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Structure and conformational equilibrium of thiacalix[4]arene by density functional theory

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Abstract

Density functional theory calculations for the structure and conformational equilibrium of thiacalix[4]arene are reported. The conformational equilibrium of thiacalix[4]arene, a heterocalixarene in which the phenol groups are bridged by sulphur atoms is compared to the conformational equilibrium of calix[4]arene. Thiacalix[4]arene conformational energies relative to the cone conformer (ΔE 's) are reduced in comparison with calix[4]arene. This conformational change is in qualitative agreement with recent NMR spectroscopy measurements of the conformational equilibrium for a tetraethylether of thiacalix[4]arene in a CDCl_3 solution which indicates an enhanced chemical exchange of thiacalixarene conformers in comparison with similar methylene bridged structures. Density functional theory results for the structure of thiacalix[4]arene are in good agreement with recent X-ray diffraction measurements. The electrostatic potentials in the cone conformers of thiacalix[4]arene and calix[4]arene suggest that their complexation or recognition abilities can be significantly different. Dipole moments of the four thiacalix[4]arene conformers are in the order: cone > 1,2-alternate > partial-cone > 1,3-alternate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiacalix[4]arenes; Density functional theory; Dipole moments

1. Introduction

Calix[n]arenes are [1_n]-metacyclophanes composed of n -phenol units bridged by methylene [1–7]. The calix[n]arene designation is related to the shape of one of the conformers, the cone conformer, that resembles a chalice [7]. Calix[n]arenes are versatile compounds in supramolecu-

lar chemistry: they can be easily modified (functionalised) and are considered basic platforms supporting different arrays of functional groups able to act as binding sites and leading to a great variety of receptors designed to specific complexing tasks [1,7]. The ability of one molecule to selectively form a complex with another species is central to molecular recognition that is mainly determined by specific intermolecular interactions [8].

The functionalisation of calix[n]arene structures has been usually based on the modification of their upper or lower rim units [7]. More recently, heterocalix[n]arenes in which phenol units are bridged by

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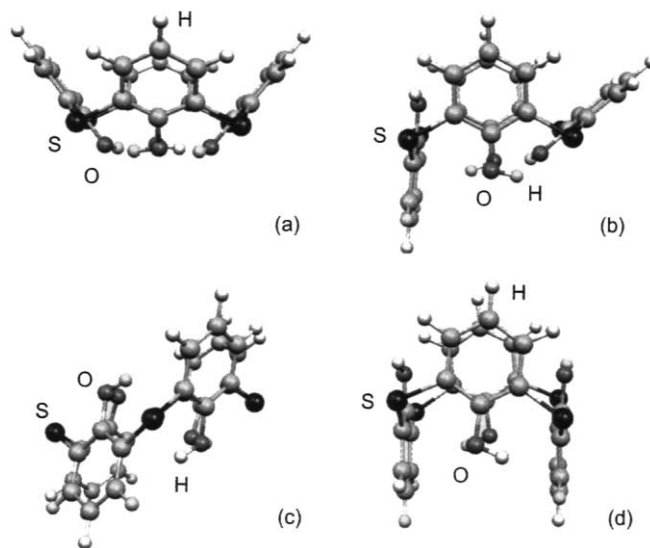


Fig. 1. Thiacalix[4]arene conformers: (a) cone (C); (b) partial-cone (PC); (c) 1,2-alternate (1,2-A); (d) 1,3-alternate (1,3-A).

heteroatoms, have been synthesised [9–21]. One of the most interesting aspects of these new structures is their special ability to include transition metal ions, [10–12] and molecules [16].

In this work we are reporting density functional theory calculations for the structure and conformational equilibrium of thiacalix[4]arene. Thiacalix[4]arenes are heterocalix[4]arenes in which the phenol units are bridged by sulphur atoms. For these new compounds, it has been demonstrated that the replacement of methylene groups by sulphur atoms leads to significant changes of their dynamics and to a large diversity in their coordination properties [16,17].

The main purposes of the present work are to provide accurate theoretical information on the conformational equilibrium and structure of thiacalix[4]arene, and to analyse how the presence of sulphur atoms as bridging units in the thiacalix[4]arene modify the binding capacities relative to calix[4]arene. In this sense, we are also reporting calculations of the electrostatic potential inside the thiacalix[4]arene and calix[4]arene cavities.

The conformational equilibrium of a tetraethylether of thiacalix[4]arene in a CDCl_3 solution has been reported [18]. The crystal phase X-ray structure of thiacalix[4]arene has been recently investigated [16].

2. Computational methods

Total energies (E) were calculated by using Eq. (1)

$$E = V_{\text{NN}} + H^{\text{CORE}} + V_{\text{ee}} + E_{\text{X}}[\rho] + E_{\text{C}}[\rho], \quad (1)$$

where V_{NN} is the nuclear–nuclear interaction, H^{CORE} a mono-electronic contribution to the total energy, including electron kinetic and electron–nuclear interaction energies, V_{ee} the Coulombic interaction between the electrons, $E_{\text{X}}[\rho]$ and $E_{\text{C}}[\rho]$, are, respectively, the exchange and correlation energies, functionals of the electronic density ρ . We have carried out full geometry optimisations (with no symmetry constraints) for the four thiacalix[4]arene conformers shown in Fig. 1 using the Becke's three parameter hybrid method (B3) [22] with the Lee, Yang, and Parr (LYP) [23] correlation functional, a combination usually denoted by B3LYP. Geometry optimisations have been carried out with the 3-21G, 3-21G(d,p) and 6-31G(d,p) basis sets. Single-point energy calculations have been carried out with the 6-311G(d,p) basis set. Hartree–Fock (HF) optimisations with the 3-21G and 3-21G(d,p) basis set are also reported. We observe that HF calculations can be seen as a particular case of density functional theory calculations where there is no correlation functional but the exchange functional is exact. Additional single-point

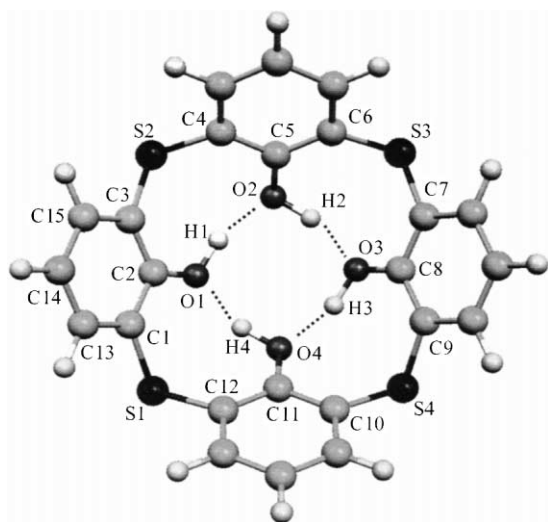


Fig. 2. Hydrogen bonding in the thiacalix[4]arene cone conformer in which the phenol units are bridged by sulphur atoms. Hydrogen bond ($\text{O}\cdots\text{H}$) distances are 1.82 Å. In calix[4]arene, a similar structure in which the phenol units are bridged by methylene groups these distances are equal to 1.58 Å.

energy calculations for the optimised structures, based on the exchange functional proposed by Gill [24] with the LYP [23] correlation functional (G96LYP), are also reported. Frequencies have been calculated at the B3LYP/3-21G(d,p) level and all the structures were characterised as local minima, i.e. all the frequencies are real. The calculations have been carried out with the GAUSSIAN-98 program [25]. The electrostatic potential surfaces have been generated with the Molekel software [26].

3. Results and discussion

3.1. Structure of thiacalix[4]arene

The structure of the four thiacalix[4]arene conformers, cone (C), partial-cone (PC), 1,2-alternate (1,2-A), and 1,3-alternate (1,3-A) are shown in Fig. 1. The thiacalix[4]arene cone conformer is shown in Fig. 2 and the set of geometric parameters are gathered in Table 1. For this conformer, recent X-ray diffraction data [16] for the structure were recently reported. The experimental results are also presented in Table 1. Although the

comparison between gas phase and condensed phase structures is not direct, we can observe a good agreement between theoretical calculations and experimental X-ray diffraction data for the crystal phase of thiacalix[4]arene [16]. We observe that the agreement between the theoretical results and experimental data for the structure of thiacalix[4]arene is not very sensitive to the theoretical level of the calculations. For the distances, rms deviations from experiment (see Table 1) are slightly lower for the B3LYP/6-31G(d,p). However, we can consider that the different theoretical levels (HF/3-21G(d,p), B3LYP/3-21G(d,p), and B3LYP/6-31G(d,p)) predict very similar structures for the cone calix[4]arene conformer. The present results show that cone thiacalix[4]arene is a four-fold symmetric structure in which the $\text{O}_1\text{--O}_3$ and $\text{O}_4\text{--O}_2$ distances (see Fig. 2) are identical and equal to 3.87 Å at B3LYP/6-31G(d,p) level. The angles ϕ (see Table 1) between opposite aromatic rings are consistent with a four-fold symmetry. This result is in contrast with the X-ray experimental data [16] that corresponds to a two-fold symmetric structure. Recent investigations [27] suggest that the cone calix[4]arene four-fold symmetry is likely to be an average over distorted conformations in condensed phases, and several NMR studies [18,28,29] support that the geometry in solution is close to a four-fold geometry.

Our results also show an enlargement of the thiacalix[4]arene cavity in comparison with calix[4]arene. This enlargement is due to the difference between the C–S bond in thiacalix[4]arene (1.78 Å) [16] and the C–C bond in calix[4]arene (1.53 Å) [30].

Hydrogen bonding in cone thiacalix[4]arene is shown in Fig. 2. $\text{O}\cdots\text{H}$ hydrogen bond distances are 1.82 Å (B3LYP/6-31G(d,p)) in comparison with 1.58 Å in calix[4]arene, [31] reflecting an enlargement of the lower rim and suggesting that the stabilisation of the conformers by $\text{O}\cdots\text{H}$ hydrogen bonding is less important in thiacalix[4]arene. It is expected that the enlargement of the thiacalix[4]arene cavity modify the conformational mobility in comparison with calix[4]arene. This is consistent with experimental information, based on chemical exchange rates between the conformers, indicating a higher internal flexibility of tetraethylethers of thiacalix[4]arene in comparison with methylene bridged analogues [18].

Table 1

Data for the structure of thiacalix[4]arene cone conformer. We present results from density functional theory (B3LYP/6-31G(d,p)), ab initio HF theory (HF/3-21G(d,p)), and experimental data (ϕ is the angle between two opposite phenol rings [16])

| | B3LYP/6-31G(d,p) | B3LYP/3-21G(d,p) | HF/3-21G(d,p) | Exp. ^a |
|--|------------------|------------------|---------------|------------------------|
| <i>Bond distances</i> (Å) | | | | |
| S ₁ –C ₁ | 1.80 | 1.79 | 1.78 | 1.76 |
| C ₁ –C ₂ | 1.41 | 1.41 | 1.39 | 1.41 |
| C ₂ –O ₁ | 1.36 | 1.38 | 1.37 | 1.36 |
| C ₂ –C ₃ | 1.41 | 1.41 | 1.39 | 1.41 |
| C ₃ –S ₂ | 1.80 | 1.79 | 1.78 | 1.76 |
| S ₂ –C ₄ | 1.80 | 1.79 | 1.78 | 1.78 |
| C ₄ –C ₅ | 1.41 | 1.41 | 1.39 | 1.40 |
| C ₅ –O ₂ | 1.36 | 1.38 | 1.37 | 1.36 |
| C ₅ –C ₆ | 1.41 | 1.41 | 1.39 | 1.39 |
| C ₆ –S ₃ | 1.80 | 1.79 | 1.78 | 1.78 |
| S ₃ –C ₇ | 1.80 | 1.79 | 1.78 | 1.78 |
| C ₇ –C ₈ | 1.41 | 1.41 | 1.39 | 1.39 |
| C ₈ –O ₃ | 1.36 | 1.38 | 1.37 | 1.38 |
| C ₈ –C ₉ | 1.41 | 1.41 | 1.39 | 1.39 |
| C ₉ –S ₄ | 1.80 | 1.79 | 1.78 | 1.78 |
| S ₄ –C ₁₀ | 1.80 | 1.79 | 1.78 | 1.78 |
| C ₁₀ –C ₄ | 1.41 | 1.41 | 1.39 | 1.39 |
| C ₁₁ –O ₄ | 1.36 | 1.38 | 1.37 | 1.36 |
| C ₁₁ –C ₁₂ | 1.41 | 1.41 | 1.39 | 1.40 |
| C ₁₂ –S ₁ | 1.80 | 1.79 | 1.78 | 1.78 |
| O ₁ –O ₂ | 2.74 | 2.59 | 2.68 | 2.80 |
| O ₂ –O ₃ | 2.74 | 2.59 | 2.68 | 2.80 |
| O ₃ –O ₄ | 2.74 | 2.59 | 2.68 | 2.80 |
| O ₄ –O ₁ | 2.74 | 2.59 | 2.68 | 2.80 |
| O ₁ –O ₃ | 3.87 | 3.66 | 3.79 | 4.21 ^b |
| O ₂ –O ₄ | 3.87 | 3.66 | 3.79 | 3.60 |
| Rms | 0.017 | 0.027 | 0.020 | |
| <i>Angles</i> (°) | | | | |
| C ₁₂ –S ₁ –C ₁ | 104.3 | 103.8 | 103.5 | 101.9 |
| S ₁ –C ₁ –C ₂ | 120.7 | 120.6 | 120.9 | 120.3 |
| C ₁ –C ₂ –O ₁ | 122.2 | 122.4 | 122.4 | 119.4 |
| C ₂ –C ₃ –S ₂ | 120.7 | 120.4 | 120.7 | 120.3 |
| C ₃ –S ₂ –C ₄ | 104.3 | 103.8 | 103.5 | 101.9 |
| S ₂ –C ₄ –C ₅ | 120.7 | 120.6 | 120.9 | 120.6 |
| C ₄ –C ₅ –O ₂ | 122.2 | 122.4 | 122.4 | 120.3 |
| C ₅ –C ₆ –S ₃ | 120.7 | 120.4 | 120.7 | 120.7 |
| C ₆ –S ₃ –C ₇ | 104.3 | 103.8 | 103.5 | 103.4 |
| S ₃ –C ₇ –C ₈ | 120.7 | 120.6 | 120.9 | 120.9 |
| C ₇ –C ₈ –O ₃ | 122.2 | 122.4 | 122.4 | 119.6 |
| C ₈ –C ₉ –S ₄ | 120.7 | 120.4 | 120.7 | 120.9 |
| C ₉ –S ₄ –C ₁₀ | 104.3 | 103.8 | 103.5 | 103.4 |
| S ₄ –C ₁₀ –C ₁₁ | 120.7 | 120.6 | 120.9 | 120.7 |
| C ₁₀ –C ₁₁ –O ₄ | 122.2 | 122.4 | 122.4 | 120.4 |
| C ₁₁ –C ₁₂ –S ₁ | 120.7 | 120.4 | 120.7 | 120.6 |
| Rms | 0.369 | 0.361 | 0.348 | |
| ϕ (°) | 77.2;77.4 | 82.2;82.2 | 76.8;76.9 | 91.7;54.5 ^b |

^a From Akdas et al. [16].

^b The experimental structure corresponds to a C₂ symmetric cone.

Table 2

Total energies (in a.u.) for the thiacalix[4]arene cone conformer. Energy differences (ΔE 's in kcal/mol) between the conformers (partial-cone, 1,2-alternate and 1,3-alternate) and the cone conformer

| | Cone | ΔE | | |
|---------------------------------|-------------|--------------|---------------|---------------|
| | Total | Partial-cone | 1,2-Alternate | 1,3-Alternate |
| <i>Thiacalix[4]arene</i> | | | | |
| HF/3-21G ^a | −2793.12214 | 22.1 | 33.7 | 30.8 |
| HF/3-21G(d,p) ^a | −2793.67636 | 19.4 | 29.9 | 27.8 |
| B3LYP/3-21G ^a | −2803.30453 | 24.6 | 44.5 | 36.1 |
| B3LYP/3-21G(d,p) ^a | −2803.84605 | 21.3 | 30.9 | 31.9 |
| B3LYP/6-31G(d,p) ^a | −2817.88206 | 10.1 | 16.5 | 13.8 |
| B3LYP/6-311G(d,p) ^b | −2818.26308 | 9.1 | 15.6 | 12.3 |
| G96LYP/6-311G(d,p) ^b | −2817.75063 | 8.2 | 13.9 | 11.5 |
| <i>Calix[4]arene</i> | | | | |
| B3LYP/6-31G(d,p) ^c | | 10.5 | 18.3 | 17.7 |
| Experiment ^d | | 14.9;13.8 | | |

^a Geometry optimised at this level of the theory.

^b Geometry optimised at B3LYP/6-31G(d,p).

^c Result for calix[4]arene from Bernardino et al. [31].

^d Free energies of activation ΔG^\ddagger in a solvent (chloroform and benzene, respectively) from Gutsche et al. [32].

3.2. Conformational equilibrium

The most stable conformer of thiacalix[4]arene is the cone (see Fig. 2). This conformer is stabilised by a cyclic array of hydrogen bonding in the thiacalix[4]arene lower rim, a feature which is also typical of cone calix[4]arene [31].

Total energies (E) for the cone conformer, which is taken as a reference conformer, and energy differences between the other conformers and the cone (ΔE) are reported in Table 2. Our results show that the conformational energies relative to the cone conformer (ΔE 's) are overestimated when the calculations are carried out with the 3-21G or 3-21G(d,p) basis sets. This conclusion is supported by calculations for calix[4]arene. In this case, experimental values for the free energy of activation ΔG^\ddagger in different solvents have been reported [32].

We are predicting a reduction of the energy differences relative to the cone conformer (ΔE 's) in thiacalix[4]arene in comparison with calix[4]arene. This reduction seems to be more important for the 1,2-alternate and 1,3-alternate conformers. At similar theoretical levels (B3LYP/6-31G(d,p)), ΔE 's for the partial-cone are 10.1 kcal/mol (thiacalix[4]arene) and 10.5 kcal/mol (calix[4]arene). It is possible that the

enlargement of the cavity size in thiacalix[4]arene affects in a similar manner the energies of cone and partial-cone conformers. However, ΔE 's for the 1,3-alternate are 13.8 kcal/mol (thiacalix[4]arene) and 17.7 kcal/mol (calix[4]arene). In this case, it seems that a more favourable orientation of the O–H hydrogens toward sulphur atoms, stabilises the 1,3-alternate conformer in thiacalix[4]arene.

The conformational equilibrium of a tetraethylether of thiacalix[4]arene in a CDCl₃ solution has been recently analysed by NMR spectroscopy [18]. This study concluded that, relative to similar methylene bridged analogues of tetraethylethers of calix[4]arene, the sulphur bridged conformers are more flexible and that the partial-cone, 1,3-alternate, and cone conformers coexist in solution at room temperature. In these systems, the ethers are attached to the oxygen atoms at the lower rim and intramolecular hydrogen bonding plays no part. From experiment, it is also suggested that the partial-cone (paco) is a central intermediate for the whole interconversion pathway [18].

Condensed phase effects can significantly modify the conformational equilibrium and complexation abilities of calix[4]arenes [7]. In some cases, the conformer distribution is dependent on the solvent polarity and the proportion of the conformers with

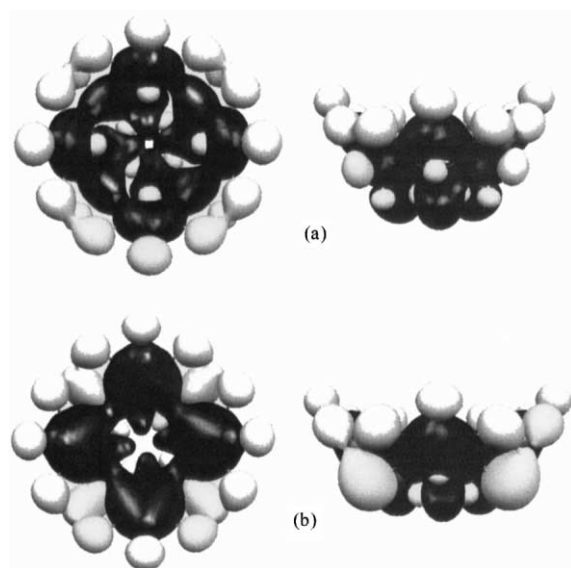


Fig. 3. Top and side views of electrostatic isopotential surfaces. The lower and upper limits of the electrostatic potential (in a.u.) ($\phi_{<}$ and $\phi_{>}$ respectively) were determined over isoelectronic density surfaces of $\rho_e = 0.0004 \text{ e/\AA}^3$. (a) cone calix[4]arene: $\phi_{<} = -0.0976$; $\phi_{>} = 0.0455$. (b) cone thiacalix[4]arene: $\phi_{<} = -0.1244$; $\phi_{>} = 0.0441$.

the greater dipole moments, increases with increasing solvent polarity [33–35]. In general, the conformational changes are due to specific interactions between the solvent and the calixarene atoms (e.g. hydrogen bonds), or by inclusion of solvent molecules in the calixarene macrocycle [36]. Molecular dynamics simulations indicate that solvation of calixarenes in water may lower the activation barrier of the inter-conversions due to hydrogen bonding formation [37]. Moreover, for the tetraethylether of thiacalix[4]arene [18], the expected energetical order of the conformers is quite different from the present system that involves hydrogen bonding at the lower rim.

3.3. Electrostatic potential, charge distribution and dipole moments

The importance of electrostatic potential surfaces as a useful qualitative guide to analyse the binding possibilities of aromatic structures, and in particular, binding modes related to cation– π interactions has been pointed out by Dougherty and collaborators [38]. Fig. 3 shows electrostatic isopotential surfaces for thiacalix[4]arene and calix[4]arene. Initially, we

have constructed electronic isodensity surfaces with $\rho_e = 0.0004 \text{ e/\AA}^3$, and determined, over this surface, the extrema of the electrostatic potential $\phi_{<}$ and $\phi_{>}$. Isopotentials surfaces corresponding to these values are represented in Fig. 3. Some interesting features are worth mentioning. For both structures, an extended isopotential surface corresponding to $\phi_{<}$ can be observed inside the macrocycle cavities. However, in the case of thiacalix[4]arene this isopotential surface is extended to the upper rim region, in contrast to calix[4]arene where the electrostatic potential in the lower rim is more negative. Experimental studies of the complexation of *p*-terbutylcalix[4]arenes with alkali metal cations [39] indicate that the larger cations (K^+ , Rb^+ , and Cs^+) are included into the calix[4]arene macrocycle. For small cations (Li^+ and Na^+) the complexes with calix[4]arenes are stabilised by electrostatic interactions with the phenolic oxygens at the lower rim [39]. Solvent extraction studies indicate the formation of stables complexes of thiacalix[4]arenes with transition metal ions and lanthanide ions [40–42]. Sulphur bridged compounds exhibits a clear preference for soft metal ions and the formation of similar complexes was not observed for the methylene bridged counterpart [40]. Although the present analysis based on the electrostatic potential is essentially qualitative, Fig. 3 suggests that the complexation of thiacalix[4]arene with larger cationic species could be favoured relative to the methylene bridged calix[4]arene structure.

Table 3 reports partial charges for the calix[4]arene and thiacalix[4]arene cone conformers. The charges have been calculated according to a Mulliken population analysis and also by using the Merz–Kollman–Singh (MK) scheme [43,44], which fits the charges to the electrostatic potential derived from quantum mechanical calculations. The results indicate that polarity of the O–H groups at the lower rim, is higher for the methylene bridged compound. In addition, carbon atoms connected to the bridging sulphur atoms (C_1 and C_3) exhibits more negative charges in comparison with the corresponding atoms in calix[4]arene.

Dipole moments are also reported in Table 3. Experimental data for thiacalix[4]arenes are apparently not available. For calix[4]arenes experimental [45,46] and theoretical [35,46] results have been reported. Theoretical results for tetramethoxycalix[4]arene in

Table 3

Atomic charges (in e) for the cone conformers, and dipole moments (μ in D) of calix[4]arene and thiacalix[4]arene conformers. The atomic charges were calculated from the Mulliken population analysis and from the Merz–Kollman–Singh (MK) scheme. In thiacalix[4]arene, the methylene group is considered as one site. We report dipole moments from the DFT calculations (B3LYP/6-31G(d,p)) and from the MK scheme. For clarity, only data for one phenol ring and the CH₂ or S bridging unit (see Fig. 2) are reported

| | Atomic charges | | | |
|---------------------------------|----------------|--------|-------------------|--------|
| | Calix[4]arene | | Thiacalix[4]arene | |
| | Mulliken | MK | Mulliken | MK |
| C ₁ | 0.138 | 0.024 | −0.161 | −0.124 |
| C ₂ | 0.238 | 0.227 | 0.373 | 0.387 |
| C ₃ | 0.143 | −0.023 | −0.164 | −0.162 |
| O ₁ | −0.648 | −0.592 | −0.598 | −0.422 |
| H ₁ | 0.354 | 0.430 | 0.373 | 0.302 |
| CH ₂ /S ₁ | −0.110 | 0.030 | 0.105 | −0.128 |
| C ₁₃ | −0.135 | −0.167 | −0.081 | 0.037 |
| C ₁₄ | −0.075 | −0.175 | −0.072 | −0.314 |
| C ₁₅ | −0.134 | −0.144 | −0.082 | 0.044 |
| | Dipole moments | | | |
| | DFT | MK | DFT | MK |
| C | 1.64 | 1.61 | 5.67 | 5.68 |
| PC | 1.22 | 1.22 | 2.15 | 2.15 |
| 1,2-A | 5.18 | 5.13 | 3.84 | 3.83 |
| 1,3-A | 0.00 | 0.01 | 0.00 | 0.02 |

which hydrogen bonding at the lower rim is not involved [35], indicate that for these compounds, the dipole moments of the four conformers are in the order: C > PC > 1,2-A > 1,3-A. We find that the dipole moments of the calix[4]arene conformers are in the order 1,2-A > C > PC > 1,3-A. The larger dipole moment of the 1,2-A calix[4]arene conformer (5.1 D) is mainly determined by the superposition of two O–H dipoles, involved in two hydrogen bonds. From the MK charges we estimate that the contribution of these groups is ~ 5.4 D, and the total dipole is 5.13 D. The dipole is directed along a C₂ axis through two bridging carbon atoms. Thiacalix[4]arene dipoles are in the order C > 1,2-A > PC > 1,3-A. The significant difference between the dipole moments of thiacalix[4]arene and calix[4]arene cone conformers (5.7 and 1.6 D, respectively, along a vertical C₄ axis) can be related to the difference between the contributions from the partial charges of the methylene groups (calix[4]arene) and sulphur atoms (thiacalix[4]arene). Our results for the dipole moments indicate that the

conformational equilibrium of calix[4]arene and thiacalix[4]arene can be significantly different in a polar solvent [33–35].

4. Conclusions

This work reports results for the structure and conformational equilibrium of thiacalix[4]arene based on HF and density functional theory calculations. Results for the structure are compared to X-ray diffraction data for the crystal phase of thiacalix[4]arene [16]. Apparently, the only related information for the conformational equilibrium of thiacalix[4]arenes is from NMR spectroscopy of a tetraethylether of thiacalix[4]arene in solution [18].

Our results show that the gas phase thiacalix[4]arene cone conformer is a four-fold symmetric structure. Although a good agreement is observed between theoretical predictions and experimental data for several structural parameters, X-ray measurements [16] indicate a two-fold symmetric cone in the crystalline phase. Some significant modifications of the thiacalix[4]arene structure in comparison with calix[4]arene were observed. The most relevant concern the hydrogen bond distances at the lower rim, and the orientation of hydrogen atoms toward sulphur bridging units in the 1,2-A and 1,3-A thiacalix[4]arene conformers, indicating the formation of energetical stabilising S...H bonds.

Experimental data suggest that the conformational equilibrium and complexation abilities of thiacalixarenes are significantly modified relative to calixarenes. We find that the present results for the gas phase structure and conformational equilibrium of thiacalixarene are consistent with the available experimental information for parent systems. A qualitative analysis, based on the electrostatic potential and charge distribution in the cone conformers may indicate an increased affinity of thiacalix[4]arene for larger cations, relative to the methylene bridged calix[4]arene.

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