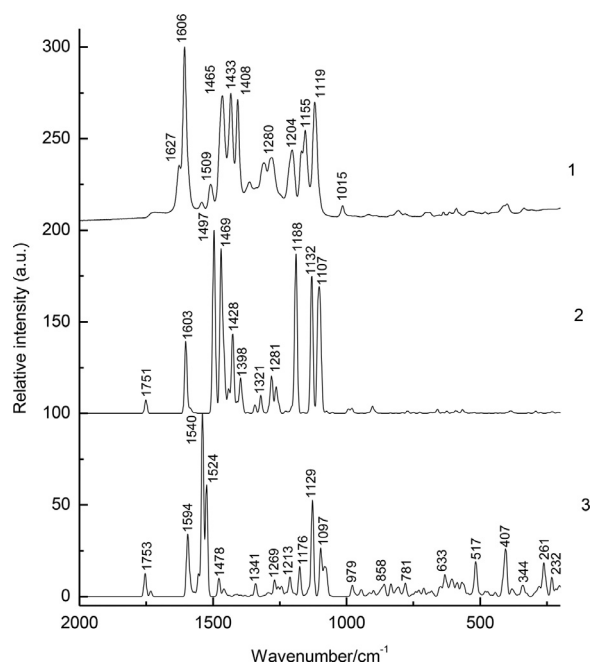
are no bands of free OH groups in the region of  $3600\text{ cm}^{-1}$  (Fig. 4), which means that all hydroxyl groups participate in the formation of H-bonds. The  $\nu(\text{OH})$  bands have frequencies at  $3400, 3151\text{ cm}^{-1}$  in the IR spectra *p*-CAC. Frequencies at  $3368, 3237\text{ cm}^{-1}$  reveal itself in the spectra of *p*-CATC. Bands at  $3429, 3271\text{ cm}^{-1}$  appear in *m*-CATC spectra. A lower vibration frequency of hydroxyl groups in calixarenes compared to thiacalixarenes indicates the formation of a stronger hydrogen bond.

CH stretching vibrations of aromatic fragments cause bands at  $3073, 3065, \text{ and } 3067\text{ cm}^{-1}$  in the spectra of the studied calixarenes (Fig. 4). Bands at  $1692, 1691, \text{ and } 1698\text{ cm}^{-1}$ , intense in the infrared spectra of *p*-CAC, *p*-CATC, and *m*-CATC, are connected with stretching vibrations of the  $\text{C}=\text{O}$  bonds of carboxylate groups. Under the action of hydrogen bonding, these bands shift to lower frequencies. The values of these frequencies indicate some weakening of the hydrogen bond in the carboxylate groups of molecule *m*-CATC.

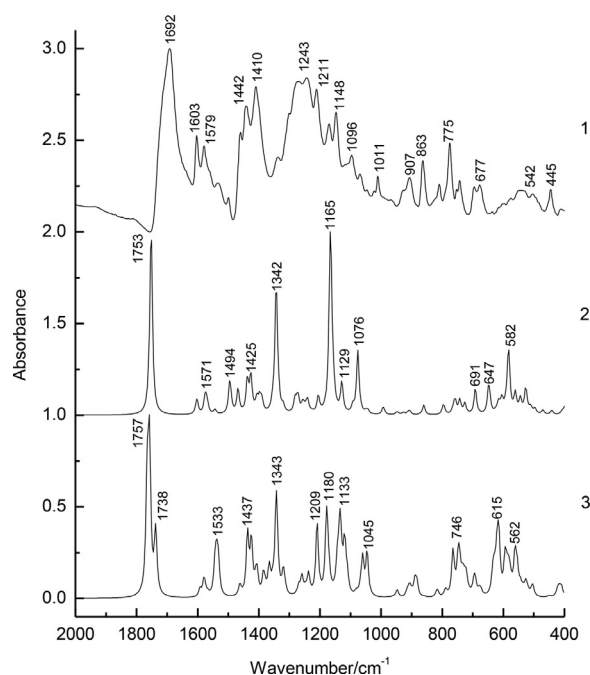
Bands at  $1623, 1602\text{ cm}^{-1}$  in the IR spectra and lines at  $1627, 1607\text{ cm}^{-1}$  in the *p*-CAC Raman spectra were attributed to CC stretching and CCH bending vibrations of aromatic moieties (Fig. 5). The vibrational spectra for para- and meta- substituted aromatic derivatives in this region differ markedly.

Asymmetric deformation vibrations of methylene groups occur at frequencies of  $1469 \text{ and } 1465\text{ cm}^{-1}$  in the vibrational spectra of *p*-CAC. Stretching vibrations of aromatic CC bonds and HCH and COH deformation vibrations cause the bands at  $1362 \text{ and } 1363\text{ cm}^{-1}$  in the vibrational spectra of *p*-CAC. The stretching vibrations

**Fig. 6.** Experimental IR spectra of *p*-CAC (1) and theoretical absorption curves of *E*- (2) and *Z*-forms (3) in the region  $1800\text{--}400\text{ cm}^{-1}$ .



**Fig. 7.** Experimental Raman spectra of *p*-CAC (1) and theoretical absorption curves of *E*- (2) and *Z*-forms (3) in the region 1800–400  $\text{cm}^{-1}$ .

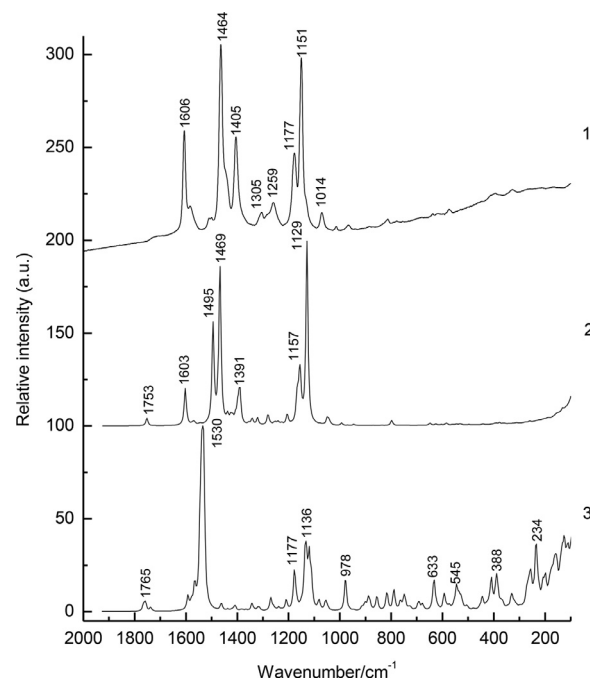


**Fig. 8.** Experimental IR spectra of *p*-CATC (1) and theoretical absorption curves of *E*- (2) and *Z*-forms (3) in the region 1800–400  $\text{cm}^{-1}$ .

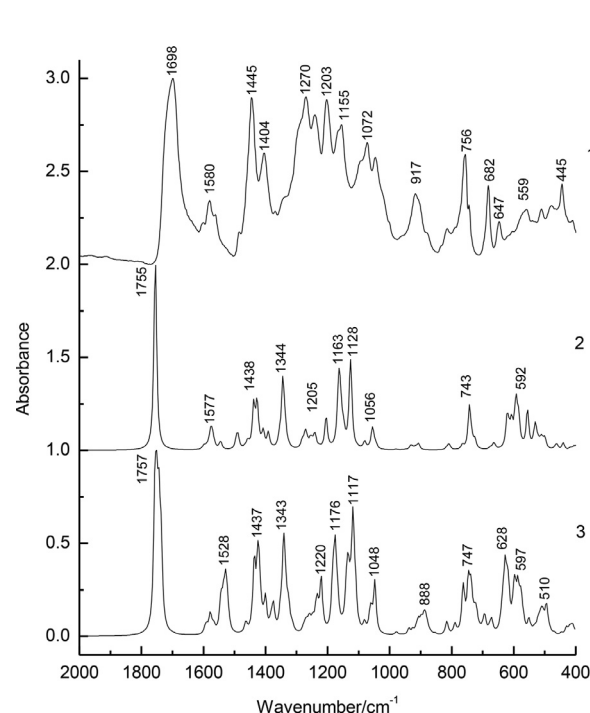
of the CC and CO bonds give rise to peaks at 1265, 1220, and 1166  $\text{cm}^{-1}$  in the infrared spectra of *p*-CAC.

The CC bonds stretching vibrations and the CCH bending vibrations give the bands 905, 862, and 832  $\text{cm}^{-1}$  in the IR spectrum of *p*-CAC. The 775  $\text{cm}^{-1}$  frequency in the infrared spectra of *p*-CAC relates to non-planar vibrations of aromatic groups.

The torsional and bending vibrations of the benzene rings result in bands of 697, 685, 662, 636, 608, 600  $\text{cm}^{-1}$  in the IR spectrum of *p*-CAC. The torsional vibrations of the benzene rings and deformation vibrations of the macrocycle cause a band 535  $\text{cm}^{-1}$  in the IR spectrum of *p*-CAC. CCC and OCC bending vibrations oc-



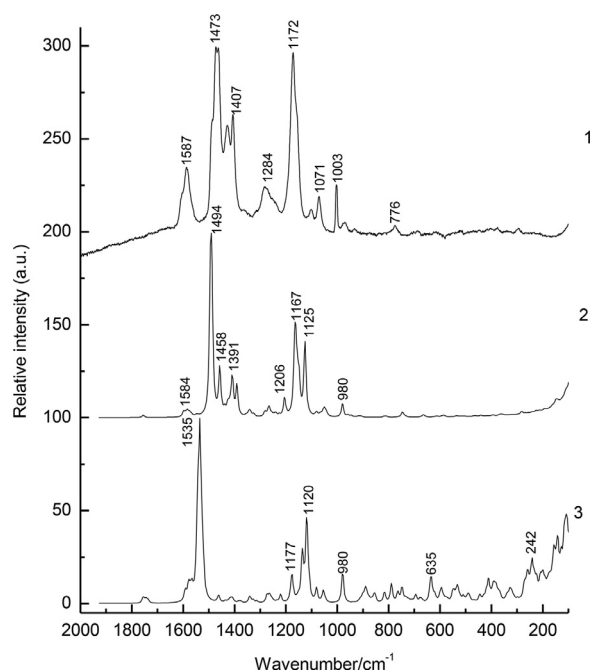
**Fig. 9.** Experimental Raman spectra of *p*-CATC (1) and theoretical absorption curves of *E*- (2) and *Z*-forms (3) in the region 1800–400  $\text{cm}^{-1}$ .



**Fig. 10.** Experimental IR spectra of *p*-CATC (1) and theoretical absorption curves of *E*- (2) and *Z*-forms (3) in the region 1800–400  $\text{cm}^{-1}$ .

cur with frequencies at 482, 410  $\text{cm}^{-1}$  in the Raman spectrum of *p*-CAC. Torsional vibrations around the CC and CN bonds appear in the Raman spectrum of *p*-CAC as bands at 400, 336, 309, 317, and 173  $\text{cm}^{-1}$ .

The consideration of the vibrational spectra of *p*-CAC and *p*-CATC allows selecting bands of methylene groups and CS bonds. Vibration bands of methylene groups at 1470, 1417, 1362, 1332, 1118, 832  $\text{cm}^{-1}$  in the spectrum of calixarene *p*-CAC are absent in the spectra of *p*-CATC.



**Fig. 11.** Experimental Raman spectra of *m*-CATC (1) and theoretical absorption curves of *E*- (2) and *Z*-forms (3) in the region 1800–400  $\text{cm}^{-1}$ .

A change in the conformation of the azobenzene fragment leads to a decrease in the size of the conjugate sections, which in turn leads to a change in the vibrational spectra of *E*- and *Z*-forms of *p*-CAC, *p*-CATC, and *m*-CATC (Figs. 6–9, Supplementary information S7–S9). The frequencies at 1433, 1417  $\text{cm}^{-1}$  in the spectra of *p*-CAC are related to N=N stretching vibrations of the azobenzene units (Figs. 6–9) [42,44]. These vibrations have frequencies of 1389  $\text{cm}^{-1}$  for the *E*-form and 1540  $\text{cm}^{-1}$  for the *Z*-form in the theoretical Raman spectra *p*-CAC (Fig. 7).

An analysis of the vibrational spectra of calixarenes allows one to distinguish the 1606  $\text{cm}^{-1}$  line in the Raman spectrum and the 1602  $\text{cm}^{-1}$  band in the IR spectrum *p*-CAC due to stretching vibrations of the carbon-carbon bonds of the benzene rings. The carboxyl groups show characteristic intense bands 1692 and 1265  $\text{cm}^{-1}$  in the IR spectrum of *p*-CAC. Stretching vibrations of the N=N azobenzene bonds reveal itself as frequencies at 1433, 1417  $\text{cm}^{-1}$  in the spectra of *p*-CAC.

## 5. Summary

Vibrational spectra of azocalix[4]arene and azothiacalix[4]arene with carboxylate groups were recorded. A comparative study of the vibrational spectra of azocalix[4]arene and azothiacalix[4]arene with carboxylate groups allows us to identify the bands characterizing the vibrations of different functional groups. The calixarenes studied have a complex system of hydrogen bonds which determines their supramolecular properties. In the infrared spectra of *p*-CAC, *p*-CATC, and *m*-CATC, there are no bands of free OH groups, which means that all hydroxyl groups participate in the formation of H-bonds. A lower vibration frequency of hydroxyl groups in calixarenes compared to thiacalixarenes indicates the formation of a stronger hydrogen bond.

The *p*-CAC, *p*-CATC, and *m*-CATC calixarene molecules retain the structure of the bowls. The most stable is the *E*-form of azobenzene groups. The energy differences between *E*- and *Z*-forms of azobenzene groups in *p*-CAC, *p*-CATC, and *m*-CATC are 254.4, 260.2, and 249.4 kJ/mol, respectively.

The calixarene molecules in the *cone* conformation are bowl-shaped and can include guest molecules. To evaluate electrostatic interactions, we calculated the charges on the atoms of the functional groups in the calixarenes. It turned out that the molecules of calixarenes contain polar OH bonds along the lower rim. The carboxylate groups have high charges on oxygen atoms. Thus, hydroxyl and carboxylate groups can participate in further reactions and actively interact with guest molecules.

Consideration of the molecular orbitals of molecules *p*-CAC, *p*-CATC, and *m*-CATC shows that conjugation encompasses azobenzene fragments. During the formation of complexes of calixarenes with metal ions, the length of conjugated fragments and the color change, which in turn leads to a change in the vibrational spectra of *E*- and *Z*-forms. We have identified bands in the vibrational spectra characteristic of various forms of azobenzene units.

## CRediT author statement

**Victor Furer:** Conceptualization, Methodology, Software, Writing- Original draft preparation and Editing

**Alexandr Vandyukov:** Investigation of IR and Raman spectra

**Zalia Ahkmetzyanova:** Synthesis of calixarenes

**Vladimir Burilov:** Synthesis of calixarenes

**Svetlana Solovieva:** Conceptualization, Methodology, Reviewing and Editing

**Igor Antipin:** 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

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