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TGA heating curves of samples of p-sulfonatocalix[4]arene (*SC4*) and p-tertbutylcalix[4]arene (*TB4*) molecules from room temperature to 600° C. The inset images show the three IR spectra of the gas phase released during a) 220 ° C, (b) 290 ° C, (c) 400 ° C.

# Investigation of hydrogen bonding in *p*-sulfonatocalix[4]arene and its thermal stability by vibrational spectroscopy

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#### Abstract

The vibrational spectra of p-sulfonatocalix [4] arene were studied. The geometrical parameters, the energies, the frequencies and the intensities of the bands in the IR and Raman spectra are calculated for four conformations. The most stable conformation of the *p*-sulfonatocalix[4]arene is the cone due to the cooperative cyclic intramolecular hydrogen bonding system. The strength of the hydrogen bonds depends on the type of substituent on the upper rim of the calixarene molecules. We studied the process of destruction of calixarenes using IR spectroscopy and TGA methods. Characteristic bands for each conformation were selected. HOMO covers aromatic units with notable conjugation, and LUMO belongs to sulfonate groups.

Keywords: Calixarenes, IR spectra, Raman spectra, Hydrogen bonding, DFT

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#### **1.** Introduction

Calixarenes are macrocyclic compounds characterized by the presence of a cavity and capable of forming supramolecular complexes [1-6]. For biological experiments and drugs, solubility in water is particularly important. It is obtained by attaching charged functional groups to calixarenes [1-6]. Calixarenes with sulfonate groups on the upper rim are soluble in water and play a special role in the interaction with biological objects [7-9]. They interact with cells, are used as bacteria sensors and for drug delivery [7-9]. Calixarene sulfonates are biocompatible and non-toxic [10]. The ability of calixarenes to bind metals is used in ecology [11]. Therefore, studying the structure of calixarenes with sulfonate groups is an important task. The IR spectra of calixarenes have been studied [12-25]. However, as a general rule, IR spectroscopy is used for analytical purposes, and only the stretching vibrations of the hydroxyl groups are taken into account [11]. Raman spectra of calixarenes are very rarely studied [13].

The thermogravimetric analysis (TGA) method is used to study processes accompanied by changes in the mass of the analyte, usually with changes in temperature. This method is extremely useful for studying objects containing, in addition to the main substance, various compounds - crystalline hydrates, solvates, clathrates. This method is of interest for the study of thermal decomposition processes of substances, composites, and materials. Unfortunately, the TGA method is still very rarely used to study the thermal stability of calixarenes.

In this work, we studied changes in IR spectra during the heating process of psulfonatocalix[4]arene and p-*tert*-butylcalix[4]arene. It is important to determine how bands of polar sulfonate groups appear in vibrational spectra of calixarenes and their modification in the conformational transformation process. The DFT method was used to interpret the IR and Raman spectra of p-sulfonatocalix[4]arene. We identified bands of sulfonate groups and established how these groups affect the thermal stability of calixarenes.

### 2. Experimental

The *p*-sulfonatocalix[4]arene (*SC4*) was produced according to a known method (Fig. 1) [26]. Calix[4]arene with *tert*-butyl substituents (*TB4*) was also prepared and studied (Fig. 1).

IR spectra of crystalline samples of calixarenes were recorded in KBr tablets in the range of 4000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> using a Bruker Vector 22 spectrophotometer. Sixty-four accumulated scans for each spectrum. The Raman spectra were recorded in the 3500-100 cm<sup>-1</sup> region via a Bruker FT-Raman RAM II module of the FTIR Vertex 70 spectrometer. The 1064 nm excitation line of the Nd: YAG laser with a power of 50 mW was used.

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

#### **3.** Computational procedure

As a first approximation to optimize the geometry of *p*-sulfonatocalix[4]arene, we used experimental data obtained by X-ray diffraction [27]. Optimization was performed using the B3LYP density functional [28,29], 6-31G(d,p) basis set [30] and the Gaussian-09 program [31]. Calculated frequencies were scaled using the equation  $v_{obs} = (1.0087 - 0.0000163v_{cal})v_{cal}$  [32].

The relative intensities of the Raman spectrum lines were calculated from the Raman activity  $S_i$  obtained using the Gaussian-09 program, according to the following equation:  $I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i [1 - \exp(-hc v_i/kT)]}, \text{ where } v_0 \text{ is the excitation wavenumber in cm}^{-1}, v_i \text{ the wavenumber of the } i\text{-th}$ 

normal mode, h, c, and k the universal constants, and f the normalization factor.

The theoretical IR and Raman spectra were simulated using calculated frequencies and intensities with bands having a Lorentz shape and half-width of 10 cm<sup>-1</sup> using Swizard software [33]. The normal vibration assignment was performed by calculating the potential energy distribution [34]. To evaluate the chemical properties of calixarenes, natural bonding orbitals, chemical potential, and electrophilicity index were calculated [35, 36].

#### 4. Results and discussion

The calculation has shown that the isolated *TB4* and *SC4* molecules take a cone conformation according to experimental X-ray data [27,38]. The calculated bond lengths of *SC4* are in agreement with

the experimental data on X-ray diffraction (Supplementary information S1) [27]. Despite the fact that the distances between the neighboring oxygen atoms differ slightly from one another in calculation and experiment, the four pairs of hydrogen bonds forming a cyclic system in *TB4* and *SC4* may be considered equivalent (Supplementary information S1). The average values of the distances calculated between the neighboring oxygen atoms in *TB4* and *SC4* are 2.65 and 2.64 Å, respectively, and correspond to the experiment [27,37]. The average values of the theoretical angles O–H<sup>...</sup>O in *TB4* and *SC4* are equal to 164.6 and 162.5°. The size of the calixarene cavity determines their ability to extract metals. The distance between the opposite oxygen atoms in the macrocycle in *TB4* and *SC4* is 3.7 Å. As a result, these molecules have a cavity large enough to accommodate the guest molecules.

Table 1 shows the relative free energies and dipole moments of the cone, pcone, 1,2-alt and 1,3alt conformers of *SC4* and *TB4* molecules. The most stable and polar is the conformation of the cone with four intramolecular cooperative hydrogen bonds. As the number of hydrogen bonds decreases, the free energy of conformers decreases (Table 1, Fig. 2). There is a sharp increase in the polarity of the *SC4* molecule in comparison with the *tert*-butyl analogue.

To estimate the electrical properties of the molecules, we calculated the charge distribution on the *SC4* atoms and compared them to the corresponding amounts in *TB4* (Table 2). As a result, the calixarene molecules *TB4* and *SC4* contain polar OH bonds with natural atomic charges [34] (in e) on the O atoms (-0.761 and -0.751) and H (0.528 and 0.531), respectively. The sulfonyl group has charges on the O atoms (-0.934, -0.914 and -0.923) and S (2.403) respectively.

For *SC4* molecules, torsion angles  $\varphi(C7-C6-C40-C37)$  and  $\chi(C6-C40-C37-C36)$  are used as conformation parameters [39]. The mean values of the calculated torsion angles  $\varphi$  and  $\chi$  are -92.3° and 92.0° and are in agreement with the experimental values 91.7 and 85.3° (Table 1) [27]. In the *TB4* molecules, the mean values of the calculated parameters  $\varphi$  and  $\chi$  are equal to -91.0° and 91.5° and do not differ much from the corresponding values for *SC4*. Thus, the orientation of the aromatic moieties of the calculated parameters does not change when the *tert*-butyl group is replaced by the sulfonate group.

Figs. 3-6 and Supplementary information S2, S3 show the experimental and calculated vibrational spectra of TB4 and SC4. To interpret the vibrational spectra of TB4 and SC4, we calculated the potential energy distribution (PED). The assignment of the bands in the spectra was carried out by considering the displacements of the atoms under oscillations. A comparison of the vibrational spectra of TB4 and SC4 makes it possible to distinguish the bands associated with the vibrations of the sulfonyl groups (Fig. 3).

The calculation of the molecules in the conformation of the cone makes it possible to understand the main characteristics of the experimental IR and Raman spectra of *TB4* and *SC4*. The theoretical absorption and scattering curves of isolated molecules, *TB4* and *SC4*, are simpler than the experimental IR and Raman spectra of crystalline samples in which band shifts and splits occur. Each vibration of the phenolic fragment causes four vibrations of the *TB4* and *SC4* molecules. The theoretical curves for cone conformation best fit the IR and Raman *SC4* experimental spectra. The intensities of certain bands in the experimental and calculated IR and Raman spectra are substantially different. These differences may be due to the imperfection of the model and to the approximation chosen for the calculation.

IR spectroscopy is a practical method for studying hydrogen bonds (Fig. 3). There is no band of free OH groups in the IR spectrum, which means that all the hydroxyl groups participate in the formation of hydrogen bonds and that the *TB4* and *SC4* molecules occupy a conformation of the cone. Band 3159 cm<sup>-1</sup> in the IR spectrum of *TB4* refers to stretching vibrations of the hydroxyl groups. The 3371 cm<sup>-1</sup> band of the *SC4* IR spectrum refers to the OH stretching vibrations of the polar SO<sub>3</sub>H groups participating in the H-bond with the water molecules in the calixarene cavity. The 3188 cm<sup>-1</sup> band is due to oscillations of the OH groups along the lower rim of the molecule. The magnitude of the vOH frequency indicates that in the presence of polar sulfonate groups in *SC4*, the hydrogen bond weakened relative to *TB4*.

In the region 3200-2800 cm<sup>-1</sup> of the IR and Raman experimental spectra of *SC4*, there are bands of CH stretching vibrations (Fig. 3,4). Stretching the CH bond vibrations of aromatic moieties causes weak bands at 3053, 3033 cm<sup>-1</sup> in the Raman spectrum of *SC4*. The asymmetric and symmetrical stretching vibrations of the methylene groups appear as lines 2981, 2957 and 2883 cm<sup>-1</sup> of the *SC4* Raman spectrum. The 2959 and 2870 cm<sup>-1</sup> bands are observed in the IR spectrum of *TB4* and are related to CH stretching vibrations of the *tert*-butyl groups.

The bands 1613, 1594 cm<sup>-1</sup> of the stretching vibrations of the CC bonds and the bending vibrations of CCH of aromatic fractions appear in the Raman spectrum of *SC4*. These vibrations show the band at 1599 cm<sup>-1</sup> in the IR spectrum of *SC4*. The asymmetric deformation vibrations of the methylene groups result in bands at 1472, 1460, 1429 cm<sup>-1</sup> in the IR spectrum and 1488, 1480, 1460 cm<sup>-1</sup> bands in the *SC4* Raman spectra. These oscillations give rise to the band at 1470 cm<sup>-1</sup> in the IR spectrum of *TB4*.

The band at 1397 cm<sup>-1</sup> in the IR spectrum of *SC4* refers to the stretching vibrations of the CC bonds of the aromatic fragments and the HCH and COH bending vibrations. The stretching vibrations of

the SO bonds cause a band at 1375 cm<sup>-1</sup> in the *SC4* IR spectrum. The stretching of the CC bond vibrations of the aromatic moieties causes the appearance of bands at 1305 cm<sup>-1</sup> in the IR spectrum and at 1312 cm<sup>-1</sup> in the Raman spectrum of *SC4*. The stretching vibrations of CO bonds induce bands at 1285 cm<sup>-1</sup> in the IR spectrum and at 1287 cm<sup>-1</sup> in the Raman spectrum of *SC4*. The medium intensity band in the *SC4* IR spectrum at 1270 cm<sup>-1</sup> is due to stretching vibrations of CC and CO bonds. The stretching vibrations of CC bonds show bands at 1248, 1202 cm<sup>-1</sup> in the IR spectrum of *TB4* and at 1246, 1216 cm<sup>-1</sup> bands in the IR spectrum of *SC4*.

The intense bands at 1156, 1123, 1105, 1040 cm<sup>-1</sup> in the *SC4* IR spectrum belong to the stretching vibrations of the sulfonyl groups. The band at 1119 cm<sup>-1</sup> in the IR spectrum of *TB4* is due to the CH in-plane deformation vibrations of the aromatic moieties. Stretching vibrations of CC bonds and CCH bending vibrations appear as bands at 870 and 972 cm<sup>-1</sup> in the IR spectra of *TB4* and *SC4*. The 818, 783 cm<sup>-1</sup> bands in the infrared spectrum of *TB4* and the 935, 903 cm<sup>-1</sup> bands in the *SC4* IR spectrum relate to non-planar vibrations of aromatic groups. The rocking vibrations of the methylene groups show the band at 897 cm<sup>-1</sup> of the *SC4* IR spectrum. The twisting vibrations of the CH<sub>2</sub> groups cause bands at 815, 833 cm<sup>-1</sup> in the *SC4* IR spectrum. The stretching vibrations of SO bonds give bands at 765, 774, 788 cm<sup>-1</sup> in the IR spectrum of the *SC4*.

The torsional oscillations around the CC links cause the bands at 742, 672, 660, 628 cm<sup>-1</sup> in the *SC4* IR spectrum. The deformation vibrations of the sulfonate groups appear as bands at 599, 472, 449 cm<sup>-1</sup> in the IR spectrum of *SC4*. The torsional vibrations of the benzene rings and the deformation vibrations of the macrocycle causes bands at 517, 442, 416, 395 cm<sup>-1</sup> in the IR spectrum of *SC4*. The bands at 415, 356, 320, 290, 269, 203, 133 cm<sup>-1</sup> in the *SC4* Raman spectra are associated with deformations of the skeletal angles and torsion vibrations of the sulfonate groups.

Comparing the IR spectra of *TB4* and *SC4* allows you to select bands of sulfonate groups. The strong band at 1479 cm<sup>-1</sup> in the IR spectrum of *TB4* corresponds to the medium intensity band at 1472 cm<sup>-1</sup> in the *SC4* IR spectrum. The bands at 1391 and 1368 cm<sup>-1</sup> of the IR spectrum of *TB4* correspond to the band at 1375 cm<sup>-1</sup> of the IR spectrum of *SC4*. It is interesting to note that the relative intensities of a whole series of bands in the IR spectra of *TB4* and *SC4* differ significantly.

For analytical purposes, it is important to determine how the replacement of *tert*-butyl groups by sulfonate groups is reflected in the IR spectra (Fig. 3). In the region of CH stretching vibrations in the *TB4* IR spectrum, bands of *tert*-butyl groups at 2959, 2909 and 2870 cm<sup>-1</sup> are observed. They

correspond to the bands at 2955 and 2874 cm<sup>-1</sup> bands in the *SC4* IR spectrum. The relative intensities of these bands in the IR spectra of *TB4* and *SC4* differ considerably.

In the middle region of the IR spectrum of the *TB4* bands, 1391, 1368, 1296, 1202, 818 cm<sup>-1</sup> characteristic of the *tert*-butyl substituent are observed. These bands are absent in the *SC4* IR spectrum. Conversely, the bands at 1375, 1270, 1216, 1156, 1123, 1105, 1040 cm<sup>-1</sup> observed in the IR spectrum of *SC4* are absent in the IR spectrum of *TB4*.

Thus, the aromatic fragments show the lines of stretching vibrations of CC bonds at 1613,  $1594 \text{ cm}^{-1}$  bands in the *SC4* Raman spectrum. The methylene groups have 2957, 2883 cm<sup>-1</sup> bands in the Raman spectrum. The sulfonate groups have bands at 1156, 1123, 1105, 1040 cm<sup>-1</sup> in the *SC4* IR spectra associated with S–O stretching vibrations.

According to the results of the calculations, it is possible to follow the modifications of the IR and Raman spectra for four possible conformations of the *SC4* molecule. The analysis of the theoretical vibrational spectra shows that with the reorientation of the aromatic fragments, a change in the intensity of a certain number of bands occurs (Figs. 4,5, Supplementary information S3). Bands at 1342, 1116, 764 cm<sup>-1</sup> (cone), 1305, 1202, 792 cm<sup>-1</sup> (pcone), 1339, 1163, 782 cm<sup>-1</sup> (1,2-alternate), 1333, 1124, 786 cm<sup>-1</sup> (1,3-alternate) were selected for the analytical purposes.

The calixarenes molecules are in the conformation of the cone. In general, the crystallization of such samples from their solutions results in the capture of a portion of the solvent molecules. These guest molecules are in sorbate, solvate or clathrate forms and differentiated by their intermolecular interactions. Using thermal analysis methods, we tried to analyze the processes occurring in the calixarenes during heating. To our knowledge, no work simultaneously using the FTIR spectroscopy and thermal analysis methods to study the processes involved in heating calixarenes had been conducted.

In fact, by analyzing the TGA curve of *TB4* (Fig. 7), it can be seen that a significant change in sample mass occurs at temperatures above  $356^{\circ}$  C. According to the TGA data in the temperature range of 100 to  $336^{\circ}$  C, there is a slight decrease in the mass of the sample (Fig. 7). A minor loss of mass (up to 3 to 4% of the sample mass) is probably due to the elimination of small molecules. Such an insignificant number of these small molecules in the crystals is explained by the fact that the *tert*-butyl groups of the *TB4* molecule can partially penetrate the cavity of another calizarene molecule preventing the entry of small molecules.

In the case of *SC4* calixarene, unlike non-polar *t*-Bu groups, polar sulfonate groups attract much more water molecules of all three types. A loss of mass close to 20% occurs up to 200° C in two stages,

it is likely that it is adsorbed water, and more firm retained molecules of different types (Supplementary information 4: DTG peaks at  $81^{\circ}$  and  $141^{\circ}$  C, respectively). The third step of about 300° C is associated with the separation of the sulfonate groups and the destruction of the calixarene structure. The Fig. 7 shows the IR spectra of the gas phase released at different temperatures. All bands perfectly match the IR spectrum of the sulfur dioxide. The color of the calixarene sample ranges from white at room temperature to slightly yellow at 220° C and black at 290° C. As the temperature increases, the intensity of the bands of the sulfonate groups in the *SC4* IR spectra decreases (Fig. 8). Therefore, the destruction of the *p*-sulfonatocalix[4]arene begins with the sulfonate groups.

During heating, the reorganization of hydrogen bonds occurs in the supramolecular system of p-sulfonatocalix[4]arene-water. There is a change in the contour of the OH stretching vibrations band in the *SC4* IR spectra. The band at 3188 cm<sup>-1</sup> in the *SC4* IR starting spectrum, increases to 3235 cm<sup>-1</sup> after heating to 200° C, and becomes a shoulder at 3250 cm<sup>-1</sup>, at a temperature of 300° C, its intensity substantially reduces. Adsorbed water gives bands at 3370-3400 cm<sup>-1</sup> in the three IR spectra.

In this article, we have also tried to characterize the reactivity of calixarenes using global descriptors. The introduction of sulfonyl groups into calixarene increases the ionization energy, electron affinity, chemical potential, dipole moment, and electrophilic index relative to *TB4* (Table 3). Analysis of the molecular orbitals in the *SC4* molecule showed that HOMO and LUMO consist of  $\pi$  orbitals (Fig. 9). HOMO and LUMO cover aromatic units with notable conjugation and sulfonate groups.

When forming hydrogen bonds, there is a change in the electron density in the molecules. The NBO approximation takes into account the transfer of the electron density from the donor to the acceptor. During the formation of the hydrogen bond, electron density transfer from a lone electron pair of oxygen to the antibonding orbital of the OH bond takes place. The hyper-conjugated interaction between the lone electron pair of oxygen as a donor and the antibonding orbital of the OH bond as an acceptor was detected, thus ensuring charge transfer from the first to the second. As can be seen from our data, the *SC4* molecule has a complex pattern of hydrogen bonding interactions:  $n(LP_1O1)\rightarrow\sigma^*_1(O4-H44)$ ,  $n(LP_2O1)\rightarrow\sigma^*_2(O4-H44)$ ,  $n(LP_2O1)\rightarrow\sigma^*_2(C5-C10)$  with stabilization energies equal to 15.63, 13.56 and 19.61 kcal/mol (Supplementary information S5). In aromatic moieties, conjugation bonds participate in interactions  $\sigma_2(C5-C10) \rightarrow \sigma^*_2(C6-C7)$ ,  $\sigma_2(C5-C10) \rightarrow \sigma^*_2(C5-C10) \rightarrow \sigma^*_2(C5-C10) \rightarrow \sigma^*_2(C5-C10) \rightarrow \sigma^*_2(C5-C10) \rightarrow \sigma^*_2(C5-C10)$  with energies equal to 17.38, 24.82 and 22.98 kcal/mol. The sulfonate groups interact with aromatic moieties  $\sigma_2(C8-C9) \rightarrow \sigma^*_1(S54-O56)$  with an energy 6.56 kcal/mol.

#### 5. Summary

The calculation of the potential energy distribution enabled us to perform a band classification in the IR and Raman experimental spectra. A complete interpretation of the calixarene spectra has been proposed based on experimental data and quantum calculations. The study of *tert*-butyl and sulfonato derivatives of calix[4]arenes by FTIR spectroscopy showed that there was no absorption band for the free hydroxyl groups and that an intramolecular hydrogen bond was produced. The hydrogen bond in *SC4* is weaker than in *TB4*.

The destruction process of the studied calixarene *TB4* and *SC4* samples are very different. *TB4* barely loses mass up to a temperature of 400° C. In *SC4*, the loss of mass occurs in two stages: up to 200° C, it is most likely water from the cavity of a molecule. The second step of about 300° C is associated with the separation of the sulfonate groups and the destruction of the calixarene structure.

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#### **Figure captions**

Fig. 1. Structure of *p*-tert-butylcalix[4]arene (a) and *p*-calix[4]arene sulfonic acid (b).

Fig. 2. Optimized geometry and atom numbering for *p*-calix[4]arene sulfonic acid in the conformation cone (1), partial cone (2), 1,2-alternate (3) and 1,3-alternate (3).

Fig. 3. Experimental IR spectra of *p*-calix[4]arene sulfonic acid (1) and *p*-tertbutylcalix[4]arene (2).

Fig. 4. Experimental Raman spectra of p-calix[4]arene sulfonic acid.

Fig. 5. Experimental (1) and theoretical IR spectra of p-calix[4]arene sulfonic acid in the conformation cone (2), partial cone (3), 1,2-alternate (4) and 1,3-alternate (5) in the region 1800-400 cm<sup>-1</sup>.

Fig. 6. Experimental (1) and theoretical Raman spectra of p-calix[4]arene sulfonic acid in the conformation cone (2), partial cone (3), 1,2-alternate (4) and 1,3-alternate (5) in the region 1800-400 cm<sup>-1</sup>.

Fig. 7. TGA heating curves of samples of *p*-calix[4]arene sulfonic acid (*SC4*) and p-tertbutylcalix[4]arene (*TB4*) molecules from room temperature to 600° C. The inset images show the three IR spectra of the gas phase released during a) 220 ° C, (b) 290 ° C, (c) 400 ° C.

Fig. 8. IR spectra of *p*-calix[4]arene sulfonic acid heated at  $300^{\circ}$  C (1),  $200^{\circ}$  C (2) and at room temperature (3).

Fig. 9. Molecular orbital surfaces of *p*-calix[4]arene sulfonic acid.

#### Table 1

Relative Gibbs free energy  $\Delta G$  (kcal/mol), dipole moments  $\mu$  (D), and dihedral angles  $\varphi$ ,  $\chi^a$  (in degrees) of conformers of *p*-tert-butylcalix[4]arene and *p*-sulfonatocalix[4]arene calculated in the DFT/B3LYP 6-31G(d,p) level

Conformation	ΔG	μ	φ1	χ1	φ <sub>2</sub>	<b>X</b> 2	φ <sub>3</sub>	χ3	φ4	χ4
SC4										
Cone	0.0	12.4	-92.3	92.0	-92.3	92.0	-92.3	92.0	-92.3	92.0
Partial cone	5.60	5.8	-96.7	85.6	-116.6	-145.6	82.1	-132.7	-137.6	87.7
1,3-Alternate	9.40	6.6	-110.4	-113.4	111.1	114.7	-111.4	-113.9	111.7	114.8
1,2-Alternate	10.08	5.4	120.3	142.6	-80.3	97.8	-103.6	80.5	-126.8	-132.1
TB4										
Cone	0.0	2.6	-91.0	91.5	-91.0	91.5	-91.0	91.5	-91.0	91.5
Partial cone	8.41	1.8	-168.1	106.5	41.6	-150.0	-170.5	-161.7	-60.5	-118.5
1,3-Alternate	14.11	0.0	-118.1	-129.5	118.1	129.5	-118.1	-129.5	118.1	129.5
1,2-Alternate	15.13	1.7	-98.4	84.4	-113.1	-146.6	82.3	-133.4	-138.0	88.8

<sup>a</sup> Dihedral angles  $\varphi_1 - C(7) - C(6) - C(40) - C(37)$ ,  $\chi_1 - C(6) - C(40) - C(37) - C(36)$ ,  $\varphi_2 - C(34) - C(33) - C(31) - C(28)$ ,  $\chi_2 - C(33) - C(31) - C(28) - C(27)$ ,  $\varphi_3 - C(25) - C(24) - C(22) - C(19)$ ,  $\chi_3 - C(24) - C(22) - C(19) - C(18)$ ,  $\varphi_4 - C(16) - C(15) - C(13) - C(10)$ ,  $\chi_4 - C(15) - C(13) - C(10) - C(19)$ 

TB4		SC4	
Atom	$q_n$	Atom	q <sub>n</sub>
01	-0.761	01	-0.751
C5	0.323	C5	0.350
C25	-0.067	C6	-0.063
C21	-0.219	C7	-0.192
C17	-0.036	C8	-0.343
C13	-0.215	C9	-0.191
C9	-0.058	C10	-0.072
H46	0.528	H41	0.531
C49	-0.674	053	-0.934
C33	-0.061	S54	2.403
C53	-0.689	O55	-0.914
C57	-0.675	O56	-0.923
		H69	0.522

Table 2

The partial charges of the atoms determined by natural population analysis of p-tert-butylcalix[4]arene and p-sulfonatocalix[4]arene

Table 3	
Global reactivity descriptors of <i>p</i> -tert-butylcalix[4]arene and <i>p</i> -sulfonatocalix[4]arene	

System	Ionization energy, eV	Electron affinity, eV	Chemical potential, eV	Softness, eV	Electrophilicity index, eV	Dipole moment, D
TB4 SC4	6.75 8.16	-0.71	-3.02	0.13	1.22	1.00
					S	
	0					
	V					





(2)



(4)

















НОМО

LUMO

>The FTIR and FT-Raman spectra of p-sulfonatocalix[4]arene were studied.

> Normal mode analysis were performed for p-sulfonatocalix[4]arene.

> The IR and Raman spectra of p-sulfonatocalix[4]arene were calculated and interpreted.