

IR and NMR spectra, intramolecular hydrogen bonding and conformations of mercaptothiacalix[4]arene molecules and their *para-tert*-butyl-derivative

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Abstract It is demonstrated that the introduction of *p-tert*-butyl groups dramatically influences the conformational behaviour of the mercaptothiacalix[4]arene molecules. Quantum-chemical computations in combination with IR and NMR spectroscopy prove that, in contrast to closely related calixarenes, the 1,3-*alternate* becomes a dominant conformer of *p-tert*-butyl-mercaptothiacalix[4]arene not only in crystal, but also in solutions and in vacuum. It is shown that the title molecules form essentially non-cooperative intramolecular hydrogen bonds: their SH groups are intramolecularly H-bonded solely to the sulfide groups bridging thiophenolic units. The enthalpy of this bonding, evaluated from Iogansen's rule, amounts to ca. 1.5 kcal mol⁻¹ per one SH...S bond, which about four times smaller than the enthalpies of cooperative intramolecular H-bonds formed by related calixarenes and thiacalixarenes.

Keywords Mercaptothiacalix[4]arenes · *p-tert*-Butyl-substitution · Conformations ·

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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 the S atoms. Both types of calixarenes, especially calix[4]arene (**1**, Fig. 1) and thiacalix[4]arene (**2**), comprising four phenolic units, and their *para-tert*-butyl derivatives (**3** and **4**, respectively) are among the most used macrocyclic frameworks [1–3]. For the parent calix[4]arene derivatives the binding of metal cations and main group elements [4] takes place at the lower rim through the OH groups. For the thiacalixarenes the replacement of methylene groups by sulphur atoms increases the number of coordination sites leading thus to a large diversity in the coordination properties [5]. Recently the synthesis of *para-tert*-butyl-tetramercaptothiacalix[4]arene (**5**), in which four OH groups were replaced by four SH groups was reported [6]. The molecule **5** offering a total of eight sulphur atoms is of interest for both its coordination features and as a backbone for the elaboration of other ligands and receptor molecules. E.g., the ability of **5** to generate a hexanuclear mercury complex was demonstrated [7].

The structural flexibility of the calixarene molecules and their capacity for hydrogen bonding represent their important features employed both in the complexation and in the elaboration of other ligands and receptor molecules [1–3, 5f–h]. Recently [8, 9] we have demonstrated that experimental IR and Raman spectroscopy combined with the scaled quantum mechanical (SQM) method [10] on the

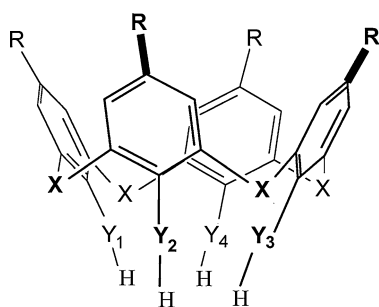


Fig. 1 1: X = CH₂, Y = O, R = H; 2: X = S, Y = O, R = H; 3: X = CH₂, Y = O, R = *t*-Bu; 4: X = S, Y = O, R = *t*-Bu; 5: X = S, Y = S, R = *t*-Bu; 6: X = S, Y = S, R = H

basis of density functional theory (DFT) [11] calculations allow to elucidate conformational and H-bonding properties of both solid calixarenes **1–4** and their solutions. It was shown that a formation of eight-membered intramolecularly H-bonded cyclic system (OH \cdots)₄ of the most highly symmetric C₄ cone conformations of the calix[4]arenes **1, 3** and thiacalix[4]arenes **2, 4** causes “duplication” of the number of OH infrared bands which is a new good indicator of cooperativity of intramolecular H-bonding of the calixarenes. The presence of the second type of proton-acceptor centers into the thiacalixarene molecules **2** and **4**, viz., S atoms, connecting phenolic units, results in the bifurcated character of the intramolecular O \cdots H \cdots S hydrogen bonds. Nevertheless the enthalpy of the cooperative intramolecular H-bonding (ΔH_{intra}) for the cone conformation of **2** and **4** (~ 20 – 21 kcal mol⁻¹) is only a little smaller than for **1** and **3** (~ 26 – 28 kcal mol⁻¹). As a consequence of this strong stabilization of the *cone* conformation, all other possible conformers of both the calix[4]arenes and thiacalix[4]arenes are not detectable spectroscopically at ambient or even elevated temperatures. The introduction of four *p*-*tert*-Bu groups into the calixarene molecules practically does not influence relative energies of their conformers and ΔH_{intra} . So, neither the presence of the *tert*-Bu groups at the upper rim and the type of interphenolic junctions results in essential changes of conformational behaviour and the H-bonding abilities of the calixarene molecules.

In marked contrast with the calixarenes **1–4** title compound **5** adopts the 1,3-alternate conformation in the crystalline phase [6]. Nevertheless, recent DFT computations of the closely related molecule tetramercaptothiacalix[4]arene **6** both in vacuum [12] and in chloroform and dichloromethane [13] show that the calculated energy of the *cone* is by ~ 2 – 6 kcal mol⁻¹ lower than the energies of other possible conformers. These results seem to contradict the X-ray data [6], though the conformation assumed by **5** in the solid state does not necessarily dominate in its solutions and, to elucidate the conformational behaviour of the

mercaptothiacalix[4]arenes, experimental spectroscopic techniques should be applied. Regrettably, it is impossible for the molecule **6**, which has not yet been synthesised. On these grounds we use in the present work the above-mentioned hyphenated spectroscopic-SQM/DFT technique, to study hydrogen bonding and conformational behaviour of the compound **5**. It is hoped to understand on this basis how the presence of different substituents at the lower and upper rims and the type of interphenolic junctions influences conformational behaviour and binding abilities of the calixarene molecules.

Experimental

The title compounds were synthesised by previously described procedures [6]. The solvent, CCl₄, 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 400–4,000 cm⁻¹ range at an optical resolution of 4 cm⁻¹. Solid samples were prepared as KBr pellets. Spectra of CCl₄ solutions were recorded in 2 cm cells. The concentrations were about 10⁻⁴ M.

Computations

All DFT calculations were done using the Gaussian-98 suite of programs [14]. We used Becke’s three-parameter exchange functional [15] in combination with the Lee–Yang–Parr correlation functional [16] (B3LYP) and standard 6-31G* basis set. 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 [17]. 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 [10, 18], including calixarenes [8, 9]. Computations of absolute chemical shieldings were carried out in the GIAO approach [19].

Results and discussion

Computed 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 the focus since the beginning of their chemistry. The calix[4]arenes and the thiacalix[4]arenes are known to have the *cone* conformation both in the solid state and CCl_4 solutions [1–3, 8, 9, 20, 21]. 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 [8, 9, 20]. According to computations by the Hartree-Fock and DFT methods [4, 8, 9, 22–24] the *cone* conformations of individual molecules 1–4 with the C_4 symmetry [25] are more energetically stable than other possible conformers—partial cone (*paco*), 1,3-alternate (1,3-*alt*) and 1,2-alternate (1,2-*alt*)—by ca. 10–20 kcal mol⁻¹. DFT computations of the molecule 6 both in vacuum [12] and in chloroform and dichloromethane [13] show that the *cone* conformation presents C_2 symmetry rather than the C_4 symmetry, as the Y_1 – Y_3 and Y_2 – Y_4 distances (Fig. 1) are not identical. The calculated energy of this *pinched cone* is only by ~ 2 –6 kcal mol⁻¹ lower than the energies of the 1,3- and 1,2-*alternates* or *partial cone*. The energetic ordering for the conformers was predicted to be: *cone* < *paco* < 1,3-*alt* < 1,2-*alt* in vacuum [12] and *cone* < 1,3-*alt* < *paco* < 1,2-*alt* in chloroform and dichloromethane [13].

In our B3LYP/6-31G* calculations both the X-ray data for 5 [6] and the B3LYP/6-31G* optimised structures of parent thiacalix[4]arene 2 and *p*-*tert*-butyl-thiacalix[4]arene 4 [9] were used as starting geometries for optimisation of molecules 5 and 6. Two possible rotameric forms of the *tert*-butyl groups were considered. The results of optimisation were always the same (Fig. 2). It should be noted that the relative electronic energies (ΔE) of the conformers 6 agree well with the corresponding values of the published quantum-chemical estimates, obtained with the use of 6-31G** or higher basis sets and various DFT functionals [12, 13]. The respective relative free energies (ΔG), which have been calculated for the first time, more or less parallel the ΔE values. The *pinched-cone* conformer also adopts C_2 symmetry while the *cone* conformation of the C_4 symmetry corresponds to the saddle point. So, the computed energy difference $E(C_4\text{-cone}) - E(C_2\text{-cone}) = 8$ kcal mol⁻¹ may be regarded as the first non-empirical estimate of the barrier ΔE^\ddagger for the $C_2 - \text{cone} \rightarrow C_2 - \text{cone}^*$ interconversion.

The conformational properties can be influenced by substituents. It is known that different substituents in the *p*-positions of calix[4]arenes [2] and thiacalix[4]arenes [9] have only minor influence on the stability of the cone conformation and on the rotational barriers, but nothing was published in concern with possible impact of the *para*-substitution on the conformational behaviour of mercaptothiacalix[4]arenes. More than that, only *p*-*tert*-Bu-mercaptothiacalix[4]arene 5 was synthesised, while the

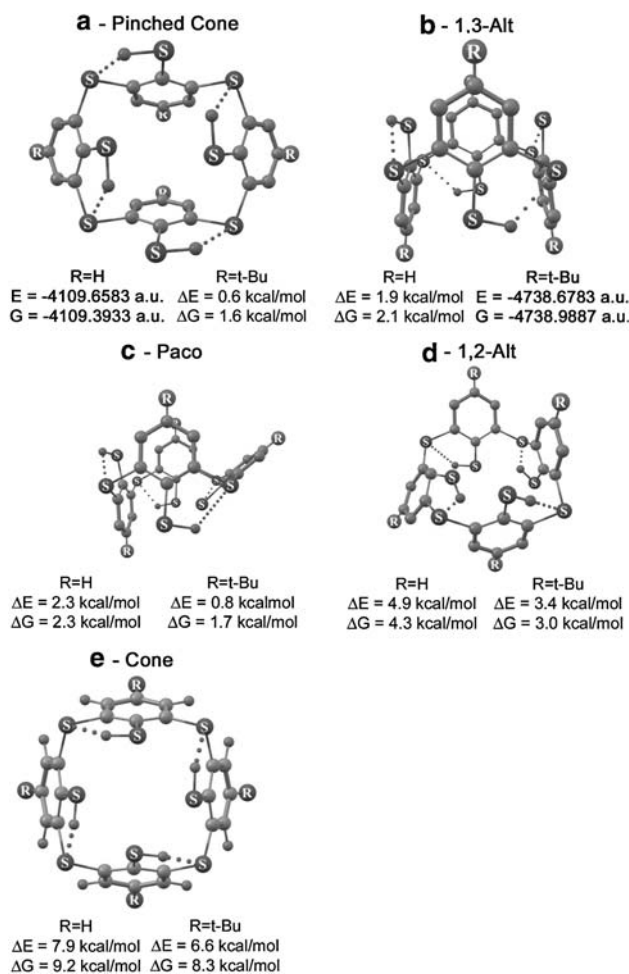


Fig. 2 (a–d) Calculated stable conformations of the molecules 5 and 6 and their conformational energies (ΔE)/free energies (ΔG) relative to the electronic energies (E)/sums of electronic and thermal free energies (G) of the most stable conformations. E and G values for the most stable conformers are printed in bold. Intramolecular hydrogen bonds are shown as dotted lines. (e) the calculated structure and corresponding computed energy differences of the “saddle points” (C_4 cone conformations) of 5 and 6

compound 6 has not yet been achieved till now. So, we have calculated all four possible conformations of 5 (Fig. 2). As in the case of 6, the *pinched-cone* conformer of C_2 symmetry corresponds to minimum on the potential energy surface of 5 while the *cone* conformation of the C_4 symmetry corresponds to the saddle point. The computed barrier ΔE^\ddagger for the $C_2 - \text{cone} \rightarrow C_2 - \text{cone}^*$ interconversion is equal to 6 kcal mol⁻¹ in this case which is a little lower in comparison with 6. The dramatic difference between the molecules 5 and 6 is in fact that the 1,3-*alt* conformation of the molecule 5 is more energetically stable than the *pinched-cone*. That is, introduction of four *p*-*tert*-Bu groups into the mercaptothiacalix[4]arene molecules essentially influences relative stabilities of their conformers, as contrasted with the case of the calix[4]arenes and

thiacalix[4]arenes. First, the predicted energetic ordering for the conformers of **5** is $1,3\text{-alt} < \text{pinched cone} < \text{paco} < 1,2\text{-alt}$ instead of $\text{pinched cone} < \text{paco} < 1,3\text{-alt} < 1,2\text{-alt}$ in case of **6**. Second, the calculated energy gaps between the conformers of **5** are even smaller than in the case of **6**: ΔE in vacuum does not exceed $3.4 \text{ kcal mol}^{-1}$ while maximal ΔG value at room temperature is equal to 3 kcal mol^{-1} . To simulate solvent effects we used the polarised continuum model (PCM) [27]. The model employs a self-consistent reaction field (SCRFF) methodology for modelling systems in solution. According to our SCRFF computations $1,3\text{-alt}$ is additionally stabilised in CHCl_3 medium. As a result, the energy gap (ΔE) between the $1,3\text{-alt}$ and the *pinched-cone* conformations grows to $1.8 \text{ kcal mol}^{-1}$. These results imply that the compound **5** should preferably exist in $1,3\text{-alt}$ instead of *pinched cone* conformation, though conformational inhomogeneity in solutions of **5** cannot be excluded. To validate the reliability of our computational predictions a comparison with available experimental data is necessary. These are described in the subsequent section.

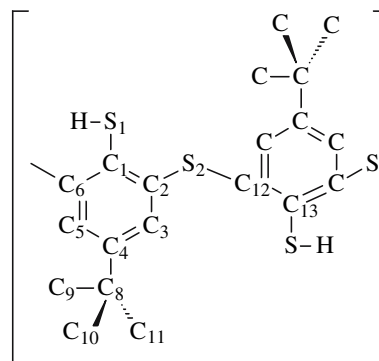
Structure, IR and NMR spectra, conformations and hydrogen bonding of **5**

In marked contrast with the calixarenes **1–4** which adopt the cone conformation, and in agreement with our computational predictions compound **5** adopts the $1,3\text{-alternate}$ conformation in the crystalline phase [6]. The calculated structural parameters of the $1,3\text{-alt}$ conformation (Table 1) are in good agreement with the X-ray data [6].

Clearly, crystal conformation of **5** does not necessarily dominate in its solutions. At the same time, solutions of the compound in neutral non-polar solvents, e.g. CCl_4 or CHCl_3 , should be regarded as systems much closer to the case of isolated molecules studied computationally. So, for real validation of our computational predictions an experimental analysis of conformational behaviour of **5** in the solutions is necessary. IR spectroscopy is known to be a versatile tool in conformational studies of both solid compounds and their solutions. So, the IR spectra of **5** were registered and analysed.

The experimental IR spectra of solid **5** and its CCl_4 solutions are shown in Fig. 3, and the band positions are listed in Table 2 together with assignments based on comparison of the spectra of the related calixarenes **2**, **4** and **5** and on the present SQM computations. The latter demonstrate a good general agreement between the calculated and the experimental wavenumbers of the fundamentals (Fig. 3, Table 2). Conformational homogeneity of **5** in crystal facilitates the assignments of the fundamentals because the computed frequencies of the

Table 1 Comparison of the results obtained from the B3LYP/6-31G* geometry optimisation for the $1,3\text{-alternate}$ conformer of *p*-tert-butylmercaptocalix[4]arene **5** with the corresponding X-ray data



Bond (Å)	X-ray ^a	Calculation	Angle (°)	X-ray ^a	Calculation
C ₁ –C ₂	1.413	1.414	C ₁ –C ₂ –C ₃	120.98	120.35
C ₂ –C ₃	1.385	1.402	C ₂ –C ₃ –C ₄	121.61	122.43
C ₃ –C ₄	1.398	1.396	C ₃ –C ₄ –C ₅	117.17	116.48
C ₄ –C ₅	1.395	1.400	C ₄ –C ₅ –C ₆	121.68	122.58
C ₅ –C ₆	1.382	1.396	C ₅ –C ₆ –C ₁	131.51	120.37
C ₆ –C ₁	1.397	1.414	C ₆ –C ₁ –C ₂	116.93	117.34
C ₁ –S ₁	1.753	1.778	S ₁ –C ₁ –C ₂	121.37	123.39
C ₄ –C ₈	1.534	1.538	S ₁ –C ₁ –C ₆	121.66	119.24
C ₈ –C ₉	1.678	1.547	C ₁ –C ₂ –S ₂	122.47	123.77
C ₈ –C ₁₀	1.317	1.540	C ₃ –C ₂ –S ₂	116.3	115.72
C ₈ –C ₁₁	1.636	1.547	C ₃ –C ₄ –C ₈	120.79	123.24
C ₂ –S ₂	1.782	1.806	C ₅ –C ₄ –C ₈	122.01	120.25
			C ₄ –C ₈ –C ₉	104.92	109.19
			C ₄ –C ₈ –C ₁₀	120.4	109.56
			C ₄ –C ₈ –C ₁₁	106.46	112.15
			C ₂ –S ₂ –C ₁₂	104.31	104.88
			C ₁ –C ₂ –S ₂ –C ₁₂	63.10	66.76
			C ₁₃ –C ₁₂ –S ₂ –C ₂	–63.31	–62.89

^a Ref. [6]

$1,3\text{-alt}$ can be matched to the experimental frequencies of the same conformer. It should be noted though that the present SQM computations do not reveal essential difference between the calculated spectra of the $1,3\text{-alt}$, *pinched-cone* and *paco* conformers of **5**. The only noticeable conformational sensitivity is found for stretching vibrations of SH groups (νSH) of the $1,2\text{-alt}$ conformer (Table 2). So, the absence of any “extra” νSH bands in the IR spectra of the CCl_4 solutions of **5** (Fig. 3, Table 2) indicates that concentration of the $1,2\text{-alt}$ is too low to be detected in the IR spectra, but does not allow to exclude a participation of the *pinched cone* and *paco* in conformational equilibrium with the $1,3\text{-alt}$.

As in the cases of the related calixarenes **2** and **4** [9] the spectra of the molecule **5** may be qualitatively analysed in

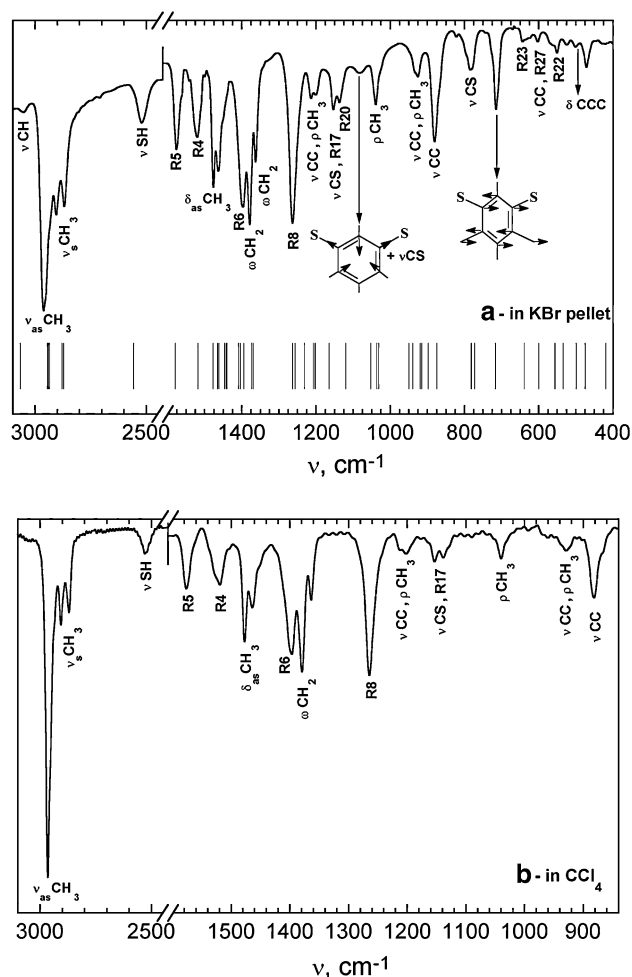


Fig. 3 (a) IR spectrum of *p*-*tert*-butylmercaptothiocalix[4]arene **5** in KBr pellet (top) and stick diagrams for the SQM computed wavenumbers of the 1,3-alternate conformer of **5** (bottom). For the detailed comparison of the computed and registered spectra see Table 2; (b) IR spectrum of **5** in CCl_4 solution. Assignments are given on the basis of SQM calculations (Table 2). The diagrams of atomic displacements during vibrations of aromatic ring corresponding to “Ring*” and “Ring**” in Table 2 are given

terms of the vibrational modes of the *para*-substituted aromatic units and those of the connecting sulphide bridges. The vibrational modes of the thiophenolic units may be qualitatively divided into vibrations of the aromatic rings and *tert*-Bu moieties, but only in part. For example, stretching vibrations of groups SH, CH and CH_3 do not mix with each other, but it is difficult to separate δSH vibrations from ρCH_3 vibrations. The notation of the aromatic ring vibrations in Table 2 and Fig. 3 differs from Wilson’s notation [28], 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 the diagrams of atomic displacements during normal vibrations, published elsewhere [9, 29]. It should be noted that not only the normal modes but also the

frequencies of the fundamentals, associated with the vibrations of the aromatic rings, practically coincide for the molecules **4** and **5**. This is further proof of the transferability of the vibrational modes of aromatic units among the related molecules [9, 29].

Vibrational interactions of these “individual” modes are less pronounced than in the case of the related calixarenes **2** and **4**, and vibrations essentially involving the whole macrocycle arise only in the spectral region below $\sim 500\text{ cm}^{-1}$. It should be noted that the dynamic interaction of four OH groups of the molecules **2** and **4** is so strong that these latter cannot be regarded as independent oscillators: owing to strong intramolecular cooperative H-bonding there arise group vibrations of eight-membered cyclic system $(\text{O}\cdots\text{H})_4$ [9]. As a result, two $\delta(\text{OH})_4$ and two $\nu(\text{O}\cdots\text{H})_4$ bands are found in the IR spectra of the most highly symmetric C_4 cone conformations of the calixarenes **1–4** [9]. The “duplication” of the number of SH infrared bands is not observed in the case of **5** because no essential dynamic interaction of SH oscillators takes place, and frequencies of all four separate SH vibrations just coincide with each other. The reason of this most striking difference between the IR spectra of **5** and the related **2** and **4** is the non-cooperative character of the intramolecular H-bonding of **5**. The OH groups in calixarene **2** form cyclic array of $\text{OH}\cdots\text{O}$ hydrogen bonds. In the thiacalixarene **4** these H-bonds are of bifurcated character $\text{O}\cdots\text{H}\cdots\text{S}$ due to the presence of the second proton-acceptor center, viz., S atom, connecting phenolic units. In case of mercaptothiacalixarenes **5** and **6** four SH groups are intramolecularly H bonded to these bridging S atoms solely (Fig. 2). They do not form H-bonds with each other. It should be noted that during the course of quantum-chemical optimisation of the molecular structure of **5** we tried various starting positions of the SH-groups, including an alternative geometry wherein the SH groups were suitably poised to take part in cooperative hydrogen bonding, but this latter starting geometry did not survive.

So, the $\text{SH}\cdots\text{S}$ bonding is not cooperative according both to the computations and to the IR spectra. This results in substantial weakening of the H-bonds as compared to **4** (see the next section). Another consequence of the above pattern is the absence of additional stabilisation of the *pinched-cone* conformation of **5** and **6**. As a result, (i) B3LYP/6-31G* energy of the *pinched-cone* conformation of **6** is only by $\sim 2\text{ kcal mol}^{-1}$ lower than the energies of the 1,3-*alt* or *paco*; (ii) maximal S \cdots S distance between the opposing SH groups of the *pinched-cone* conformation of **5** and **6** (6.60 and 6.83 Å, respectively) is essentially enlarged in comparison with the corresponding O \cdots O distance of the *cone* conformer of **2** and **4** (3.88 and 3.89 Å, respectively); (iii) because of this, bulky *tert*-Bu groups in *para*-positions to the abovementioned mercapto groups of

Table 2 IR spectra of *p-tert*-butylmercaptiothiacalix[4]arene **5**

Experiment	Computations										Assignment ^d	
	1,3-alternate					Cone						
	ν/cm^{-1} , I^a	ν/cm^{-1} , b	f_{IR}^a	ν/cm^{-1} , b	f_{IR}^a	ν/cm^{-1} , b	f_{IR}^a	ν/cm^{-1} , b	f_{IR}^a	ν/cm^{-1} , b		f_{IR}^a
3188 m	3102, 3102, 3102, 3102	3095, 3095, 3092, 3092	6	3106, 3104, 3097, 3081	5	3104, 3096, 3095, 3093	5	3104, 3096, 3095, 3093	5	3104, 3096, 3095, 3093	5	ν CH (Ring)
3051 m	3065, 3065, 3065, 3065	3080, 3080, 3069, 3069	16	3080, 3073, 3070, 3067	17	3085, 3074, 3073, 3070	15	3085, 3074, 3073, 3070	15	3085, 3074, 3073, 3070	15	ν CH (Ring)
2961 vs (2965 vs)	2944, 2944, 2944, 2944	2953, 2948, 2945, 2945	141	2947, 2947, 2947, 2945	131	2950, 2948, 2947, 2946	136	2950, 2948, 2947, 2946	136	2950, 2948, 2947, 2946	136	ν_{as} CH ₃
	2943, 2943, 2943, 2943	2945, 2944, 2942, 2942	269	2944, 2944, 2942, 2942	207	2944, 2943, 2942, 2942	231	2944, 2943, 2942, 2942	231	2944, 2943, 2942, 2942	231	ν_{as} CH ₃
2905 vs (2908 m)	2941, 2941, 2940, 2940	2942, 2941, 2940, 2940	164	2941, 2941, 2941, 2940	318	2941, 2941, 2940, 2940	290	2941, 2941, 2940, 2940	290	2941, 2941, 2940, 2940	290	ν_{as} CH ₃
	2939, 2939, 2939, 2939	2938, 2938, 2937, 2937	131	2939, 2937, 2936, 2935	78	2939, 2938, 2937, 2937	87	2939, 2938, 2937, 2937	87	2939, 2938, 2937, 2937	87	ν_{as} CH ₃
2869 vs (2870 m)	2934, 2934, 2934, 2934	2935, 2935, 2933, 2933	26	2935, 2933, 2933, 2933	52	2935, 2934, 2934, 2934	14	2935, 2934, 2934, 2934	14	2935, 2934, 2934, 2934	14	ν_{as} CH ₃
	2933, 2933, 2933, 2933	2932, 2932, 2931, 2931	21	2933, 2932, 2932, 2932	16	2933, 2933, 2932, 2931	19	2933, 2933, 2932, 2931	19	2933, 2933, 2932, 2931	19	ν_{as} CH ₃
2870 vs (2870 m)	2878, 2878, 2878, 2878	2881, 2879, 2877, 2877	86	2878, 2878, 2878, 2877	109	2880, 2879, 2878, 2878	98	2880, 2879, 2878, 2878	98	2880, 2879, 2878, 2878	98	ν_{s} CH ₃
	2871, 2871, 2871, 2871	2873, 2873, 2870, 2870	94	2871, 2871, 2871, 2870	82	2873, 2872, 2872, 2871	87	2873, 2872, 2872, 2871	87	2873, 2872, 2872, 2871	87	ν_{s} CH ₃
2521 m (2530 w)	2870, 2870, 2870, 2870	2870, 2870, 2869, 2869	100	2870, 2870, 2869, 2869	102	2870, 2870, 2869, 2869	101	2870, 2870, 2869, 2869	101	2870, 2870, 2869, 2869	101	ν_{s} CH ₃
	2557, 2557, 2557, 2557	2552, 2552, 2549, 2549	124	2564, 2561, 2555	65	2567, 2561, 2552, 2550	77	2567, 2561, 2552, 2550	77	2567, 2561, 2552, 2550	77	ν SH
1576 m (1575 m)	1581, 1579, 1579, 1577	1580, 1580, 1574, 1574	26	1582, 1579, 1578, 1575	41	1580, 1578, 1577, 1575	31	1580, 1578, 1577, 1575	31	1580, 1578, 1577, 1575	31	Ring 5
	1541 sh			2596	7							ν SH
1520 m (1520 m)	1521, 1518, 1517, 1514	1518, 1517, 1510, 1509	33	1522, 1519, 1517, 1513	30	1519, 1517, 1515, 1511	17	1519, 1517, 1515, 1511	17	1519, 1517, 1515, 1511	17	Ring 4
1476 s (1476 s)	1477, 1477, 1477, 1477	1478, 1478, 1476, 1475	43	1477, 1476, 1476, 1475	53	1479, 1477, 1477, 1476	49	1479, 1477, 1477, 1476	49	1479, 1477, 1477, 1476	49	δ_{as} CH ₃
	1465, 1465, 1465, 1465	1466, 1463, 1462, 1462	22	1464, 1464, 1464, 1463	18	1467, 1466, 1465, 1464	22	1467, 1466, 1465, 1464	22	1467, 1466, 1465, 1464	22	δ_{as} CH ₃
1463 s (1463 m)	1461, 1461, 1461, 1461	1460, 1460, 1459, 1458	20	1461, 1461, 1461, 1460	25	1461, 1461, 1460, 1458	23	1461, 1461, 1460, 1458	23	1461, 1461, 1460, 1458	23	δ_{as} CH ₃
	1446, 1446, 1446, 1446	1449, 1448, 1445, 1445	2	1447, 1446, 1445	3	1449, 1447, 1447, 1446	3	1449, 1447, 1447, 1446	3	1449, 1447, 1447, 1446	3	δ_{as} CH ₃
1396 s (1399 s)	1442, 1442, 1441, 1441	1443, 1441, 1441, 1440	0	1442, 1442, 1441, 1440	2	1443, 1442, 1441, 1440	2	1443, 1442, 1441, 1440	2	1443, 1442, 1441, 1440	2	δ_{as} CH ₃
	1439, 1439, 1439, 1439	1438, 1438, 1437, 1434	1	1438, 1438, 1438, 1438	1	1439, 1438, 1438, 1435	1	1439, 1438, 1438, 1435	1	1439, 1438, 1438, 1435	1	δ_{as} CH ₃
1378 vs (1377 m)	1413, 1408, 1408, 1402	1411, 1411, 1405, 1404	6	1413, 1411, 1407, 1405	5	1412, 1409, 1406, 1405	6	1412, 1409, 1406, 1405	6	1412, 1409, 1406, 1405	6	Ring 7
	1405, 1404, 1404, 1404	1404, 1403, 1403, 1402	157	1403, 1403, 1403, 1402	181	1404, 1403, 1403, 1402	149	1404, 1403, 1403, 1402	149	1404, 1403, 1403, 1402	149	δ_{s} CH ₃
1363 m (1365 m)	1395, 1394, 1394, 1393	1398, 1397, 1390, 1389	97	1397, 1395, 1393, 1389	78	1396, 1394, 1393, 1391	84	1396, 1394, 1393, 1391	84	1396, 1394, 1393, 1391	84	Ring 6
	1373, 1373, 1373, 1373	1374, 1373, 1373, 1373	116	1373, 1373, 1371, 1371	15	1374, 1373, 1373, 1371	18	1374, 1373, 1373, 1371	18	1374, 1373, 1373, 1371	18	δ_{s} CH ₃
1262 vs (1262 s)	1369, 1369, 1369, 1369	1369, 1368, 1367, 1366	6	1368, 1368, 1367, 1366	6	1369, 1368, 1368, 1367	6	1369, 1368, 1368, 1367	6	1369, 1368, 1368, 1367	6	δ_{s} CH ₃
	1260, 1256, 1256, 1253	1257, 1256, 1254, 1253	158	1259, 1256, 1255, 1253	187	1258, 1257, 1255, 1253	169	1258, 1257, 1255, 1253	169	1258, 1257, 1255, 1253	169	Ring 8
1213 m (1213 w)	1264, 1262, 1262, 1262	1264, 1261, 1260, 1259	70	1264, 1263, 1262, 1260	64	1264, 1262, 1261, 1260	61	1264, 1262, 1261, 1260	61	1264, 1262, 1261, 1260	61	ν CC
	1235, 1231, 1231, 1227	1233, 1233, 1228, 1226	5	1235, 1232, 1229, 1226	5	1235, 1232, 1231, 1229	5	1235, 1232, 1231, 1229	5	1235, 1232, 1231, 1229	5	Ring 10
1201 m (1201 w)	1207, 1207, 1207, 1207	1207, 1207, 1206, 1206	12	1208, 1208, 1207, 1207	11	1208, 1207, 1207, 1207	12	1208, 1207, 1207, 1207	12	1208, 1207, 1207, 1207	12	ν CC, ρ CH ₃
	1203, 1202, 1201, 1201	1203, 1202, 1201, 1200	3	1204, 1203, 1201, 1201	4	1203, 1203, 1202, 1201	3	1203, 1203, 1202, 1201	3	1203, 1203, 1202, 1201	3	ν CC, ρ CH ₃
1153 m (1152 w)	1164, 1164, 1164, 1164	1167, 1165, 1160, 1159	50	1167, 1166, 1163, 1160	42	1166, 1165, 1163, 1162	40	1166, 1165, 1163, 1162	40	1166, 1165, 1163, 1162	40	Ring 17, ν CS

Table 2 continued

Experiment	Computations						Assignment ^d		
	1,3-alternate		Cone	1,2-alternate		Partial cone			
	ν/cm^{-1}	f_{IR}^a		ν/cm^{-1}	f_{IR}^b	ν/cm^{-1}		f_{IR}^c	
IR, solid (CCl ₄)									
ν/cm^{-1} , I ^a									
1137 m (1137 w)	1127, 1121, 1119, 1112	2	1128, 1118, 1117, 1109	1	1127, 1121, 1115, 1110	3	1127, 1118, 1117, 1109	3	Ring 20
1083 w	1056, 1052, 1052, 1047	27	1054, 1050, 1048, 1044	2	1057, 1052, 1050, 1045	3	1055, 1052, 1049, 1045	11	Ring *, ν CS
	1036, 1036, 1036, 1036	0	1037, 1036, 1036, 1036	36	1037, 1036, 1035, 1034	20	1036, 1036, 1036, 1034	10	ρ CH ₃
1039 m (1037 w)	1031, 1031, 1030, 1030	10	1031, 1030, 1028, 1028	19	1030, 1029, 1029, 1029	24	1031, 1031, 1030, 1030	30	ρ CH ₃
	950, 950, 949, 949	2	950, 950, 949, 949	1	949, 948, 948, 947	1	950, 949, 948, 947	1	ρ CH ₃
	946, 939, 938, 933	29	930, 929, 923, 922	4	936, 931, 925, 923	6	940, 935, 927, 923	20	δ CSH, ρ CH ₃
926 w (927 w)	919, 919, 919, 919	8	920, 919 \times 2, 917	32	919, 918, 917	30	921, 919, 918, 918	21	ν CC(Bu), ρ CH ₃
	915, 915, 914, 914	2	917, 917, 914, 914	5	917, 917, 915, 914	7	918, 916, 915, 914	5	Ring 16
	898, 897, 897, 897	28	897, 896, 887, 886	39	896, 894, 890, 885	34	897, 893, 893, 890	34	Ring 14
880 m (878 m)	876, 874, 874, 871	29	874, 870, 870, 868	20	876, 873, 872, 869	31	874, 873, 871, 870	25	ν CC (ring-C)
823 vw									
784 w	783, 783, 782, 776	12	782, 781, 775, 774	5	784, 779, 776, 776	6	782, 779, 779, 774	7	ν CS
	774, 773, 773, 768	8	772, 772, 770, 770	24	772, 771, 770, 770	24	773, 772, 770, 766	17	ν CC (Bu)
715 m	722, 716, 716, 712	43	726, 722, 713, 709	37	723, 717, 714, 708	36	726, 719, 717, 711	44	Ring **
643 vw	645, 641, 641, 627	0	643, 640, 633, 623	4	641, 637, 634, 622	4	645, 640, 637, 625	1	Ring **, Ring 23
602 vw	600, 600, 600, 598	9	601, 601, 600, 596	7	600, 599, 598, 584	9	602, 599, 597, 588	8	Ring 27, ν CC
551 vw	556, 556	19	558, 555	18	562, 558	17	563, 551	18	Ring 22
524 vw	535, 534, 534, 534	4	530, 527, 527, 519	4	542, 528, 527, 524	4	534, 531, 529, 527	6	Ring 25
501 vw	502, 501, 500, 491	15	499, 496, 495, 491	6	506, 505, 496, 493	6	501, 497, 495, 493	10	δ CCC
471 w	479, 477, 475, 468	19	480, 474, 472, 466	19	482, 475, 472, 470	27	479, 475, 473, 467	25	Macrocycle
420 vw	420, 419, 419, 419	0	421, 420, 418, 418	3	421, 419, 418, 418	3	421, 420, 420, 419	5	Macrocycle

^a w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad

^b SQM computed wavenumbers

^c km mole⁻¹

^d ν , stretch; δ , bend; ω , wagging; τ , twisting; ρ , rocking; s, symmetrical; as, antisymmetrical

“Ring” is used for the vibrations of the phenyl rings [9, 29]. The diagrams of atomic displacements during vibrations of aromatic ring corresponding to “Ring *” and “Ring **” are given in Fig. 3

5 come within short distances of each other and destabilise appreciably the *pinched-cone* conformation, and the 1,3-*alt* becomes a dominant conformer.

Strictly speaking, this latter statement is supported only by the X-ray experiment [6], and cannot be proved on the basis of present IR spectra of CCl₄ solutions, because the vibrational frequencies of the 1,3-*alt*, *paco* and *pinched-cone* conformers are practically indistinguishable. So, we have to resort instead to NMR spectra of **5** in CDCl₃ solution, which were discussed in [6]. The ¹H NMR spectrum at 25 °C was extremely simple and comprised a singlet (7.84 ppm) corresponding to the aromatic protons and two other singlets at 1.25 and 4.72 ppm corresponding to the *t*-butyl and SH groups, respectively. Such an observation may be compatible with a frozen conformer, and for symmetry reasons this conformer cannot be *paco*. However, the observation may be explained by a rapidly equilibrating conformational process leading thus to averaged signals between different conformations. As 1,2-*alt* participation in the equilibrium may be excluded on the basis of our IR spectroscopic results, discussed above, both the observed in crystal 1,3-*alt* and a possible rapid 1,3-*alt* ⇌ *pinched-cone*1 ⇌ *pinched-cone*2 conformational exchange process seem reasonable on the basis of the ¹H NMR spectrum [6].

We have tried to discern these two variants by means of a comparison of chemical shifts computed for 1,3-*alt* and *pinched-cone* with the experimental chemical shifts [6]. The results are presented in Fig. 4.

They demonstrate a good general agreement between the calculated and the experimental chemical shifts for both conformers, though the δ values predicted for 1,3-*alt* match the experiment [6] better. The δ value, corresponding to the proton of the SH group, is the most conformationally sensitive (Fig. 4). In case of rapid *pinched-cone*1 ⇌ *pinched-cone*2 conformational exchange process two computed $\delta^1\text{H}$ for the *pinched-cone* in CDCl₃ solution (6.00 and 6.26 ppm) would result in the averaged value of 6.13 ppm. The deviation of this prediction from the corresponding experimental value (4.72 ppm) essentially exceeds standard deviation. So, this simple comparison suggests that 1,3-*alt* conformer dominates not only in crystal but also in CDCl₃ solution of **5**, though a presence of the *pinched-cone* conformers as minor forms in the solutions cannot be excluded. The latter assumption fit well with our computations (Fig. 2), which predict rather small energy gap between the 1,3-*alt* and the *pinched-cone* conformations.

The enthalpy of the intramolecular H-bonding of the *p*-*tert*-butyl-mercaptothiocalixarene **5**

The abovementioned weakening of the intramolecular H-bonds in **5** in comparison with the related calixarenes

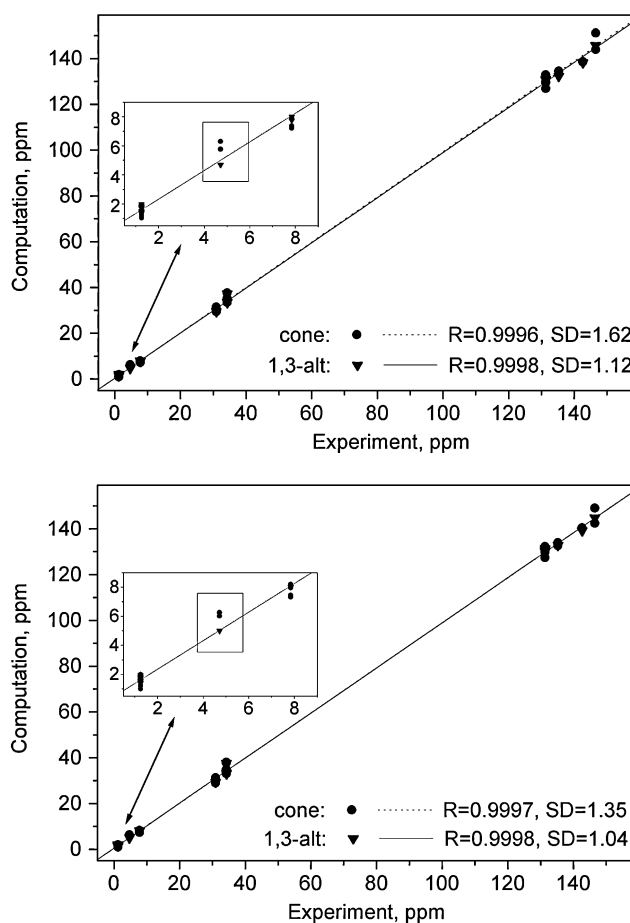


Fig. 4 Experimental chemical shifts of *p*-*tert*-butylmercaptothiocalix[4]arene **5** versus calculated for *pinched-cone* and 1,3-*alt* conformers in vacuum (top) and in chloroform (bottom)

1–4 can be easily demonstrated on the IR bands of stretching SH vibrations (νSH). The very strong cooperative intramolecular hydrogen bond in **1–4** 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). Namely, $\Delta\nu\text{OH}$ amounts to ca. 300 cm^{-1} in case of the thiocalixarenes **2, 4** and to ca. 450 cm^{-1} in case of the calixarenes **1, 3** [8, 9]. Corresponding redshifts $\Delta\nu\text{SH}$ can be evaluated by comparison of the experimental νSH frequency of the mercaptothiocalixarene **5** with ν_0 values of related thiophenols in diluted CCl₄ solutions where the molecules are free from intermolecular H-bonding. This ν_0 value of thiophenol [30] comprises 2,590 cm^{-1} . So, $\Delta\nu\text{SH} = \nu_0 - \nu\text{SH}(\mathbf{5}) = 2,590 - 2,530 = 60 \text{ cm}^{-1}$, which is much smaller than the abovementioned red shifts $\Delta\nu\text{OH}$ of the related calixarenes **1–4**. To evaluate quantitative parameters of the intramolecular H-bonds of the molecule **5** we used an extensive quantitative correlation of spectral and thermodynamic parameters for intermolecular H-bonding of phenols ([31] and references cited therein):

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

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

Applicability of the Eq. 1 to evaluation of the enthalpy of intramolecular H-bonds ($-\Delta H_{\text{intra}}$) of hydroxyl groups has been shown [32]. Of course, the Eq. 1 is not supposed for use in the case of νSH vibrations. Nevertheless, we apply it to rough estimation of the $-\Delta H_{\text{intra}}$ value of the SH...S bond in **5**, which according to (1) amounts to ca. 1.5 kcal mol⁻¹. For comparison, the enthalpy per one OH...O hydrogen bond of the calixarenes **1–4** is about four times greater than this value.

Conclusions

We have demonstrated for the first time that the introduction of *p-tert*-butyl groups dramatically influences the conformational behaviour of the mercaptothiacalix[4]arene molecules. Application of quantum-chemical computations in combination with IR and NMR spectroscopy has allowed to prove that the 1,3-*alternate* becomes a dominant conformer of *p-tert*-butyl-mercaptothiacalix[4]arene not only in crystal, but also in solutions and in vacuum. The comparison of the computed and experimental IR and NMR spectra also reveals simple spectroscopic markers of the 1,2-*alternate* (IR), cone and 1,3-*alternate* conformers (NMR) of mercaptothiacalix[4]arenes.

Essentially non-cooperative character of the intramolecular H-bonding of *p-tert*-butyl-mercaptothiacalix[4]arene **5** was for the first time demonstrated. In contrast to calix[4]arenes and thiacalix[4]arenes, the molecules **5** do not form cyclic array of intramolecular hydrogen bonds: their SH groups are intramolecularly H-bonded solely to the sulfide groups, bridging thiophenolic residues. The enthalpy of the intramolecular SH...S bonding of **5**, evaluated from Iogansen's rule, amounts to ca. 1.5 kcal mol⁻¹, which is about four times smaller than the enthalpies of cooperative H-bonds formed by related calixarenes and thiacalixarenes. As a consequence of this weakness and the non-cooperative character of the intramolecular H-bonding no essential dynamic interaction of SH oscillators takes place, and frequencies of all four separate SH stretching vibrations of **5** just coincide with each other. This is the most striking difference between the IR spectra of **5** and the related molecules **2** and **4** where the "duplication" of the number of OH infrared bands is observed.

In summary, present studies reveal the role of different substituents at the lower and upper rims and the type of interphenolic junctions in conformational behaviour and binding abilities of the calixarene molecules: (i) for the

thiacalixarenes the replacement of methylene bridging groups by sulphur atoms increases the number of H-bonding acceptor sites leading thus to a bifurcated character of the intramolecular hydrogen bonds of OH groups; (ii) further replacement of OH groups by SH groups in mercaptothiacalixarenes results in essential lost of cooperativity of the intramolecular H-bonding: four SH groups are intramolecularly H bonded to the bridging S atoms solely; (iii) as a result, the SH...S bonding almost equally stabilises all the conformations, and the energy gap between the *cone* and other conformations of **6** is much smaller than in the case of calixarenes **1–4**; (iv) another consequence of the replacement of OH groups in the thiacalixarenes by SH groups in the mercaptothiacalixarenes is a transformation of cone conformation to *pinched-cone* conformer; (v) owing to these changes in the shape of the cone conformer, introduction of four *tert*-butyl groups into upper rim of the molecule **5** increases destabilization of the *cone*, which, in turn, results in domination of the 1,3-*alternate* conformer where the repulsion of the *tert*-butyl groups is minimal.

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