Vibrational spectra, co-operative intramolecular hydrogen bonding and conformations of calix[4]arene and thiacalix[4]arene molecules and their *para-tert*-butyl derivatives†

Sergey Katsyuba,*[a] Valeri Kovalenko,[a] Alla Chernova,[a] Elena Vandyukova,[a] Vladislav Zverev,[a] Roald Shagidullin,[a] Igor Antipin,[a,b] Svetlana Solovieva,[a] Ivan Stoikov[b] and Alexander Konovalov[a,b]

[a] *A.E.Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, Arbuzov str. 8, 420088 Kazan, Russia. E-mail: katsyuba@iopc.knc.ru; Fax: +7-8432732253; Tel: +7-8432731892*
[b] *Kazan State University, Kremlevskaja str. 18, 420008 Kazan, Russia*

The IR and Raman spectra and conformations of calix[4]arene, thiacalix[4]arene and their *p-tert*-butyl derivatives have been analysed within the framework of scaled quantum mechanics (SQM). It is shown that the introduction of four *p-tert*-Bu groups into the calixarene molecules influences the relative energies of their conformers and the enthalpy of the cooperative intramolecular H-bonding (ΔH_{intra}) almost negligibly. ΔH_{intra}, evaluated from Iogansen's rule, amounts to ∼26–28 kcal mol^{-1} for the calixarenes and ∼20–21 kcal mol^{-1} for the thiacalixarenes, which essentially exceeds the enthalpies of non-cooperative H-bonds formed by related phenols. As a result of this strong bonding, bands of stretching, bending and torsion vibrations of an eight-membered cyclic system $(OH\cdots)_4$ arise, *e.g.*, two $\delta(OH)_4$ bands are observed in the IR spectra of the most highly symmetric C_4 cone conformations of calix[4]arene and thiacalix[4]arene. The "duplication" of the number of OH infrared bands is a good new indicator of cooperativity of intramolecular H-bonding of the calixarenes.

Introduction

Calixarenes are macrocyclic compounds consisting of phenol rings that are connected *via* the *ortho* positions by methylene groups. In thiacalixarenes, the methylene bridges are replaced by S atoms. The structural flexibility of the calixarene molecules and their capacity for hydrogen bonding are important features employed in the complexation of cations, anions and neutral molecules.[1–4] Vibrational spectroscopy is known to be a versatile tool in conformational and in H-bonding studies of both liquid and solid compounds or their solutions. However, an interpretation of the IR and Raman spectra of calixarenes and their derivatives is rather complex, and this is the reason why vibrational spectroscopy is not widely applied. Recently[5–8] we have tried to overcome these limitations using the scaled quantum mechanical (SQM) method[9] on the basis of density functional theory (DFT)[10] calculations. We were able to elucidate conformational properties and establish a reliable interpretation of the spectra of comparatively simple models of calixarene building blocks: diphenylmethane[5] (**1**), bis(2-hydroxyphenyl)methane[6] (**2**), and 2-benzylphenol[7] (**3**). It was demonstrated that the νCH_2 vibrations of the bridging methylene groups of the model compounds are very sensitive to conformational changes thus providing a probe to study the conformations of these kinds of molecules.

The conformations and vibrational spectra of the 2,6-dimethylanisole (**4**) and *n*-propyl-2,6-dimethylphenyl ether (**5**) molecules were also analysed.[8] These compounds were chosen as the simplest models of alkyl substituted calixarenes which are widely used in calixarene chemistry. It was shown that the major part of the vibrational spectra of molecules **4** and **5** can be approximated by the sum of the vibrational modes of their constituent groups, these modes being transferable among the related molecules.

In all cases, conformational distribution observed experimentally was reflected by quantum chemical computations. The vibrational frequencies calculated by the SQM method were in good agreement with the experimental values, the high quality of the SQM predictions being especially impressive for νOH frequencies of the intramolecularly H-bonded systems **2** and **3**. The deviations from the corresponding νOH frequencies, measured in highly diluted CCl_4 solutions, did not exceed ∼0.5%. On these grounds, we use the same approach in the present work to study normal modes, hydrogen bonding and conformational behaviour of the title compounds. It is hoped to establish on this basis a better understanding of various factors influencing vibrations of the calixarene molecules and relate their frequencies to conformations of the macrocycles and to the type of H-bonds they are able to form.

Experimental

The title compounds were synthesised by previously described procedures.[11,12] The solvent, CCl_4, was stored prior to use on molecular sieves, 3 or 4 Å, to remove traces of water. All solution preparations were carried out in a glove box with exclusion of moisture. IR spectra of the compounds were recorded on a FTIR spectrometer «Vector 22» (Bruker) in the 400–4000 cm^{-1} range at a resolution of 1 cm^{-1}. Solid samples were prepared as KBr pellets. Spectra of CCl_4 solutions were recorded in 2 cm cells. The concentrations were about 10^{-4} M. Raman spectra were recorded on a Coderg PHO spectrometer with a double monochromator using a He–Ne laser (LG-36A, $\lambda = 632.8$ nm, power 30 mW). The samples were placed in standard glass capillaries.

Computations

All DFT calculations were done using the Gaussian-98 suite of programs.[13] We used Becke's three-parameter exchange functional[14] in combination with the Lee–Yang–Parr correlation functional[15] (B3LYP) and standard 6-31G* basis set.

† Electronic supplementary information (ESI) available: Tables 1S–4S and Fig. 1S. See http://www.rsc.org/suppdata/ob/b5/b504448k/

1   **2**   **3**

4   **5**
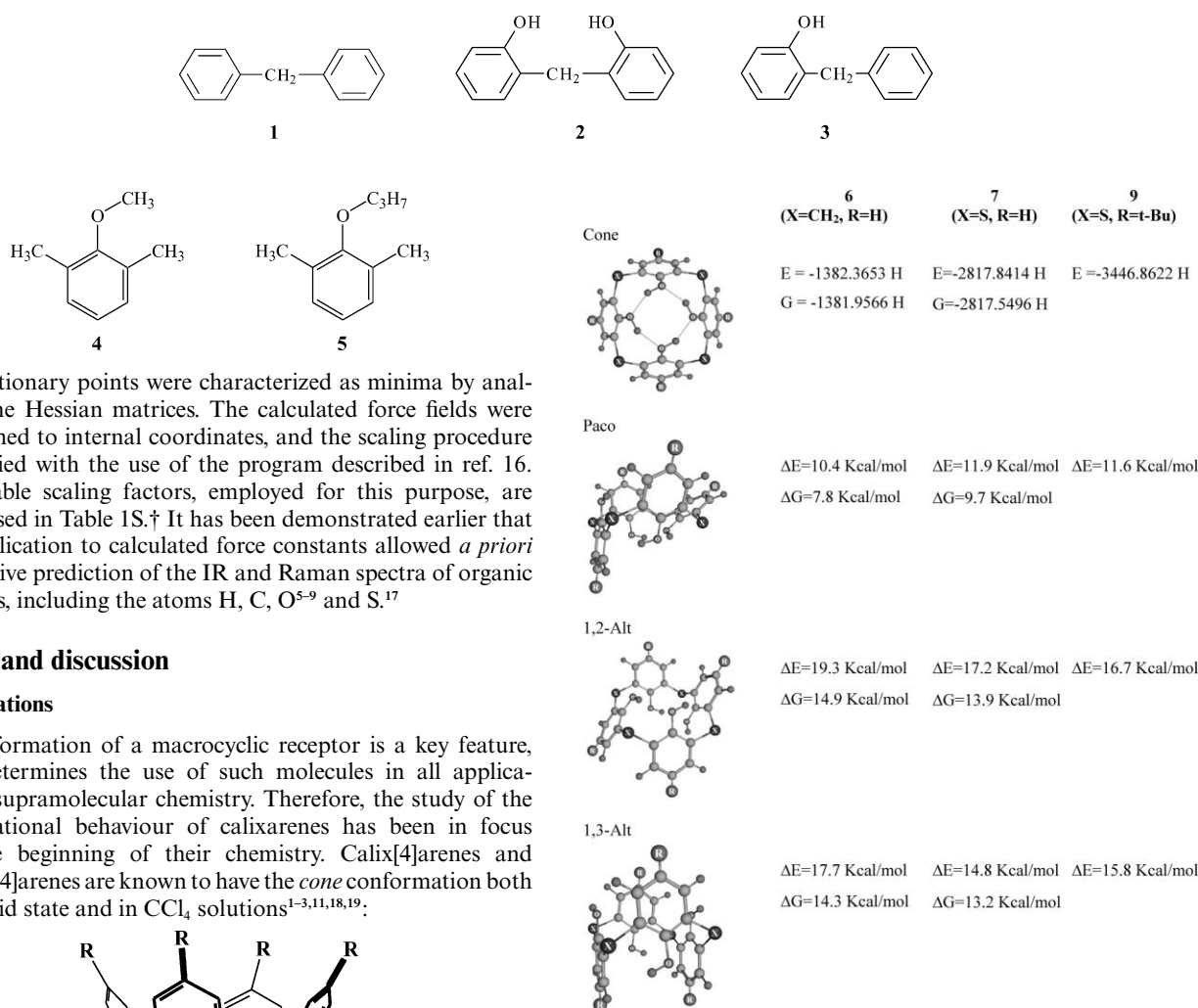
All stationary points were characterized as minima by analysis of the Hessian matrices. The calculated force fields were transformed to internal coordinates, and the scaling procedure was applied with the use of the program described in ref. 16. Transferable scaling factors, employed for this purpose, are summarised in Table 1S.† It has been demonstrated earlier that their application to calculated force constants allowed *a priori* quantitative prediction of the IR and Raman spectra of organic molecules, including the atoms H, C, O[5–9] and S.[17]

Results and discussion

Conformations

The conformation of a macrocyclic receptor is a key feature, which determines the use of such molecules in all applications of supramolecular chemistry. Therefore, the study of the conformational behaviour of calixarenes has been in focus since the beginning of their chemistry. Calix[4]arenes and thiacalix[4]arenes are known to have the *cone* conformation both in the solid state and in CCl₄ solutions[1–3,11,18,19]:
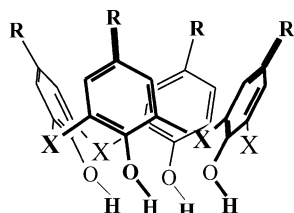
6: X = CH₂, R = H; **7**: X = S, R = H; **8**: X = CH₂, R = *t*-Bu; **9**: X = S, R = *t*-Bu

This conformation is stabilised by the very strong cooperative intramolecular hydrogen bond, which is indicated by a strong decrease in the νOH frequency in their IR spectra.[3,19] According to both published[4,19–21] and present *ab initio* computations by Hartee–Fock and DFT methods, the *cone* conformations of individual molecules **6** and **7** with C_4 symmetry[22] are much more energetically stable than other possible conformers—partial cone (*paco*), 1,3-alternate (*1,3-alt*) and 1,2-alternate (*1,2-alt*). Our calculations of the relative electronic energies (ΔE) of the conformers agree well with the corresponding averaged values[4] of all the published quantum chemical estimates, obtained with the use of 6-31G* or higher basis sets (Fig. 1). The respective relative enthalpies (ΔH) and free energies (ΔG), which have been calculated for the first time, more or less parallel the ΔE values, although ΔG values are considerably lower than ΔE values for the *1,2-alt* and *1,3-alt* conformations of molecule **6**. The lowest energy pathway for the *cone → cone** interconversion proceeds *via* either the former or the latter conformations.[1,2,24] So, the $\Delta G^{\neq}$ value of about 15 kcal mol⁻¹, measured for the inversion process by NMR spectroscopy,[24] can be compared with our non-empirical ΔG estimates for the *1,2-alt* and *1,3-alt* conformers, this comparison being much more favourable than with the corresponding ΔE values (Fig. 1 and ref. 4).

The conformational properties can be influenced by substituents. It is known that different substituents in the *p*-positions of calix[4]arenes have only a minor influence on the stability of the cone conformation and on the rotational barriers,[2] but

	6 (X=CH₂, R=H)	**7** (X=S, R=H)	**9** (X=S, R=t-Bu)
Cone	E = -1382.3653 H G = -1381.9566 H	E=-2817.8414 H G=-2817.5496 H	E =-3446.8622 H
Paco	ΔE=10.4 Kcal/mol ΔG=7.8 Kcal/mol	ΔE=11.9 Kcal/mol ΔG=9.7 Kcal/mol	ΔE=11.6 Kcal/mol
1,2-Alt	ΔE=19.3 Kcal/mol ΔG=14.9 Kcal/mol	ΔE=17.2 Kcal/mol ΔG=13.9 Kcal/mol	ΔE=16.7 Kcal/mol
1,3-Alt	ΔE=17.7 Kcal/mol ΔG=14.3 Kcal/mol	ΔE=14.8 Kcal/mol ΔG=13.2 Kcal/mol	ΔE=15.8 Kcal/mol

Fig. 1 Calculated stable conformations of molecules **6**, **7** and **9** and their conformational energies (ΔE)/free energies (ΔG) relative to the electronic energies (E)/sums of electronic and thermal free energies (G) of the cone conformations.

nothing was published that was concerned with the possible impact of *para*-substitution on the conformational behaviour of thiacalix[4]arenes. To eliminate this gap, we have calculated all four possible conformations of the *p-tert*-Bu-thiacalix[4]arene **9** (Fig. 1). A comparison of the computed relative energies of molecules **7** and **9** demonstrates that the introduction of four *p-tert*-Bu groups into the thiacalix[4]arene molecules influences the relative stabilities of their conformers almost negligibly, like in the case of the calix[4]arenes.

So, the *cone* conformations of individual molecules **6–9** are much more energetically stable than other possible conformers. As a result, the latter conformations are not detectable at ambient or even elevated temperatures, and experimental data on the structure and spectra of calixarenes **6–9** are available for the *cone* conformations exclusively. So, only *cone* conformers will be discussed in the following subsections.

The calculated structural parameters of the *cone* conformations (Table 2S†) are in good agreement with the X-ray data,[11,18] except that owing to crystal packing, the experimental X-ray structures of **6** and **7** correspond to C_2 symmetric cones. Molecules **8** and **9** retain C_4 symmetry in the solid state, probably because of the presence of bulky and symmetric *tert*-butyl substituents, protecting them from distortions.[19]

Vibrational spectra of calix[4]arene (6)

The conformational homogeneity of **6** facilitates the assignments of the fundamentals. Table 1 and Fig. 2a give these assignments

Table 1 IR spectra of calix[4]arene **6**

Experiment		Computations			
IR, solid (CCl₄)	Raman, solid		I_{IR}	I_{Ra}	Assignment[c]
ν/cm⁻¹, I[a]	ν/cm⁻¹, I[a]	ν/cm⁻¹[b]	km/mole	Å⁴/amu	
3247 s	3225 vw	3240	0	122	ν_1 OH (B)[d]
3147 vs (3173 vs)		3197, 3197	3478	13	ν_2 OH (E)[d]
3091 w (3102 w)		3102	13	263	ν_3 OH (A)[d]
(3067 vw)	3055 vw	3068, 3068, 3068, 3068	121	812	Ring 1
3045 sh (3047 vw)		3046, 3046, 3046, 3044	81	184	Ring 3
3030 sh (3033 w)	3017 vw	3041, 3039, 3039, 3038	0	214	Ring 2
2934 m (2951 m)		2928, 2928, 2928, 2928	31	188	ν_{as}CH₂
2868 m (2879 w)		2891, 2891, 2891, 2891	102	126	ν_sCH₂
1609 m	1610 m	1610, 1606, 1606, 1602	20	69	Ring 4
1593 m	1590 m	1598, 1592, 1592, 1589	26	59	Ring 5
1467 vs (1469 m)		1493, 1487, 1487, 1486	73	13	Ring 6
		1476, 1471, 1471, 1465	104	68	Ring 7
1450 vs (1454 m)		1463, 1461, 1459, 1459	274	6	δCH₂
1412 s (1422 w)		1426	1	0	δ_1 OH (A)[d]
1377 s (1384 w)		1370, 1370	104	1	$\delta_{2,3}$OH (E)[d]
1350 sh		1351	0	0	δ_4OH (B)[d]
		1325, 1313, 1312, 1312	4	24	ωCH₂
1298 m (1300 vw)		1310, 1307, 1307, 1286	4	12	Ring 8
1261 s	1265 m	1260, 1254, 1251, 1251	102	56	Ring 9
1244 s	1240 m	1245, 1234, 1234, 1221	80	16	Ring 10
1211 sh	1214 w	1203, 1203	11	3	Ring 11
1199 s	1199 w	1202, 1202	29	8	Ring 11
1152 sh	1157 w	1164, 1163, 1163, 1162	0	16	Ring 12
1146 m (1145 w)	1147 w	1152, 1146, 1146, 1141	11	10	τCH₂
1094 m	1095 m	1094	16	27	Ring 13, τCH₂
1078 m	1082 w sh	1081, 1081, 1066	24	4	Ring 13, τCH₂
1030 m					
964 w		963, 952, 952	5	7	ρCH₂, νAr–C
		942	42	1	Ring 14
951 sh		941	1	1	νAr–C
		939, 939, 936	2	0	Ring 14
		915	1	9	Ring 16
914 w	916 s	912	51	22	ρCH₂
		904	1	0	Ring 16
		890	0	0	Ring 16
898 m		887, 887	2	1	ρCH₂, νAr–C
870 w	873 w	871	238	10	Tors OH
		862	0	0	νAr–C, Ring 16
		848	13	3	ρAr–O
840 m		836, 836	56	0	Ring 17
	818 w	831	0	5	Ring 17, tCH₂
777 s	776 w	797	74	8	Ring 17
		796, 796, 774	9	0	Ring 18
752 vs	758 w	756, 752, 752	312	18	Ring 19
732 sh		731	0	0	Ring 19
697 m	708 vw	711, 711	47	0	Tors OH
	691 m	697	0	1	Bending of macrocycle
665 sh		686, 682, 682	10	11	Ring 20
652 w	654 s	642	2	64	Breathing of macrocycle
629 w		610, 610	12	8	Bending of macrocycle
599 m		602	0	4	Tors OH
565 m	566 m	573, 569, 569	32	3	Ring 21
551 w		561	5	3	Ring 22
530 w	528 m	543	0	1	Ring 23
525 w		543, 543	2	0	Ring 21
		535	0	2	Ring 22
512 m	512 m	533	3	8	Ring 21
		522	8	1	Ring 23
		512	0	8	Ring 24
485 m	483 vw	497, 497, 496	14	1	Tors of macrocycle, Ring 25
461 m		466, 466, 454, 446	15	2	Tors of macrocycle, Ring 25
		388, 388	24	0	Tors of macrocycle
		362	0	0	Tors of macrocycle
	328 m	322	1	4	Tors of macrocycle
	318 m	317, 317	3	2	Macrocycle
	306 w	288	5	0	Macrocycle
	288 m	282, 282	33	5	Macrocycle
	268 m	270	0	9	Macrocycle
	251 w	258	6	0	Macrocycle
	223 s	234	0	3	Macrocycle
	208 w	205, 205	1	5	Macrocycle
	181 s	192	0	0	Macrocycle

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad. [b] SQM scaled wavenumbers. [c] ν, stretch; δ, bend; ω, wagging; τ, twisting; ρ, rocking; s, symmetrical; as, antisymmetrical. "Ring" is used for the vibrations of the phenyl rings. [d] See Fig. 3. In parenthesis—symmetry type of the vibrations.
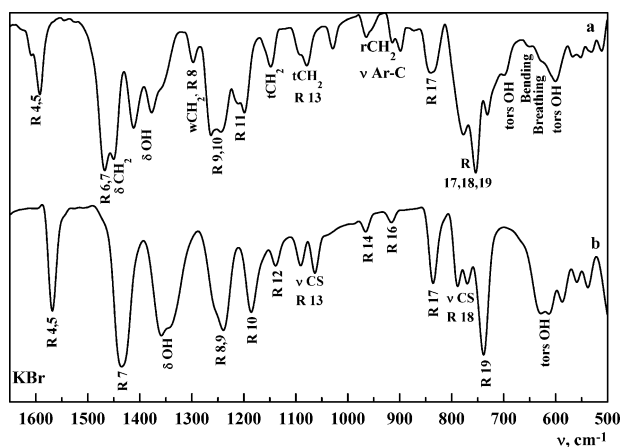
Fig. 2 IR spectra of calix[4]arene **6** (a) and thiacalix[4]arene **7** (b) in KBr pellets in the spectral region of 500–1650 cm^{-1}. Assignments are given on the basis of SQM calculations (Tables 1 and 2).

based on the present SQM computations, which demonstrate quite good general agreement between the calculated and the experimental frequencies of the fundamentals.[25]

As in the cases of model compounds **1–5**[5–8] the spectra of molecule **6** may be qualitatively analysed in terms of the vibrational modes of the methylene bridges and those of the rings. The notation of the aromatic ring vibrations in Table 1 and Fig. 2a differs from Wilson's notation,[26] which is most frequently used to describe the normal modes of benzene. Wilson's notation is not suitable for the normal modes of polysubstituted benzenes, and we resort instead to diagrams of atomic displacements during normal vibrations, published elsewhere.[8] It should be noted that it is not only the normal modes but also the frequencies of the fundamentals, associated with the vibrations of the aromatic rings, that practically coincide for 2,6-dimethylphenol, molecules **4**, **5** (Table 5 of ref. 8) and calixarene **6** (Table 1). This is further proof of the transferability of the vibrational modes of phenolic units among the related molecules.[8]

There are two exceptions to the abovementioned rule. Firstly, medium- and low-frequency modes of adjoining structural units are liable to couple with each other. As a result, two "Ring 13" bands (1094 and 1078 cm^{-1}), two "Ring 14" bands (964 and 951 cm^{-1}), *etc.*, are observed in the spectra. Vibrational interactions are most pronounced in the lower spectral region $\sim$700 cm^{-1}, where assignments to "individual" vibrations of aromatic rings become rather arbitrary. Some modes definitely involve the whole molecule: for example, "torsions of macrocycle" (485 and 461 cm^{-1}), "bendings of macrocycle" (697 and 629 cm^{-1}) and "breathing of macrocycle" (652 cm^{-1}). The line at 652 cm^{-1} is the strongest line in the experimental Raman spectrum, as is often the case with breathing vibrations of cyclic molecules, which seems to simplify their assignments.

Secondly, hydroxyl vibrational modes of calixarene **6** are dramatically different from those of molecules **2** and **3**. Because of very strong co-operative H-bonding, four OH-groups of calixarene interact with each other significantly. As a result, group vibrations of an eight-membered cyclic system (O–H $\cdots$)$_4$ arise, which will be discussed in detail later together with the corresponding vibrations of molecules **7–9**. It should be emphasized here that these OH interactions are dynamic in nature in contrast to the aforementioned coupling of "ring" modes, which is mainly kinematical.

Vibrational spectra of thiacalix[4]arene (7)

The assignments of the fundamentals of molecule **7** are presented in Table 2 and Fig. 2b. As with calix[4]arene **6**, the spectra may be qualitatively analysed in terms of the vibrational modes of the rings and those of the C–S–C bridges. The frequencies of

the vibrations of the phenolic residues of the thiacalixarenes and the calixarenes diverge, sometimes appreciably, because the masses of sulfur atoms connecting the rings in molecule **7** are much different from those of the methylene bridges of calixarene **6**. Nevertheless, the notation of the aromatic units' vibrations, introduced for calixarene building blocks,[8] is still quite suitable for normal modes of **7**. The fundamentals, associated with CSC vibrations, resemble those of Ph–S–Ph and Me–S–Ph molecules.[27] Vibrational interactions of these "individual" modes are less pronounced than in the case of calixarene **6**, and vibrations essentially involving the whole macrocycle arise only at about 600 cm^{-1} and in the spectral region below $\sim$300 cm^{-1}. In particular, a "breathing" vibration of the macrocycle does not exist, in contrast to molecule **6**. Nevertheless, group vibrations of the eight-membered cyclic system (O–H $\cdots$)$_4$ still persist, in spite of the weakening of the co-operative intramolecular H-bonding.[19] They are discussed in the next subsection.

Vibrations of OH groups of calixarenes 6 and 7

Each molecule (**6** and **7**) has four hydroxyl groups. If these OH groups could be regarded as independent oscillators, the frequencies of their stretching vibrations would coincide, because all phenolic units of the C_4 symmetric cone conformer are absolutely equivalent to each other. However our computations demonstrate that owing to intramolecular cooperative H-bonding, a strong dynamic interaction of all four oscillators arises. As a result, their vibrations are not just vibrations of separate OH groups. They may be thought of as four stretching vibrations of an eight-membered cyclic system (O–H $\cdots$)$_4$ with four different frequencies (Fig. 3a). According to C_4 symmetry, two of them are doubly degenerate, and computations predict that the only strong IR band corresponds just right to these vibrations of an E symmetry type ($\nu_{2,3}$ in Fig. 3a). One of the remaining two bands is very weak (ν_4 in Fig. 3a) and another band has zero intensity by symmetry rules (ν_1 in Fig. 3a). So, two ν(O–H)$_4$ bands should be expected in the IR spectra, one of them being of negligible intensity. The IR spectra of diluted CCl$_4$ solutions of calixarenes **6** and **7** (Fig. 4a, b), indeed, exhibit a single strong band in the spectral region of OH stretching vibrations (3173 and 3310 cm^{-1} respectively). A weak satellite band at 3102 cm^{-1} in the spectrum of **6** should probably be assigned to the vibration of an A symmetry type (ν_4 in Fig. 3a), though assignment to combinations or overtones cannot be excluded.
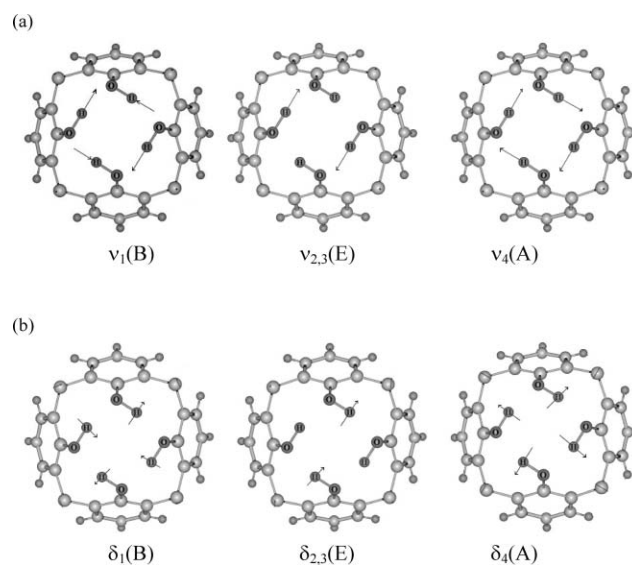
(a)

(b)

Fig. 3 Diagrams of atomic displacements during (a) OH stretching vibrations of calixarenes **6–9**, and (b) OH bending vibrations of calixarenes **6** and **7**. In parenthesis—symmetry type of the vibrations.

Table 2 Vibrational spectra of thiacalix[4]arene **7**

Experiment		Computations			
IR, solid (CCl₄)	Raman, solid		I_{IR}	I_{Ra}	Assignment[c]
ν/cm⁻¹, I[a]	ν/cm⁻¹, I[a]	ν/cm⁻¹[b]	km/mole	Å⁴/amu	
		3334	0	73	ν_1OH (B)[d]
3343 s					
(3310 vs)		3309, 3309	2075	12	$\nu_{2,3}$OH (E)[d]
3268 vs		3263	21	251	ν_4OH (A)[d]
(3072 vw)	3108 vw	3082, 3081, 3081, 3081	66	904	Ring 1
3062 m (3055 sh)		3073, 3073, 3073, 3072	9	210	Ring 3
(3028 vw)		3060, 3060, 3060, 3060	10	242	Ring 2
1655 w					
1610 w					
1568 vs	1573 m	1576, 1572, 1572, 1571	35	78	Ring 5
		1563, 1563, 1563, 1561	42	60	Ring 4
1503 w					
1478 w		1462, 1461, 1461, 1460	78	2	Ring 6
1439 vs (1440 m)		1445	220	4	Ring 7
1427 vs (1430 m)		1430, 1430, 1423	174	10	Ring 7
1358 s (1360 s)		1367	91	1	δ_1OH (A)[d]
1341 s (1340 sh)		1335, 1335	104	0	$\delta_{2,3}$OH (E)[d]
		1328	0	2	δ_4OH (B)[d]
	1273 m	1267	4	70	Ring 9
1256 sh		1257, 1257, 1253	71	27	Ring 9
		1250	16	1	Ring 8
1239 s		1238, 1238, 1230	44	8	Ring 8
1186 s	1183 vw	1201, 1191, 1191, 1179	23	4	Ring 10
1138 m	1138 vw	1146, 1146, 1146, 1146	8	15	Ring 12
1101 m	1093 w	1096	15	42	νC–S (in-phase)
1090 m		1086, 1086, 1078	15	20	νC–S, Ring 13
1063 m	1063 m	1072, 1070, 1070, 1066	14	11	Ring 13, νC–S
1035 vw					
1005 vw					
988 vw					
965 m		956, 955, 955, 953	2	0	Ring 14
939 vw					
915 m		923, 919, 919, 916	0	1	Ring 16
836 s	838 m	838, 833, 833	45	43	Ring 17
820 w sh		829	0	6	Ring 17
790 s		792	3	7	Ring 18
		787, 787	22	0	Ring 18, νCS
		782	0	6	νCS
771 m		778, 775, 775, 775	2	1	ν_{as}CS
736 vs	728 vw	745, 737, 737, 728	158	3	Ring 19, Ring 18
697 vw					
680 vw					
673 w	670 vw				
663 w sh					
629 s		640	254	4	Tors OH
611 s		609, 607, 607	264	4	Tors OH, νCS
603 sh	603 m	601	0	1	Macrocycle
590 m		587	28	35	Macrocycle
581 sh		564, 564	131	6	Macrocycle
559 m		558, 555, 555, 553	66	16	Ring 22
544 sh		547, 547, 544, 542	4	3	Ring 21
537 w		540, 540	4	0	Ring 23
		527	0	1	Tors OH
494 s		491	0	0	Ring 23
429 m	433 m	439	17	11	ν_sCS–δCSC
412 m		422, 416, 415	15	3	νCS
407 w		402, 390, 390, 382	5	6	νCS
		357	0	0	Ring 26
		322, 322	6	0	Ring 26
	288 m	288, 288, 279, 279, 270, 270	9	12	Macrocycle
	243 m–w	251, 250	0	4	Macrocycle
		226, 226	12	0	Macrocycle
	178 m	185, 181, 181, 180	3	9	Macrocycle

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad. [b] SQM scaled wavenumbers. [c] ν, stretch; δ, bend; ω, wagging; τ, twisting; ρ, rocking; s, symmetrical; as, antisymmetrical. "Ring" is used for the vibrations of the phenyl rings. [d] See Fig. 3. In parenthesis—symmetry type of the vibrations.
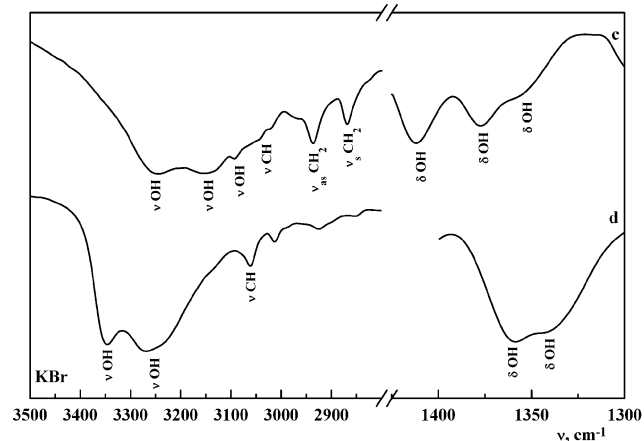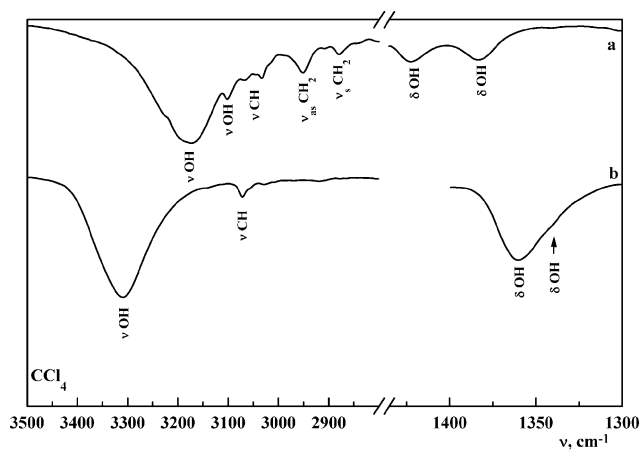
Fig. 4 IR spectra of calix[4]arenes **6** and **7** in the spectral regions of νOH and δOH vibrations: (a) **6** in CCl₄ solution; (b) **7** in CCl₄ solution; (c) **6** in KBr pellet; (d) **7** in KBr pellet.
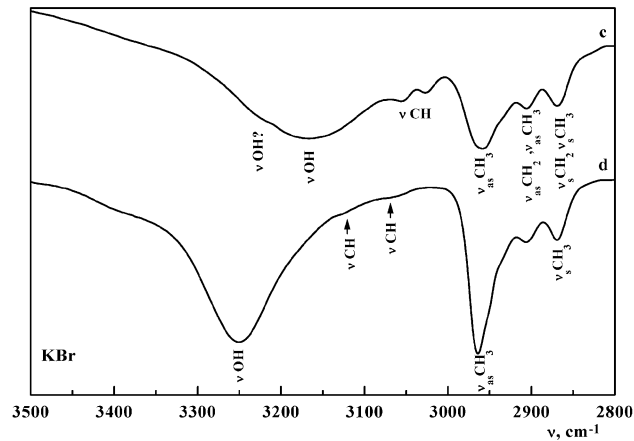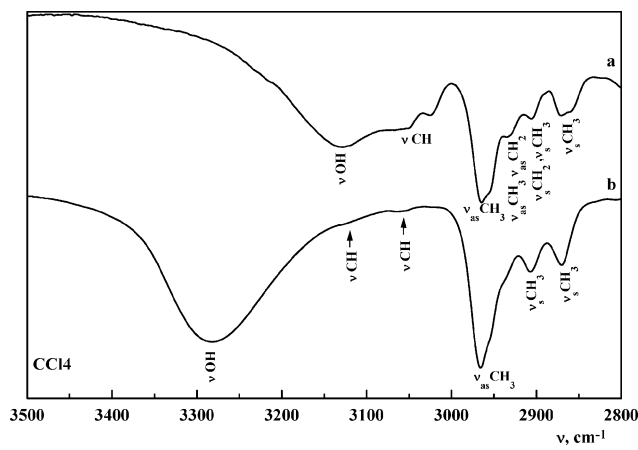

Fig. 5 IR spectra of *p-tert*-Bu-calix[4]arenes **8** and **9** in the spectral region of νOH vibrations: (a) **8** in CCl₄ solution; (b) **9** in CCl₄ solution; (c) **8** in KBr pellet; (d) **9** in KBr pellet.

The IR spectra of the crystalline calixarenes **6** and **7** (Fig. 4c, d) exhibit triplet bands in the spectral region of OH stretching vibrations. The presence of three νOH frequencies cannot be explained by Davydov splitting or other crystalline effects.[19] In both cases, complex band contours seem to be a result of the deviation of molecules **6** and **7** from the C_4 symmetry affected by the crystal packing. According to X-ray data,[11,18] the O···O distances become slightly nonequivalent, the differences between the distances being only about 0.03 Å. Nevertheless, the symmetry decreases to C_2, symmetry rules change, and all νOH vibrations become IR active. Again, like in the case of the IR spectra of diluted CCl₄ solutions, "extra" bands could be assigned to overtones, *etc.* However, the former explanation is supported by an inspection of the OH stretching region of calixarenes **8** and **9**. Their molecules in crystal form have C_4 symmetry,[11,18] and the spectra of the solid samples exhibit only one strong νOH band (Fig. 5).

Similar to OH stretchings, OH bendings and torsions must also be regarded as four bending and four torsion vibrations of an eight-membered cyclic system (O–H···)₄. Again, by C_4 symmetry rules, two of the four bending (or torsion) vibrations are doubly degenerate, and the vibration of a B symmetry type gives rise to an IR band of zero intensity (Fig. 3b). So, two δ(OH)₄ and two torsion (OH)₄ bands should be expected in the IR spectra. According to computations, the differences in intensities of these bands are not so dramatic as in the case of $ν_{2,3}$ and $ν_4$ (Tables 1 and 2), and the recorded IR spectra, indeed, demonstrate two bending OH bands (Tables 1 and 2, Fig. 4). A reliable assignment of the IR bands to torsion (OH)₄ is hampered by overlapping with bands of other vibrations of calixarenes **6** and **7** (Tables 1 and 2, Fig. 2), but experimental evidence of the splitting of δ(OH)₄ bands is especially clear because the

corresponding spectral ranges ∼1350–1430 cm⁻¹ (**6**) and ∼1320–1370 cm⁻¹ (**7**) are free from overlapping. Besides, the appearance of bands of overtones or combinations is less probable for this region than for a νOH spectral interval, and crystal effects can be excluded by comparison of the solid-state and the solution spectra (Fig. 4).

So, the most striking distinguishing feature of a C_4 symmetric array of hydroxyl groups in the IR spectra of calixarenes **6** and **7** is the presence of the "doubled" number of OH infrared bands, which is the result of dynamic interaction of the OH vibrations, induced by the strong cooperative intramolecular H-bonding. As was mentioned before, hydroxyl vibrational modes of the calixarenes are dramatically different from those of model molecules **2** and **3**. Neither computations nor experiments demonstrated any detectable splitting of νOH or δOH bands in the spectra of the latter,[6,7] obviously because the intramolecular hydrogen bonding of molecules **2** and **3** is non-cooperative and much weaker than the H-bonding of the title compounds. Quantitative parameters of H-bonds of calixarenes **6**–**9** and the related phenols **2** and **3** will be compared and discussed in a separate subsection.

Vibrational spectra of *p-tert*-Bu-calixarenes (8) and (9)

Complete interpretation of the spectra of molecules **8** and **9** is presented in Tables 3S and 4S.† The IR spectra of solid samples and CCl₄ solutions of calixarenes **8** and **9** are compared in Figs. 5 and 6. As in the case of calixarenes **6** and **7**, it is possible to analyse the spectra of their *p-tert*-Bu derivatives in terms of the vibrational modes of the *para*-substituted phenolic units and those of the connecting methylene or sulfide bridges. The vibrational modes of the phenolic units may be qualitatively divided into vibrations of the aromatic rings and *tert*-Bu
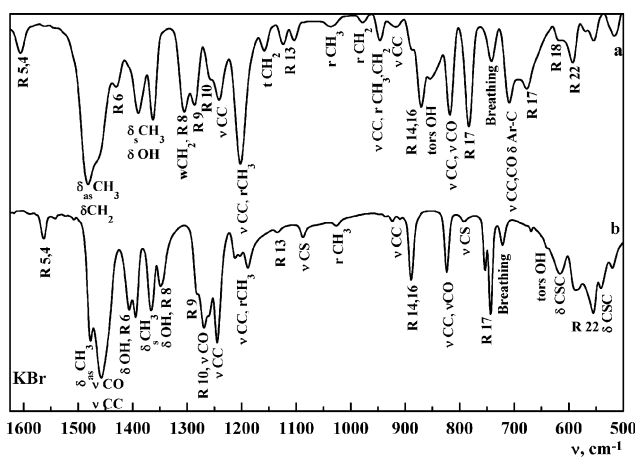
Fig. 6 IR spectra of *p-tert*-Bu-calix[4]arene **8** (a) and *p-tert*-Bu-thiacalix[4]arene **9** (b) in KBr pellets in the spectral region of 500–1650 cm⁻¹. Assignments are given on the basis of SQM calculations (Tables 3S and 4S).†

moieties, but only in part. For example, stretching vibrations of groups OH, CH and CH$_3$ do not mix with each other, but it is difficult to separate δOH vibrations from δ_sCH$_3$ and the "Ring" vibrations.

It should be pointed out that although we use the same notation of aromatic ring vibrations for both calixarenes **6** and **7** and their *p-tert*-Bu-substituted derivatives **8** and **9**, its meaning in Tables 3S and 4S† (and in Figs. 5 and 6) differs from that in Tables 1 and 2 (and in Fig. 2). The diagrams of atomic displacements during normal vibrations of the *p-tert*-Bu-substituted aromatic units of calixarenes **8** and **9** are very close to the corresponding diagrams of the aromatic ring of 2,6-dimethyl-4-*tert*-Bu-phenol (**10**) shown in Fig. 1S.† These diagrams resemble to some extent the diagrams of the normal modes of 2,6-dimethyl-phenols published elsewhere,[8] and that is the reason why we hold the "Ring" notation for all the title compounds. The extent to which various vibrations of the phenolic units of calixarenes **8** and **9** are non-additive can be evaluated by comparison of their frequencies (Tables 3S and 4S) with the corresponding frequencies of molecule **10** (Fig. 1S).†

The abovementioned vibrational "interactions" of hydroxyl groups with the rest of the molecule complicate the elucidation of the effects of intramolecular H-bonds on the bending and torsion OH vibrations. Nevertheless, it is quite possible to analyse these effects on νOH bands, because four stretching vibrations of an (OH)$_4$ cyclic array (Fig. 3a) remain well separated from all other vibrations of the macrocycle. It is easily seen from Tables 3S and 4S† that, like in the case of calixarenes **6** and **7** (Tables 1 and 2), four stretching vibrations of an eight-membered cyclic system (O–H $\cdots$)$_4$ with three different frequencies arise. A close similarity of the νOH region both in the calculated and registered spectra of CCl$_4$ solutions where all the molecules **6–9** have C_4 symmetry (Fig. 4 and 5) implies that all the studied calixarenes form very similar hydrogen bonds. This will be discussed in the next subsection.

The enthalpy of the intramolecular H-bonding of calixarenes 6–9

The very strong cooperative intramolecular hydrogen bond in calixarenes **6–9** is indicated by a substantial red shift ($\Delta\nu$) of the νOH IR bands as compared to the spectra of "free" molecules of the related phenols (ν_0). An extensive quantitative correlation of spectral and thermodynamic parameters for the intermolecular H-bonding of phenols has been published (ref. 28 and references cited therein):

$$-\Delta H = 0.3_3(\Delta\nu - 40)^{1/2} \qquad (1)$$

Here $-\Delta H$ is the enthalpy of the H-bond (in kcal mol⁻¹).

Applicability of eqn. (1) to the evaluation of the enthalpy of intramolecular H-bonds ($-\Delta H_{\text{intra}}$) of hydroxyl groups has been shown.[29] It is suitable for large non-strained cycles, locked by an intramolecular OH $\cdots$ A bond, where geometrical conditions are very similar to the case of intermolecular hydrogen bonding.[28,29] In calixarenes **6–9**, the intramolecular OH $\cdots$ O bonds lock eight-membered cycles (Fig. 3), and O–H $\cdots$ O angles are about 152–165°. Of course, eqn. (1) is not suitable for use in the case of group (OH $\cdots$)$_4$ vibrations. Nevertheless, it is worth trying to apply it to a rough estimation of the $-\Delta H_{\text{intra}}$ value, the more so that splitting of νOH bands because of the dynamic interactions of four OH oscillators (Tables 1, 2 and 3S, 4S) is much smaller than their shifts $\Delta\nu$ caused by hydrogen bonding. Hence, as a first approximation, it is possible to assume that (i) these four OH oscillators do not depend on each other; (ii) all vibrate with a frequency equal to the peak position of the νOH band; (iii) the overall energy of their H-bonding is equal to the sum of four energies of "individual" OH $\cdots$ O hydrogen bonds.

Another assumption we use is that redshifts, $\Delta\nu$, can be evaluated by comparison of the experimental OH frequencies of calixarenes **6–9** with the ν_0 values of related phenols. The use of the model compounds for the measurement of frequencies (ν_0) undisturbed by hydrogen bonding is inevitable because all OH-groups of the studied calixarenes **6–9** participate in a cyclic H-bond. A comparison of the ν_0 values obtained for different phenols (Table 3) demonstrates that a concrete choice of model compound does not dramatically influence the resulting $-\Delta H_{\text{intra}}$ estimates.

For comparison purposes, $-\Delta H_{\text{intra}}$ of the closely related molecule **2** was also evaluated employing eqn. (1), the estimate being equal to 3.2 kcal mol⁻¹. The enthalpy per one OH $\cdots$ O hydrogen bond of calixarenes **6–9** (Table 3) is about twice as large as this value. The duplication of the enthalpy of the H-bonding is indicative of a strong cooperativity effect: the hydrogen bond of the first hydroxy group to a second hydroxy group polarizes the OH bond in this second hydroxy group, so that its hydrogen bond to a third oxygen atom is strengthened.[3] As a result, the enthalpy of the whole cyclic array of H-bonds amounts to *ca.* 20–30 kcal mol⁻¹ (Table 3).

The data presented in Table 3 demonstrate that $-\Delta H_{\text{intra}}$ of calixarenes **6** and **8** is half as much as the $-\Delta H_{\text{intra}}$ of thiacalixarenes **7** and **9**. The weakening of the H-bond in the thiacalixarenes, at least partly, can be ascribed to the bifurcated

Table 3 Redshifts ($\Delta\nu$) of peak positions of OH stretching bands in the IR spectra of CCl$_4$ solutions of calixarenes **6–9** (ν^a) relative to CCl$_4$ solutions of model phenols (ν_0) and enthalpies of intramolecular H-bonding ($-\Delta H_{\text{intra}}$) of calixarenes **6–9** evaluated with the use of Iogansen's rule:[28] $-\Delta H_{\text{intra}} = 0.33(\Delta\nu - 40)^{1/2}$

Compound	$\Delta\nu$OH/cm⁻¹	$-\Delta H_{\text{intra}}$ per one OH group (kcal/mole)	$-\Delta H_{\text{intra}}$ per molecule[b] (kcal/mole)
6	439[c], 440[d], 429[e]	6.6[c], 6.6[d], 6.5[e]	26.4[c], 26.4[d], 26.0[e]
7	302[c], 303[d], 292[e]	5.3[c], 5.4[d], 5.2[e]	21.4[c], 21.4[d], 21.0[e]
8	483[c], 484[d], 473[e]	6.9[c], 7.0[d], 6.9[e]	27.8[c], 27.8[d], 27.5[e]
9	273[c], 274[d], 263[e]	5.0[c], 5.0[d], 4.9[e]	20.1[c], 20.1[d], 19.7[e]

[a] Measured as a wavenumber corresponding to the strongest peak of the νOH band. *[b]* $-\Delta H_{\text{intra}}$ per molecule is determined as 4·($-\Delta H_{\text{intra}}$ per one OH group). *[c]* Relative to phenol ($\nu_0 = 3612$ cm⁻¹).[30] *[d]* Relative to 3,5-dimethylphenol ($\nu_0 = 3613$ cm⁻¹).[31] *[e]* Relative to **2** ($\nu_0 = 3602$ cm⁻¹).[6]

character of this O⋯H⋯S bonding due to the presence of the second proton-acceptor center, *viz.*, S atom, connecting phenolic units.[19] The introduction of four *p-tert*-Bu groups into the calixarene molecules results in practically negligible changes of the enthalpy of the hydrogen bonds.

Conclusions

We have demonstrated that SQM in B3LYP/6-31G* formulation successfully reproduced the conformational behavior and vibrational spectra of calixarenes **6–9**. The computations reveal that the normal modes of phenolic residues of molecules **6** and **7** rather closely resemble those of 2,6-disubstituted phenols or their alkyl ethers. Nevertheless, integration of the four aromatic units into one macrocycle gives rise to a vibrational interaction of their "individual" modes. The interaction is especially strong for low-frequency vibrations of the heavy atoms and the vibrations of the hydroxyl groups. In both cases, separate structural units cannot be regarded as individual oscillators. Instead, either stretching, bending and torsion vibrations of the whole macrocyclic backbone or stretching, bending and torsion vibrations of the eight-membered cyclic hydrogen bonded system $(O–H⋯)_4$ arise. Because of symmetry rules, the number of $(O–H⋯)_4$ IR bands and their intensities are very sensitive to small conformational reorganisations of molecules **6** and **7**. Even for the most highly symmetric C_4 cone conformation of the calixarenes, the number of OH infrared bands is "doubled", which is a good new indicator of cooperativity of the intramolecular H-bonding of calixarenes.

It is shown that the introduction of four *p-tert*-Bu groups into calixarene molecules results in a rather pronounced mixing of vibrations of aromatic rings, hydroxyl groups and *tert*-Bu moieties. Nevertheless, vibrational modes and frequencies of stretching vibrations of an eight-membered cyclic system $(O–H⋯)_4$ practically do not depend on *para*-substitution. The same is true for the relative energies of all conformers of calixarenes and the enthalpy of their cooperative intramolecular H-bonding (ΔH_{intra}). $-\Delta H_{intra}$, evaluated from Iogansen's rules, amounts to ~21–26 kcal mol^{-1} for calixarenes and ~15–21 kcal mol^{-1} for thiacalixarenes, which essentially exceeds the enthalpies of non-cooperative H-bonds formed by related phenols.

References

1 (*a*) C. D. Gutsche, Calixarenes, *Monographs in Supramolecular Chemistry*, ed. J. F. Stoddart, The Royal Society of Chemistry, Cambridge, UK, 1989; (*b*) C. D. Gutsche, Calixarenes Revisited, *Monographs in Supramolecular Chemistry*, ed. J. F. Stoddart, The Royal Society of Chemistry, Cambridge, UK, 1998.
2 *Calixarenes 2001*, eds. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001.
3 L. C. Groenen, E. Steinwender, B. T. G. Lutz, J. H. van der Maas and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1893.
4 J. Schatz, *Collect. Czech. Chem. Commun.*, 2004, **69**, 1169 and references cited therein.
5 S. A. Katsyuba, J. Grunenberg and R. Schmutzler, *J. Mol. Struct.*, 2001, **559**, 315.
6 S. Katsyuba, A. Chernova, R. Schmutzler and J. Grunenberg, *J. Chem. Soc., Perkin Trans. 2*, 2002, 67.
7 S. Katsyuba, A. Chernova and R. Schmutzler, *Org. Biomol. Chem.*, 2003, **1**, 714.
8 S. A. Katsyuba, R. Schmutzler, U. Hohm and C. Kunze, *J. Mol. Struct.*, 2002, **610**, 113.
9 J. Baker, A. Jarzecki and P. Pulay, *J. Phys. Chem. A*, 1998, **102**, 1412.
10 R. G. Parr and W. Yang, *Density Functional Methods of Atoms and Molecules*, Oxford University Press, New York, 1989.
11 H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. Cian and J. Fischer, *Tetrahedron Lett.*, 1998, **39**, 2311.
12 C. D. Gutsche, J. A. Lovine and P. K. Sujeeth, *J. Org. Chem.*, 1985, **50**, 5802.
13 *Gaussian 98 (Revision A.2)*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA., USA, 1998.
14 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
15 C. Lee, W. Yang and R. G. Parr, *Phys. Rev.*, 1988, **B41**, 785.
16 (*a*) V. A. Sipachev, *J. Mol. Struct.*, 2001, **567–568**, 67; (*b*) V. A. Sipachev, *Struct. Chem.*, 2000, **2/3**, 167.
17 S. A. Katsyuba and E. E. Vandyukova, *Chem. Phys. Lett.*, 2003, **377**, 658.
18 (*a*) G. D. Andreetti, R. Ungaro and A. Pochini, *J. Chem. Soc., Chem. Commun.*, 1979, 1005; (*b*) R. Ungaro, A. Pochini, G. D. Andreetti and V. Sangermano, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1979.
19 V. I. Kovalenko, A. V. Chernova, E. I. Borisoglebskaya, S. A. Katsyuba, V. V. Zverev, R. R. Shagidullin, I. S. Antipin, S. E. Solovieva, I. I. Stoikov and A. I. Konovalov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 762; V. I. Kovalenko, A. V. Chernova, E. I. Borisoglebskaya, S. A. Katsyuba, V. V. Zverev, R. R. Shagidullin, I. S. Antipin, S. E. Solovieva, I. I. Stoikov and A. I. Konovalov, *Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 825.
20 (*a*) R. J. Bernardino and B. J. C. Cabral, *J. Phys. Chem. A*, 1999, **103**, 9080; (*b*) R. J. Bernardino and B. J. C. Cabral, *Supramol. Chem.*, 2002, **14**, 57.
21 R. J. Bernardino and B. J. C. Cabral, *J. Mol. Struct.*, 2001, **549**, 253.
22 According to HF/4-31G* computations (ref. 23), the symmetry of the cone conformer of calix[4]arene is C_2. Probably, this result differs from other quantum chemical data (ref. 18–20) because of the comparatively small basis set.
23 F. Billes and I. Mohammed-Ziegler, *Supramol. Chem.*, 2002, **14**, 451.
24 D. C. Gutsche and L. J. Bauer, *J. Am. Chem. Soc.*, 1985, **107**, 6052.
25 Experimental and HF/4-31G* calculated wavenumbers of calix[4]arene vibrational frequencies are partially published in ref. 23. These data mainly agree with present results, except some obvious misassignments (*e.g.*, a week IR band at 3565 cm^{-1} is assigned to OH stretchings of the calixarene, instead of very strong and broad IR bands in the region ~3250–3150 cm^{-1}).
26 E. B. Wilson, Jr., *Phys. Rev.*, 1934, **45**, 706.
27 The detailed tables of calculated and experimental frequencies of PhSPh and MeSPh molecules together with the assignments, based on computed potential energy distributions, are available on request from the authors of ref. 17.
28 (*a*) A. V. Iogansen and B. V. Rassadin, *Zh. Prikl. Spektrosk.*, 1969, **11**, 828; (*b*) A. V. Iogansen, in *Vodorodnaya Svyaz (The Hydrogen Bond)*, ed. N. D. Sokolov, Nauka, Moskow, 1981, pp. 112–155.
29 R. R. Shagidullin, A. V. Chernova, S. A. Katsyuba, L. V. Avvakumova and R. R. Shagidullin, *Russ. Chem. Bull.*, 2004, **53**, 55.
30 A. V. Iogansen, *Spectrochim. Acta, Part A*, 1999, **55**, 1585.
31 B. T. G. Lutz, G. Astarloa, J. H. Van der Maas, R. G. Janssen, W. Verboom and D. N. Reinhudt, *Vib. Spectrosc.*, 1995, **10**, 29.