



# DFT study of conformation, hydrogen bonds, IR, and Raman spectra of the sodium salt of *p*-hexasulfonatocalix[6]arene DFT

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## ABSTRACT

The vibrational spectra of *p*-hexasulfonatocalix[6]arene hexasodium salt (SC6) and *p*-*tert*-butylcalix[6]arene (TB6) were studied. The comparison of the IR spectra SC6 and TB6 allows to distinguish bands of *tert*-butyl and sulfonate groups. The structure and the vibrational spectra of the SC6 molecule were calculated for the conformations of the *compressed cone* and the *double partial cone*. For the molecule SC6, the conformation of a *compressed cone* is the most stable, and the conformation of a *double partial cone* is 43.6 Kcal/mol less stable. When replacing *tert*-butyl groups with sulfonate groups, the cavity size of calixarene molecules increases from 5.22 (TB6) to 7.80 Å (SC6).

In the sodium salt of the SC6 molecule, six sodium ions are coordinated with the oxygen atoms of the sulfonate groups. Under the influence of sodium ions, the electron density is redistributed in the SC6 molecule, and its supramolecular properties change. The transition from TB6 to SC6 increases the ionization energy, electronic affinity, chemical potential and dipole moment. In the SC6 molecule, the frontal orbitals are located on aromatic and sulfonate groups. Due to these orbitals, calixarenes interact with biological objects.

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## 1. Introduction

Calixarenes are cup-shaped macrocyclic compounds that occupy an important place in supramolecular chemistry [1–4]. The solubility in water is particularly important when using calixarenes in biology and medicine. The addition of charged groups to calixarenes allows to solve this problem [5,6]. Calixarene sulfonates are water-soluble, interact with proteins, cells, are used as bacteria sensors and for drug transport [7–9]. Calixarenes form complexes with proteins by interaction with amino acids [7–9]. They are biocompatible and nontoxic [10]. Calixarenes are used to purify water and solve environmental problems with nuclear waste [11]. Calixarene compounds are used as transistors, nonlinear optical devices, liquid crystals, and catalysts [12–15].

The supramolecular properties of calixarenes depend on their conformation; therefore, studying the relationship between hydrogen bonds and the shape of molecules seems important [1–7]. IR spectra are one of the most informative methods for studying hydrogen bonds in calixarenes [16–21]. A complete analysis of the dy-

namics of vibrations is only carried out for a few simple calixarene molecules [16].

In this work, our objective was to determine the conformation of the molecules and the nature of intramolecular interactions by studying the vibrational spectra of the sodium salt of *p*-sulfonatocalix[6]arene (SC6). The IR spectra and structure of calixarene molecules with *tert*-butyl and sulfonate substituents were compared, and the vibration bands of different substituents were assigned.

## 2. Experimental

The synthesis of the *p*-*tert*-butylcalix[6]arene (TB6) and *p*-sulfonatocalix[6]arene (SC6) was performed out according to [22,23] (Fig. 1).

IR spectra of crystalline samples were recorded in KBr tablets by a Brook Vector spectrometer. The Raman spectra were excited by an Nd: YAG laser and recorded by a Vertex 70 FTIR-spectrometer equipped with a Bruker FT-Raman RAM II module.

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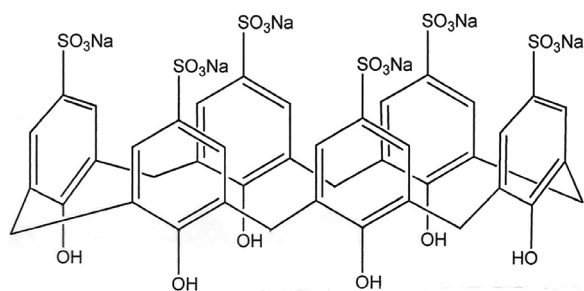


Fig. 1. Structure of SC6.

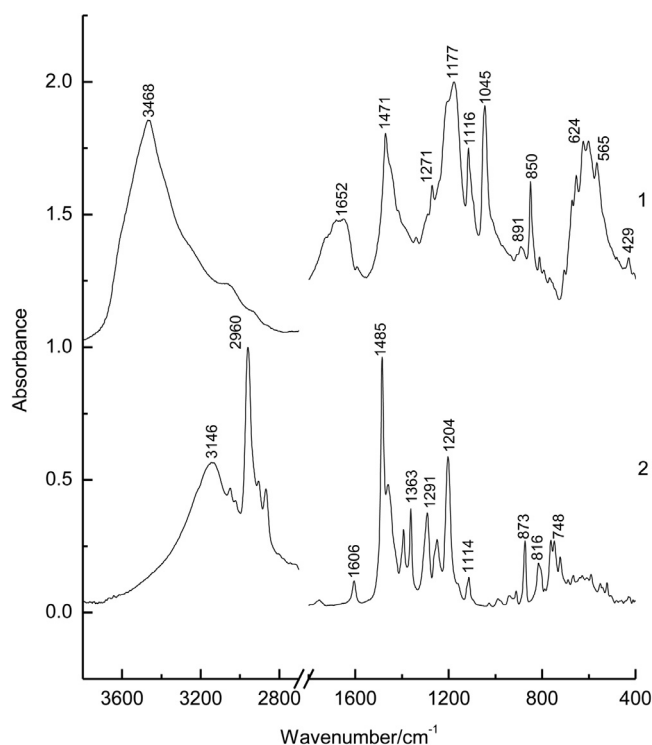


Fig. 2. Experimental IR spectra of crystalline SC6 (1) and TB6 (2).

### 3. Computational procedure

As a first approximation to optimize the geometry of the molecules SC6 and TB6, the experimental data obtained by the X-ray method were chosen [24–26]. The calculation was performed at a DFT/B3LYP/6–31G(d,p) level using a GAUSSIAN 09 W program package [27]. The bands in the vibrational spectra were assigned using the distribution of potential energy [28].

### 4. Results and discussion

It is known that due to the ring system of hydrogen bonds, the most stable structure of calix[6]arenes with unsubstituted hydroxyl groups is the conformation of the *compressed cone*. This has been demonstrated by X-ray data and IR spectroscopy [18,24]. In the solid-state, *p*-sulfonatocalix[6]arenes can be found in the conformations of a *compressed cone* and a *double partial cone* [25,26]. For the molecule SC6, the conformation of a *compressed cone* is the most stable, and the conformation of a *double partial cone* is 43.6 Kcal/mol less stable.

In the region of stretching vibrations of the hydroxyl groups in the IR spectra TB6 and SC6, bands at 3146 and 3468 cm<sup>−1</sup> are observed, respectively (Fig. 2). Such a large difference in the band frequencies indicates that these bands belong to different types of

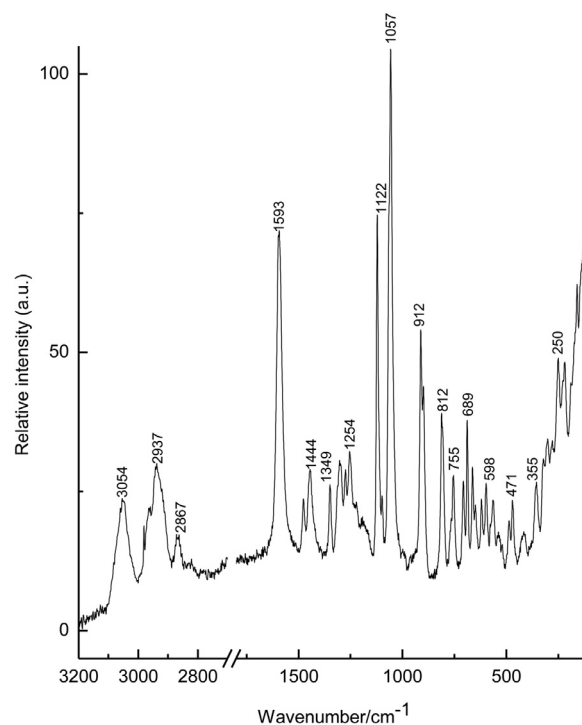


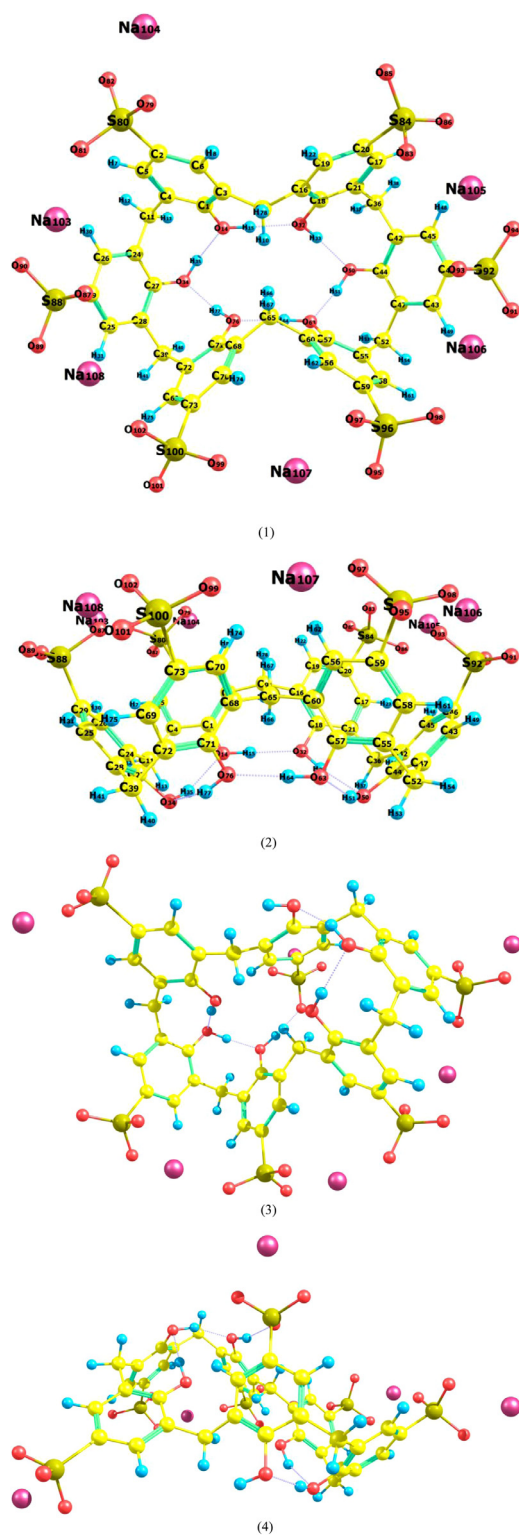
Fig. 3. Experimental Raman spectra of crystalline SC6.

H-bonds. In the case of TB6, the band at 3146 cm<sup>−1</sup> refers to the vibrations of the hydroxyl groups of the hydrogen bonds along the lower rim of the molecule. In the IR spectrum of SC6, the peak of 3468 cm<sup>−1</sup> can be attributed to the vibrations of the sulfonate groups involved in the formation of hydrogen bonds. This oscillation appears as a shoulder of 3136 cm<sup>−1</sup> in the IR spectrum SC6. These vibrations do not appear in the Raman spectrum of SC6 (Fig. 3).

Calculations show that the structure of the *compressed cone* in which six oxygen atoms of the lower rim of the molecule are in “boat” conformation is implemented in SC6 (Fig. 4). The SC6 molecule can also occupy a *double partial cone* conformation in which three neighboring sulfonate groups are oriented upwards and three downwards (Fig. 4) [25,26]. The theoretical geometric parameters of the SC6 molecules in different conformations correspond to the experiment (Supplementary information S1).

Although the distances between the adjacent oxygen atoms on the lower rim of the SC6 molecule in the *compressed cone* conformation are slightly different from each other, in calculations and experiments, six pairs of hydrogen bonds forming a ring can be considered equivalent. The average value of the calculated distances between adjacent oxygen atoms in the SC6 in the *compressed cone* conformation molecule is equal to 2.81 Å. In the *double partial cone* conformation of the SC6 molecule, two groups of three oxygen atoms separated by 2.72 Å participate in the formation of H-bonds. In the TB6 molecule, the H-bonds are almost linear with angles O – H···O equal to 169.2°. In the molecule SC6, this angle is 164.6° for the *compressed cone* conformation and 159.5° for the *double partial cone* conformation.

The covalent and H-bonded macrocycles of the SC6 molecule influence each other. The aromatic fragments rotate to ensure the formation of H-bonds. The torsion angles of methylene groups can be used to characterize the conformation of calixarene molecules[29]. For the SC6 molecule, torsion angles  $\varphi$ (C5–C4–C11–C24) and  $\chi$ (C4–C11–C24–C26) are chosen as conformational parameters. The sizes and signs of angles are characteristic of *compressed cone* conformation (Table 1). In the SC6



**Fig. 4.** Optimized geometry and atom numbering for SC6 in the conformation *compressed cone* and *double partial cone* upper view (1, 3), side view (2, 4).

molecule, two methylene bridges are directed inside the macrocycle to ensure the formation of a ring system of H-bonds. Four H-bonds are realized in molecule SC6 in *double partial cone* conformation.

In the formation of complexes, the shape of the molecules and the size of their cavity are of great importance. The main values of the gyration tensor characterize the shape of the molecules. The

**Table 1**

Dihedral angles (in degrees) of SC6 in the *compressed cone* and in the *double partial cone* conformation.

Dihedral angles	<i>Compressed cone</i>		<i>Double partial cone</i>	
	Exp.	Calc.	Exp.	Calc.
C(5)–C(4)–C(11)–C(24)	–119.7	–91.4	–84.8	–129.4
C(4)–C(11)–C(24)–C(26)	83.3	66.3	108.7	78.8
C(25)–C(28)–C(39)–C(72)	–76.3	–71.3	–74.5	–75.4
C(28)–C(39)–C(72)–C(69)	92.1	94.3	106.7	86.5
C(70)–C(68)–C(65)–C(60)	105.2	75.8	103.5	20.2
C(68)–C(65)–C(60)–C(56)	–84.3	–84.0	–0.7	54.0
C(58)–C(55)–C(52)–C(47)	–113.4	–89.5	84.7	96.0
C(55)–C(52)–C(47)–C(43)	78.2	74.3	–108.6	–70.0
C(45)–C(42)–C(36)–C(21)	–75.8	–68.2	74.5	106.0
C(42)–C(36)–C(21)–C(17)	103.6	84.2	–106.7	–80.1
C(19)–C(16)–C(9)–C(3)	95.0	98.4	–103.6	–44.7
C(16)–C(9)–C(3)–C(6)	–81.3	–94.1	0.7	114.1

**Table 2**

The partial charges of the atoms determined by natural population analysis of TB6 and SC6.

TB6 Atom	SC6 $q_n$	Atom	$q_n$
C1	0.336	C1	0.357
C2	–0.041	C2	–0.352
C3	–0.073	C3	–0.065
C4	–0.060	C4	–0.060
C5	–0.217	C5	–0.222
C6	–0.219	C6	–0.208
C9	–0.497	C9	–0.492
O14	–0.767	O14	–0.754
H15	0.537	H15	0.540
C79	–0.061	S80	2.452
C80	–0.674	O81	–1.070
C81	–0.688	O79	–1.068
C82	–0.675	O82	–1.057
		Na104	0.945

ratios of the principal values  $I_1/I_3$  and  $I_2/I_3$  of the moment of gyration tensor are 0.51 and 0.63 (TB6) and 0.44 and 0.72 (SC6), and therefore these molecules have an asymmetric shape. The distance between opposite oxygen atoms equal to 5.22 (TB6) and 7.80 Å (SC6) characterize the cavity size of calixarene molecules.

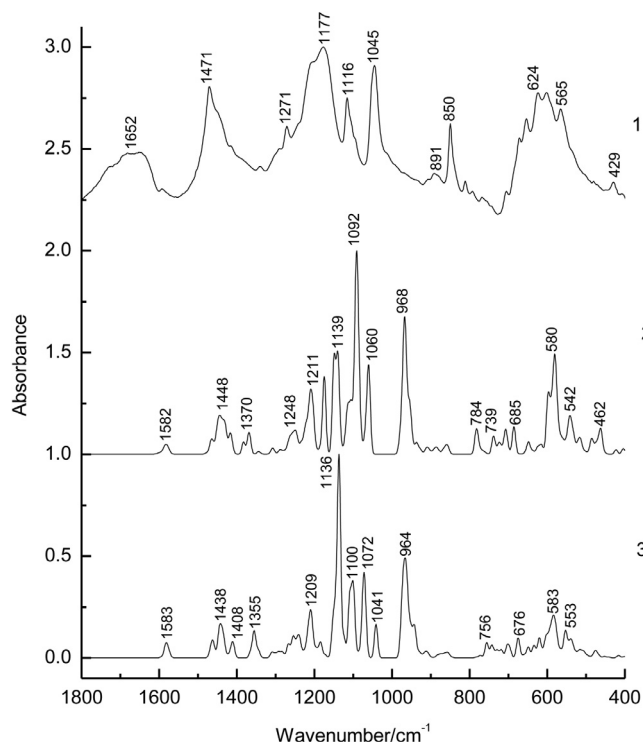
Upon the formation of H-bonds, the electron cloud of molecules changes. Charge transfer values were estimated using the NBO theory [30]. In the molecule SC6, the interaction of the lone electron pair of oxygen and the antibonding orbital of the hydroxyl group  $n(LP1O6) \rightarrow \sigma^*_1(O10-H87)$  with the energy of 11.37 kcal/mol is realized (Supplementary information S2).

In aromatic fragments, due to the conjugation of CC bonds, occur interactions  $\sigma_2(C20-C21) \rightarrow \sigma^*_2(C21-C22)$ ,  $\sigma_2(C20-C21) \rightarrow \sigma^*_2(C18-C19)$ ,  $\sigma_2(C20-C21) \rightarrow \sigma^*_2(C22-C3)$ ,  $\sigma_2(C21-C22) \rightarrow \sigma^*_2(C20-C21)$  with energies equal to 4.52, 17.03, 20.69 and 4.30 kcal/mol. Benzene rings interact with sulfonate groups  $\sigma_2(C20-C21) \rightarrow \sigma^*_1(S3-O7)$  with energy equal to 4.19 kcal/mol. Lone electron pairs of oxygen atoms of sulfonate groups interact with anti-bonding orbitals of SO bonds  $n(LP2O7) \rightarrow \sigma^*_1(S3-C21)$ ,  $n(LP2O7) \rightarrow \sigma^*_1(S3-O8)$ ,  $n(LP3O7) \rightarrow \sigma^*_1(S3-O9)$  with energies 11.00, 15.13, and 8.31 kcal/mol.

The formation of complexes of molecules often occurs due to electrostatic interactions. To estimate the energy of these interactions, we calculated the charges on the atoms of the TB6 and SC6 molecules (Table 2). It turned out that molecules TB6 and SC6 contain polar hydroxyl groups with charges (in e) on atoms O (–0.767 and –0.754) and H (0.537 and 0.540). Phenol has charges on atoms O (–0.693) and H (0.490), respectively. Therefore, during the formation of hydrogen bonds in the calixarenes TB6 and SC6, charge transfer occurs.

**Table 3**  
Global reactivity descriptors of TB6 and SC6.

System	Ionization energy, eV	Electron affinity, eV	Chemical potential, eV	Softness, eV	Electrophilicity index, eV	Dipole moment, D
TB6	6.54	−0.61	−2.97	0.14	1.23	1.53
SC6	7.36	1.23	−4.30	0.16	3.01	4.89



**Fig. 5.** Experimental (1) and theoretical IR spectra of SC6 in the conformation *compressed cone* (2), *double partial cone* (3) in the region 1800–400  $\text{cm}^{-1}$ .

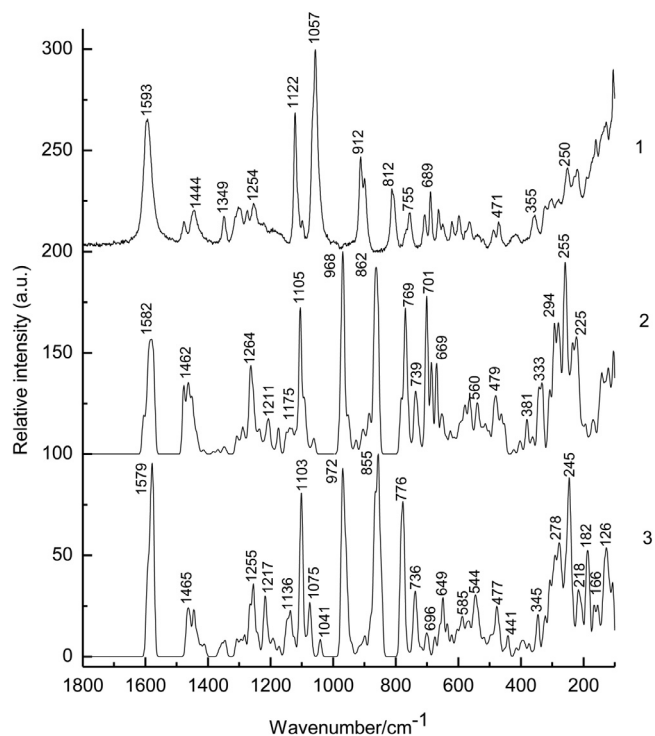
The theoretical and measured vibrational spectra of SC6 are presented in (Figs. 5,6 Supplementary information S3). The main bands in the experimental spectra of compound SC6 can be explained based on the calculation of the molecule in the conformation of the *compressed cone*.

The bands at 3067 and 3054  $\text{cm}^{-1}$  in the vibrational spectra of SC6 refer to the CH stretching of the aromatic fragments. The frequencies at 2937, 2935, and 2867  $\text{cm}^{-1}$  in the SC6 spectra are associated with asymmetric and symmetrical stretching vibrations of the methylene groups.

1597, 1593, and 1592  $\text{cm}^{-1}$  bands in the SC6 spectra are due to CC stretch vibrations and CCH bending vibrations of the benzene rings. The bands at 1477, 1471, 1451, and 1444  $\text{cm}^{-1}$  in the SC6 spectrum refer to asymmetric deformation vibrations of the methylene groups. The 1341  $\text{cm}^{-1}$  band in the IR spectrum and the 1349  $\text{cm}^{-1}$  band in the Raman spectrum of SC6 have been attributed to the COH deformation vibrations. The bands in the 1300–1200  $\text{cm}^{-1}$  region of the SC6 spectrum are associated with stretching of the CC and CO bonds.

Bands in the area 1130–1040  $\text{cm}^{-1}$  were assigned to the stretch of the SO bonds. Bands in the 920 to 800  $\text{cm}^{-1}$  range of the SC6 spectrum have been assigned as CC bonds stretching vibrations and methylene groups rocking vibrations.

Bands in the region 810–700  $\text{cm}^{-1}$  of the SC6 spectra are caused by non-planar vibrations of benzene rings. Bands in the 650–550  $\text{cm}^{-1}$  region of the SC6 spectra have been attributed to torsional and bending vibrations of the aromatic fragments. Bands of 450 to 400  $\text{cm}^{-1}$  have been attributed to the torsional vibra-



**Fig. 6.** Experimental (1) and theoretical Raman spectra of SC6 in the conformation *compressed cone* (2), *double partial cone* (3) in the region 1800–400  $\text{cm}^{-1}$ .

tions of the aromatic fragments and the deformation vibrations of the macrocycle.

Guest-host interactions play an important role in the supramolecular chemistry of calixarenes. We have tried to characterize these interactions by calculating global descriptors [31]. The transition from TB6 to SC6 increases the ionization energy, electronic affinity, chemical potential, and dipole moment (Table 3).

The comparison of IR spectra SC6 and TB6 shows that they differ significantly (Fig. 2). A broad  $\nu(\text{OH})$  band with a maximum of 3468  $\text{cm}^{-1}$  in the IR spectrum of SC6 has two weak shoulders at 3067 and 2937  $\text{cm}^{-1}$ . This vibration is shifted to 3146  $\text{cm}^{-1}$  in the IR spectrum of TB6, which characterizes the formation of a stronger H-bond. The CH stretching vibrations of the *tert*-butyl group appear in the region 2960–2860  $\text{cm}^{-1}$  of the IR spectrum of TB6. The intense band at 2960  $\text{cm}^{-1}$  can be used for analytical purposes to determine the content of *tert*-butyl fragments.

The bands at 1394, 1363, 1291, 1250, 1204  $\text{cm}^{-1}$  in the IR spectrum of TB6 are absent in the IR spectrum of SC6 and relate to the vibrations of *tert*-butyl groups. The bands of sulfonate groups at 1177, 1116, 1045, 624, 565  $\text{cm}^{-1}$  in the IR spectrum of SC6 are absent in the IR spectrum of TB6.

The calculation makes it possible to determine the bands in the vibrational spectra for the conformations of a *compressed cone* and a *double partial cone* of the SC6 molecule. It turned out that when the conformation changes, the frequencies change much less than the intensities of bands (Figs. 5,6, Supplementary information S2). Bands at 1370, 1149, 1092, 1069  $\text{cm}^{-1}$  (*compressed cone*), 1335,



1136, 1100, 1072  $\text{cm}^{-1}$  (double partial cone) are characteristic of these conformations.

## 5. Summary

The study of IR and Raman spectra in combination with the calculation of normal vibrations by the DFT method gives detailed information on the structure, conformation, hydrogen bonding, and electronic properties of calixarene molecules with different types of substitution. For the molecule SC6, the conformation of a *compressed cone* is the most stable, and the conformation of a *double partial cone* is 43,6 Kcal/mol less stable. The distance between opposite oxygen atoms equal to 5.22 (TB6) and 7.80 Å (SC6) characterize the cavity size of calixarene molecules.

This approach allows a complete interpretation of the spectra and significantly expands the capabilities of the study of the complexation of calixarenes.

## CRediT author statement

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

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

**Sofia Kleshnina:** 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

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130892.

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