Russian Chemical Bulletin, International Edition, Vol. 51, No. 5, pp. 825—827, May, 2002 825

Cooperative intramolecular hydrogen bond and conformations of thiocalix[4]arene molecules

V. I. Kovalenko,[a] A. V. Chernova,[a] E. I. Borisoglebskaya,[a] S. A. Katsyuba,[a] V. V. Zverev,[a] R. R. Shagidullin,[a] I. S. Antipin,[a] S. E. Solov´eva,[a] I. I. Stoikov,[b] and A. I. Konovalov[a]

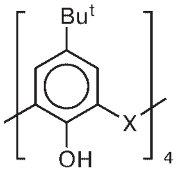
[a]*A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Research Center,*
Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: koval@iopc.kcn.ru
[b]*Kazan State University,*
18 ul. Kremlevskaya, 420008 Kazan, Russian Federation.
Fax: +7 (843 2) 38 7418. E-mail: iantipin@ksu.ru

The joint FTIR spectroscopic study and *ab initio* quantum-chemical calculations (HF/3-21G and PBE/TZ2P methods) showed that thiocalix[4] arene molecules adopt the cone conformation in CCl_4 solutions. The weakening of the cooperative intramolecular H bond in thiocalix[4]arenes compared to the corresponding calix[4]arenes can be due to the larger thiocalixarene macrocycle, bifurcated hydrogen bond in it, and electron density transfer from the bridging S atom to the benzene ring.

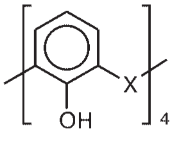
Key words: FTIR spectroscopy, *ab initio* quantum-chemical calculations, UV spectroscopy, cone conformation, cooperative hydrogen bond, bifurcated hydrogen bond, thiocalix[4]arenes, calix[4]arenes.

Calix[4]arenes (CA) are known to have the cone conformation both in the solid state and CCl_4 solutions. This conformation is stabilized by the very strong cooperative intramolecular hydrogen bond (IHB), which is indicated by a strong decrease in the ν(OH) frequency in their IR spectra: to 3160 cm^{-1} (in KBr pellets) and 3137 cm^{-1} (in solutions of CCl_4).[1] Thiocalix[4]arenes (TCA) in which methylene bridges connecting the phenol fragments are replaced by the S atoms, according to the X-ray structural data,[2—4] also adopt the cone conformation, which is more flexible than that in CA.[4,5]

In this work, FTIR spectroscopy and quantum-chemical calculations were used to study the nature of the hydrogen bond and conformations of the thiocalix- (**1**, **2**) and calix[4]arene (**3**, **4**) molecules.



1: X = S
3: X = CH_2



2: X = S
4: X = CH_2

Experimental

IR spectra (4000—400 cm^{-1}) were recorded on a Vector 22 Fourier spectrometer (Bruker) with a resolution of 1 cm^{-1}. UV spectra were obtained on a Specord UV—Vis spectrophotometer (Karl Zeiss Jena) with a resolution of 30 cm^{-1} and a recording speed of 8500 cm^{-1} min^{-1}.

Water-free CCl_4 was used as the solvent. The concentration of solutions was ~$1 \cdot 10^{-4}$ mol L^{-1}, and the layer thickness in cells was 2 cm (IR spectra) and 0.2 cm (UV spectra). All procedures on preparation of solutions were conducted in a dry box.

Ab initio calculations with the full geometry optimization at the HF/3-21G* level were performed by the GAMESS (US) program,[6] and calculations in the framework of the density functional theory (DFT) were performed by the PRIRODA program.[7] For DFT calculations with the exchange-correlation PBE potential[8] the three-exponent basis set with two polarization functions (TZ2P) was used.[7] The advantages of the PBE/TZ2P approach were discussed earlier.[7,8]

Compounds **1**,[9] **2**,[2] **3**,[10] and **4** [11] were synthesized by previously described procedures.

Results and Discussion

The IR spectrum of thiocalixarene **1** (Fig. 1, *a*) exhibits a singlet symmetric ν(OH) band, whose position changes slightly on going from crystals (3249 cm^{-1} in KBr) to a solution (3281 cm^{-1} in CCl_4). A similar behavior of the absorption peak of ν(OH) is observed for the corresponding calixarene **3** (3165 cm^{-1} in KBr, 3137 cm^{-1} in a solution of CCl_4). This indicates that four OH groups in the molecules of **1** and **3** are equiva-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 762—764, May, 2002.

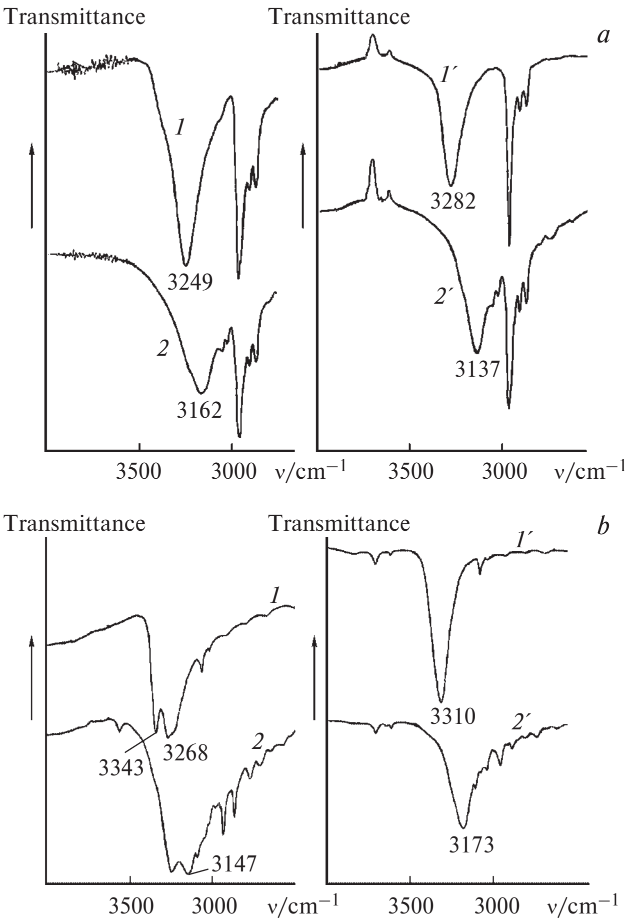


Fig. 1. IR spectra of calix[4]arenes (*a*) **1** (*1*, *1′*) and **3** (*2*, *2′*) and calix[4]arenes (*b*) **2** (*1*, *1′*) and **4** (*2*, *2′*) in KBr pellets (*1*, *2*) and in CCl_4 solutions (*1′*, *2′*).

lent and suggests that the cone conformation with the C_4 symmetry is retained in a solution for both molecules. The spectrum of a solution of thiocalixarene **1** in CS_2 exhibits the high-frequency shift of the ν(OH) band by 57 cm^{-1} relative to that in CCl_4. A similar effect was observed[1] for analogous solutions of calixarene **3** and attributed to the formation of an inclusion compound with CS_2, due to which, in authors′ opinion, the cooperative character of the H bond somewhat decreases.

The ν(OH) band in the spectrum of the crystalline **2** is observed as a doublet at 3343/3268 cm^{-1} with prevailing of the low-frequency component (Fig. 1, *b*). The doublet contour of ν(OH) at 3247/3147 cm^{-1} is also present in the spectrum of crystalline calixarene **4**. The doublet character of the ν(OH) bands is not connected to the conformational heterogeneity of the compounds because, according to the X-ray structural data,[2—5] all the molecules under discussion in crystal exist in the single cone conformation. The presence of two ν(OH) frequencies cannot be explained by the Davydov splitting or other crystalline effects because the difference in frequencies between the components of doublets is rather high. In both cases, doublet band contours seem to be a result of the deviation of molecules **2** and **4** from the C_4 symmetry affected by the crystal packing. Due to a decrease in the symmetry of the cone in crystal to C_2, the O...O distances become nonequivalent,[2,4] which results in the appearance of two ν(OH) bands in the spectra of the solid samples of compounds **2** and **4**. Molecules **1** and **3** in crystal have the C_4 symmetry[2,12] and, hence, the spectra of the solid samples exhibit only one ν(OH) peak. It is likely that the presence of bulky and rather symmetric *tert*-butyl substituents in the molecules **1** and **3** plays a decisive role, whereas noticeable distortions of the cone symmetry in crystal are possible when these "shielding" groups are absent. In fact, in the spectra of solutions of **2** and **4** in CCl_4 the single bands ν(OH) (3173 cm^{-1} for **4** and 3310 cm^{-1} for **2**) appear. Perhaps, in solution the distorting effects of the environment disappear, and molecules **2** and **4** adopt conformations with the C_4 symmetry.

The cone conformation with the C_4 symmetry of individual molecules **2** and **4** is also predicted by our *ab initio* calculations by the Hartree—Fock methods and density functional theory PBE/TZ2P. Some results of these calculations are presented in Table 1. It can be seen that the elongation of the unbound $C_{ar}...C_{ar}$ side of the bridging C_{ar}—X—C_{ar} triangle on going from X = CH_2 to X = S is accompanied by an increase in the dihedral angle (α) between the planes of the opposite phenyl rings and the distance between the O atoms. These theoretical predictions agree with the X-ray structural data,[13] according to which the O...O distances are 2.80—2.76 and 2.66—2.63 Å for thiocalixarene **2** and calixarene **4**, respectively. The calculated O—H bonds in thiocalixarene **2** are shorted and the H...O distances are longer than those in calixarene **4**, which implies weaker IHB in molecule **2** compared to that in molecule **4** (see Table 1).

Table 1. Geometric parameters of calixarene molecules **2** and **4** $[(—C_6H_3OH)—X—]_4$ (X = CH_2, S) calculated in the framework of the density functional theory (PBE/TZ2P [PRIRODA])

Parameter	Value	
	X = CH_2	X = S
Interatomic distances/Å		
$C_{ar}...C_{ar}$	2.552	2.838
O...O	2.622	2.760
O—H	1.010	0.996
O...H	1.633	1.855
X...H	2.492	2.507
Angle α/deg	68.4	75.2

The weakening of the cooperative H bond in thiocalixarenes compared to that in calixarenes can result from an increase in the macrocycle size when the methylene bridges are replaced by sulfide ones. The above-mentioned increase in the dihedral α angle in the thiocalix[4]arene molecules compared to the calix[4]arene molecules only partially compensates the elongation of the bridging bonds and, as a result, the O...O distance elongates[2,4] by ~0.1—0.2 Å.

Another reason for the weakening of the cooperative H bond in thiocalixarenes can be the formation of the bifurcated O...H...S hydrogen bond due to the presence of the second proton-acceptor center, *viz.*, S atom. As known,[14] bifurcated bond formation is usually accompanied by an increase in the $\nu(\mathrm{OH_{bond}})$ frequency over the normal two-centered H bond. A possibility of the weak IHB OH...S was indicated[4] in discussion of the molecular structure of the crystalline complex of *p-tert*-butylcalix[4]arene with 1,2-$Cl_2C_2H_4$. This assumption was based on the formal geometric criteria accepted in X-ray structural analysis: short S...O (average 3.023 Å) and S...H (2.59 Å) distances and O—H...S angle 115°. Note that the last value also corresponds to the optimum geometric parameters of three-centered bifurcated H bonds obtained by *ab initio* calculations.[15] The possibility of the formation of the bifurcated O...H...S hydrogen bond is also indicated by our quantum-chemical calculations, according to which the OH groups of the fragments in molecule **2** are oriented simultaneously to both proton-acceptors, *viz.*, O and S.

In addition to two factors considered above, one should take into account the electron influence of the bridging heteroatom on the thiocalixarene molecules. In order to reveal their role, we recorded the UV spectra of solutions of **1**—**4** in CCl_4. The UV spectra of thiocalixarenes exhibit the typical of calixarenes long-wave absorption in the form of a doublet (296/305 nm for **1** and 292/301 nm for **2**) bathochromically shifted by 16 nm relative to the spectra of calixarenes **3** and **4**, respectively. The ratio of the peak intensities of the components of the doublet D_{290}/D_{300} is on the average 1.3, which corresponds to the value presented for calix[4]arenes.[16] A similar shift of the long-wave band was observed in the UV spectra of hexane solutions of thioanisole (278 nm) and toluene (261 nm), which can be considered as structural units of thiocalixarene and calixarene molecules, respectively. The bathochromic shift has previously[17] been attributed by the quantum-chemical calculations to the considerable electron density transfer in anisoles from the heteroatom to the benzene ring. This transfer can result in a decrease in the proton-donating capability of the OH group and weakening of the IHB in thiocalixarenes.

When considering the nature of the cooperative H bond in thiocalix[4]arenes, one should take into account all factors mentioned above: sizes of the macrocycle, the bifurcated character of the H bonds, and electronic effect of the bridging S atom.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 01-03-33056, 01-03-32079, and 05-00-15).

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Received July 20, 2001