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REGULAR ARTICLE

Theoretical study on the structure and conformational features of distally dibromo-dipropoxythiacalix[4]arene derivatives and their Zn^{2+} complexes

A. Suwattanamala · A. L. Magalhães ·
J. A. N. F. Gomes

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Abstract A comparative DFT study of distally dibromo-dipropoxythiacalix[4]arene and dipropoxythiacalix[4]arene was performed. The hydrogen bonds OH$\cdots$O at the lower rim play an important role in stabilizing all the conformers, and *cone* is predicted to be the most stable. The structure and energetic ordering of the conformers are not affected by the bromination at upper rim. The inclusion of the solvent effect keeps the energetic orderings unchanged, but leads to a reduction in the energy gaps between conformers. Concerning the 1:1 neutral Zn^{2+} complexes, only one binding mode was found which presented the metal ion coordinated to four oxygen atoms at lower rim. This is in good agreement with our previous study on the Zn^{2+} complex with thiacalix[4]arene carrying opposite phenolate groups. The results thus support the idea that the position of the phenolate groups at lower rim is crucial to define the structural binding mode pattern of metal complexes.

Keywords Dipropoxythiacalix[4]arene · Conformational equilibrium · Solvent effect · Zinc complexes · DFT

1 Introduction

Thiacalixarenes [1] have emerged recently as novel members of the well-known calixarene family. The presence of four sulfur atoms in place of the typical methylene linkages induces some novel properties [2,3]. Some noteworthy examples of such properties, that have never been referred in the previous 'classical' calixarenes, are the different cavity sizes, different conformational preferences, easy oxidation of bridges and excellent complexation abilities towards transition metal ions with contribution of sulfur atoms to coordination. Recently, these compounds have attracted considerable interest as good candidates in building blocks and/or molecular scaffolds for the design of more complicated molecular systems in the broad field of supramolecular chemistry [2–5]. Unfortunately, these potential applications of thiacalix[4]arenes are still rather restricted, mainly due to the unknown chemistry of these compounds and the lack of knowledge about general derivatisation methods.

Several previous studies [6–11] on the electrophilic substitution at the upper rim of thiacalix[4]arene revealed a completely different chemical behavior of these new systems when compared to the well-known 'classical' calix[4]arenes. One interesting example is bromination because bromosubstituted thiacalix[4]arene would represent extremely useful intermediates with many possible synthetic applications. Upper rim bromination of thiacalix[4]arene using the same procedures as in 'classical' calix[4]arenes chemistry was attempted in a previous experimental study but, unfortunately, all the synthesis failed [6]. The bromination of tetrapropoxythiacalix[4]arene was also unsuccessful [6]. On the other hand, a distally disubstituted compound, namely dipropoxythiacalix[4]arene, used as starting material

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A. Suwattanamala (✉) · A. L. Magalhães · J. A. N. F. Gomes
REQUIMTE, Departamento de Química,
Faculdade de Ciências, Universidade do Porto,
Rua do Campo Alegre, 687, Porto 4169-007, Portugal
e-mail: asuwatta@fc.up.pt

A. Suwattanamala
Department of Chemistry, Faculty of Science,
Burapha University, Chonburi 20131, Thailand

yielded successfully dibromo- and tetrabromo-dipropoxythiacalix[4]arene derivatives [6]. This surprising chemical process might shed some light into the subsequent derivatization at the upper rim of this compound.

Recently, density functional theory (DFT) methodology has been successfully applied in the structural and energetic studies of thiacalix[4]arene [12] and its tetraamino- and tetramercapto- derivatives resulting from the lower rim substitution [13]. Moreover, the complexation of Zn^{2+} with each conformer of tetraaminothiacalix[4]arene [14] and a comparative study on the complexation features of thiacalix[4]arene towards Zn^{2+} and Cu^{2+} were also analyzed by DFT methods [15]. In this work, the comparative structural analysis of the main conformers of dibromo-dipropoxythiacalix[4]arene (**1**) and dipropoxythiacalix[4]arene (**2**) are investigated at DFT level. The main goal is to understand how the presence of bromine atoms at the upper rim affects the conformational preference relative to the corresponding unsubstituted compound. In addition, the effect of the presence of chloroform was also included in this theoretical study because it is one of the most common solvents used in experimental studies. In order to understand the coordination ability of both compounds **1** and **2** towards transition metal ions, structural and energetic data of Zn^{2+} complexes are also investigated in this work. We hope both compounds might be considered as interesting alternatives for the application of novel molecular receptors in supramolecular chemistry.

2 Computational methods

The structures of the four main conformers of **1** and **2** namely *cone, partial cone (paco), 1,2-alternate (1,2-alt)* and *1,3-alternate (1,3-alt)* were obtained by complete optimization without any geometrical constraints using hybrid density functional theory methods based on the generalized gradient approximation (GGA) functional and Hartree–Fock (HF) theories. Among these hybrid functionals, the most popular B3LYP (the Becke's three-parameter hybrid exchange functional [16] combined with the correlation functional of Lee et al. [17]) and the more modern PBE1PBE (or sometimes called PBE0, [18,19] the one-parameter hybrid exchange functional of Perdew et al. combined with their correlation functional) were selected along with the 6-31G(d) basis set. Electronic energies were also obtained by additional single point calculations using the B3LYP functional with the 6-31G+(d,p) basis set. In order to include the electrostatic influence of the solvent chloroform on the conformational equilibrium, self-consistent reaction field calculation using integral equation formalism of the polarizable continuum model (IEF-PCM) of Tomasi and co-workers [20–22] was performed at both B3LYP/6-31G(d) and PBE1PBE/6-31G(d) levels. Each solute was placed into a cavity with an appropriate shape based on interlocking atomic spheres centered on its non-hydrogen atoms, as defined by the united atom topology model (UATM) [23]. The cavity was inserted in a continuum medium characterized by a uniform dielectric constant of $\varepsilon = 4.9$ for chloroform.

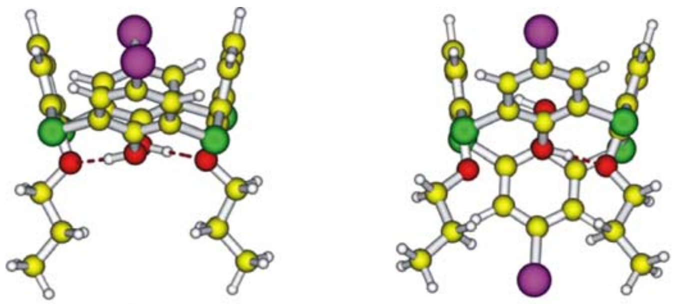
The geometry of the Zn^{2+} complexes with the two-fold deprotonated species in *cone* conformation was completely optimized at B3LYP/DFT level. Different structures based on the distinct binding modes of Zn^{2+} at lower rim were considered as starting points for the optimization procedure. A variety of basis sets, such as 6-31G(d), MIDI! [24,25] and the correlation consistent polarized valence triple zeta (cc-pVTZ) [26–30], were employed for the ligands, whereas an effective core potential CEP-31G basis set (CEP is sometimes called SBKJC potential, which stands for Stevens–Basch–Krauss–Jasien–Cundari [31–33]) was used for Zn^{2+}. The binding energy of each complex is calculated as the difference between the total energy of the metal complex and the sum of the total energies of the most stable structures of the isolated moieties. All the calculations have been performed with the GAUSSIAN 03 program package [34] and graphics of all the optimized structures were displayed by the MOLDEN package [35].

3 Results and discussion

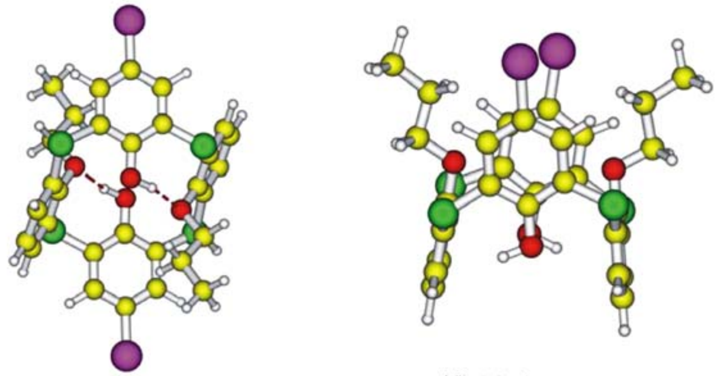
3.1 Structures and hydrogen bonds

The optimized structures of the four main conformers, namely *cone, paco, 1,2-alt* and *1,3-alt*, of **1** and **2** are depicted in Fig. 1. Both DFT functionals point out the *cone* as the most stable conformer for either compounds, which is in good agreement with previous differential ^{1}H NMR NOE and X-ray crystal experimental studies on **1** [6,36]. Two different patterns of hydrogen bonds, labeled **I** and **II**, were found in that *cone* conformation, as shown in Fig. 2. A small energy gap between the two patterns suggests that the interconversion between them can easily occur after rotation of hydroxyl groups.

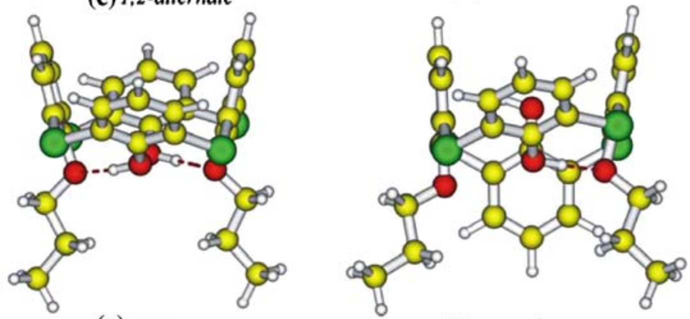
The calculated values of some relevant geometric parameters for two adjacent units of the *cone* conformer are reported in Table 1, and the complete information of all units are presented in supplementary material. All the calculations indicate that the *cone* conformer possesses C_2-like symmetry rather than C_4 symmetry



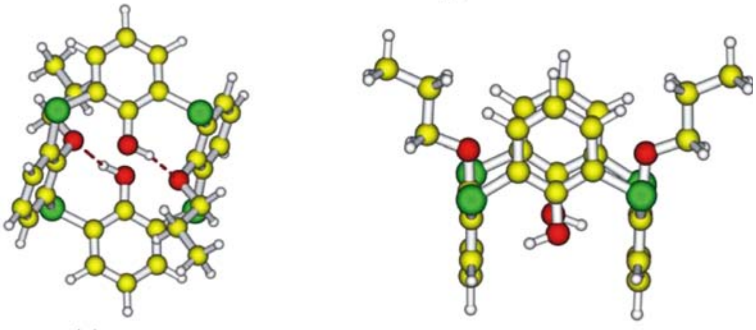
(a) *cone* **(b)** *partial cone*



(c) *1,2-alternate* **(d)** *1,3-alternate*



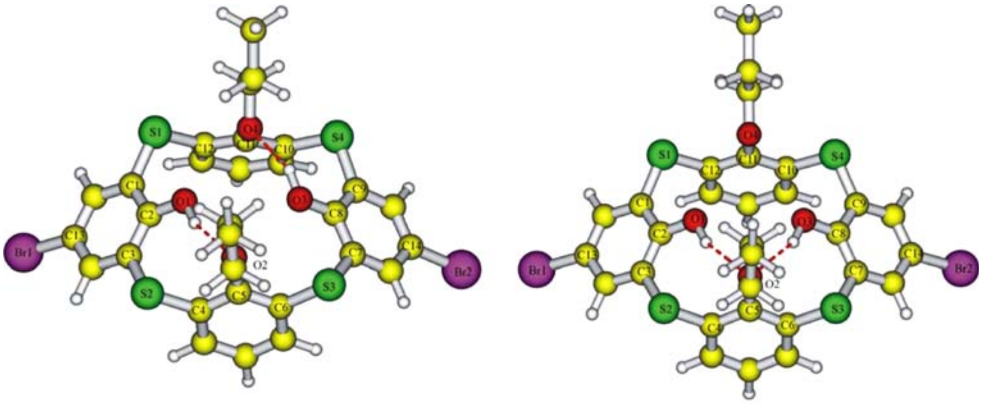
(e) *cone* **(f)** *partial cone*



(g) *1,2-alternate* **(h)** *1,3-alternate*

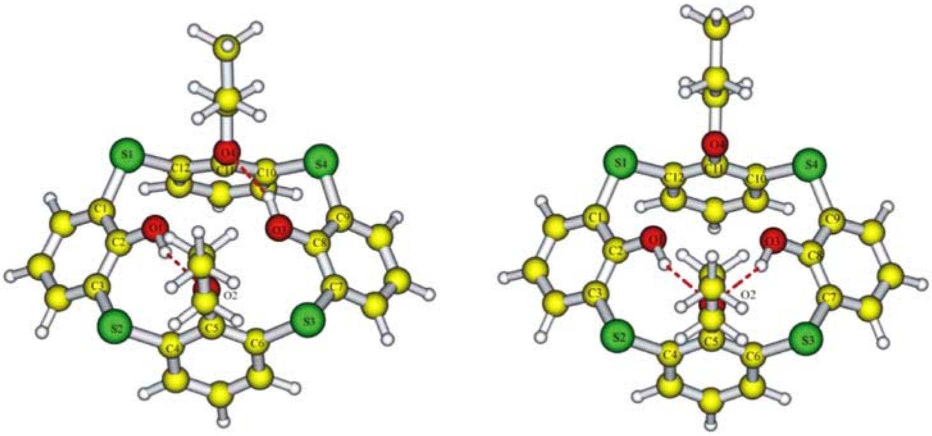
Fig. 1 Optimized geometries of the four main conformers of **a**–**d** dibromo-dipropoxythiacalix[4]arene (**1**) and **e**–**h** of dipropoxythiacalix[4]arene (**2**), obtained at PBE1PBE/6-31G(d) level

found in the thiacalix[4]arene [12]. Accordingly, neither the O_1–O_3 and O_2–O_4 distances nor the two angles ϕ formed by two opposite benzene rings are identical (see Table 1). A *cone* conformer possessing C_2 symmetry is called pinched *cone* and it seems to be a quite usual conformational behavior in thiacalix[4]arene derivatives [2,37,38]. The lower rim substitution of two propoxy groups at opposite rings leads to a decrease of the angle ϕ_2 between them, while the other angle ϕ_1 becomes wider when compared with the identical angle in the thiacalix[4]arene ($\phi = 78°$) [15]. The majority of the bond distance parameters seem to remain unchanged in both patterns of *cone* conformer except the O–O distances, whereas most bond angles seem to differ slightly



(a) pattern **I** of **1**

(b) pattern **II** of **1**



(c) pattern **I** of **2**

(d) pattern **II** of **2**

Fig. 2 Optimized *cone* structures showing two different hydrogen bond patterns of dibromo-dipropoxythiacalix[4]arene (**1**) and dipropoxythiacalix[4]arene (**2**) obtained at PBE1PBE/6-31G(d) level

in both cases. The pattern **II** of both compounds leads to a decrease of angle ϕ_2 by *ca* 15° and an increase of angle ϕ_1 by about 5° when compared with the pattern **I**. The distances between the two distal sulfur atoms (S_1–S_3, S_2–S_4), which are related to the size of the *cone* cavity, are slightly different in both patterns. Although condensed phase structures cannot be directly compared with those predicted in gas phase, there is a good agreement between theoretical predictions, especially with PBE1PBE, and the experimental X-ray crystal data for **1**. However, the DFT prediction overestimates both angles ϕ by about 7–9°. It is interesting to indicate that the bromination at the upper rim does not affect the structural parameters very much, size of cavity and angles ϕ, when compared with the corresponding unsubstituted dipropoxythiacalix[4]arene. The modern PBE1PBE yielded almost the same results as B3LYP but the majority of the values seem to be slightly decreased. Therefore, a modern hybrid functional can be an alternative method to study this molecular system.

As shown in Figs. 1 and 2, the number of hydrogen bonds $OH \cdots O$ at the lower rim seems to be the reason for the energy stabilization of these conformers, and they are two in the *cone* and *1,2-alt*, one in *paco*, and none in the *1,3-alt*. The hydrogen bonding parameters for *cone* are also reported in Table 1. In compound **2**, the hydrogen bond distances seem to be slightly lengthened in pattern **II** when compared with pattern **I**, whereas the hydrogen bond angle is reduced by about 3–4°. However, these hydrogen bond parameters seem to be almost unchanged upon bromination (compound **1**).

3.2 Energetics and conformational equilibrium

Taking the total energy of the most stable structure as a reference, the energy difference (ΔE) to the other conformers are reported in Table 2. All the calculations point out the following energetic ordering for both compounds : *cone* **I** < *1,2-alt* < *cone* **II** < *paco* < *1,3-alt*,

Table 1 Structural parameters for the *cone* conformer of the compounds **1** and **2** in both patterns **I** and **II**

	Dibromo-dipropoxythiacalix[4]arene (**1**)					Dipropoxythiacalix[4]arene (**2**)			
	B3LYP **I**	B3LYP **II**	PBE1PBE **I**	PBE1PBE **II**	X-ray[a]	B3LYP **I**	B3LYP **II**	PBE1PBE **I**	PBE1PBE **II**
Bond distance (Å)									
S_1–C_1	1.80	1.79	1.78	1.78	1.78	1.80	1.80	1.78	1.78
C_1–C_2	1.42	1.42	1.41	1.41	1.39	1.42	1.42	1.41	1.41
C_2–O_1	1.34	1.34	1.33	1.33	1.34	1.34	1.34	1.33	1.33
C_2–C_3	1.42	1.41	1.41	1.41	1.40	1.42	1.41	1.41	1.41
C_3–S_2	1.80	1.80	1.78	1.78	1.77	1.80	1.80	1.78	1.78
S_2–C_4	1.80	1.81	1.79	1.79	1.77	1.80	1.81	1.79	1.79
C_4–C_5	1.41	1.41	1.40	1.40	1.41	1.41	1.41	1.40	1.40
C_5–O_2	1.37	1.38	1.36	1.37	1.38	1.37	1.38	1.36	1.37
C_5–C_6	1.41	1.41	1.40	1.40	1.39	1.41	1.41	1.40	1.40
C_6–S_3	1.80	1.81	1.79	1.79	1.79	1.80	1.81	1.79	1.79
C_{13}–Br_1	1.91	1.91	1.89	1.89	1.89				
O_1–O_2	2.78	2.85	2.77	2.84	2.91	2.79	2.86	2.78	2.85
O_2–O_3	3.14	2.85	3.10	2.84	2.83	3.11	2.86	3.11	2.85
O_3–O_4	2.78	3.36	2.77	3.37	3.85	2.79	3.33	2.78	3.36
O_4–O_1	3.14	3.36	3.10	3.37	3.78	3.11	3.33	3.10	3.36
O_1–O_3	3.54	3.52	3.50	3.49	3.62	3.53	3.54	3.53	3.52
O_2–O_4	4.70	5.02	4.65	5.04	5.54	4.66	4.99	4.64	5.03
S_1–S_3	7.65	7.89	7.61	7.82	7.82	7.68	7.89	7.61	7.82
S_2–S_4	8.11	7.89	8.02	7.82	7.73	8.09	7.89	8.02	7.82
O_1–H_1	0.98	0.98	0.98	0.98		0.98	0.98	0.98	0.98
H_1–O_2	1.85	1.93	1.84	1.93		1.86	1.95	1.85	1.94
O_3–H_3	0.98	0.98	0.98	0.98		0.98	0.98	0.98	0.98
H_3–O_4	1.85		1.84			1.86		1.85	
H_3–O_2		1.93		1.93			1.95		1.94
Bond angle (°)									
C_{12}–S_1–C_1	102.0	100.4	101.5	99.7	97.2	102.3	100.6	101.7	99.9
S_1–C_1–C_2	120.8	120.7	120.4	120.3	120.6	120.7	120.6	120.3	120.1
C_1–C_2–O_1	117.4	117.5	117.6	117.7	118.2	117.5	117.5	117.6	117.7
C_2–C_3–S_2	121.6	121.0	121.1	120.4	119.9	121.4	120.8	120.9	120.2
C_3–S_2–C_4	103.4	104.5	102.9	103.9	101.2	103.5	104.5	102.9	104.0
S_2–C_4–C_5	119.7	120.2	119.4	119.8	120.0	119.8	120.3	119.5	119.9
C_4–C_5–O_2	118.9	119.6	119.0	119.6	120.1	118.9	119.6	118.9	119.6
C_5–C_6–S_3	121.0	120.2	120.7	119.8	119.9	121.2	120.3	120.9	119.9
O_1–H_1–O_2	158.1	155.1	157.4	153.6		157.2	154.6	156.6	153.3
O_3–H_3–O_4	158.1		157.4			157.1		156.5	
O_3–H_3–O_2		155.1		153.7			154.6		153.3
ϕ_1 [b]	108.2	113.8	109.0	114.5	105.4	109.5	111.9	107.7	112.9
ϕ_2 [b]	29.0	15.9	27.0	11.2	3.9	29.6	17.6	27.4	12.4

Calculations performed with different DFT functionals and the 6-31G(d) basis set (atom numbering corresponding to Fig. 2)

[a] See [36]

[b] $\phi_1$is the angle between two opposite phenol rings, whereas $\phi_2$is the angle between two opposite propoxy benzene rings

which shows that the most stable conformer is *cone* **I**. This suggests that bromination at the upper rim does not affect the energetic ordering. However, this ordering is slightly different from an early theoretical study on thiacalix[4]arene [12]. A large reduction of ΔE for all the conformers was observed when compared with thiacalix[4]arene at the same DFT level, as shown in Table 2. It may be suggested that the weaker intramolecular hydrogen bonds in both compounds reduce the relative stabilization of the conformers, because the breaking of a hydrogen bond when the molecule changes to a less stable conformer is not so energetically unfavorable. The small energy gaps between conformers may suggest that these compounds are more flexible than thiacalix[4]arene, and the conformational interconversion can occur easily. It is interesting to note that for **1**, PBE1PBE reduces ΔE more than B3LYP by about 0.9 kcal mol^{-1} for *paco* and *1,3-alt*, and 0.3 kcal mol^{-1} for *1,2-alt*. On the other hand, concerning **2**, PBE1PBE seems to reduce ΔE by *ca* 0.4 kcal mol^{-1} for all the conformers. Adding polarization and diffuse functions as B3LYP/6-31+G(d,p) reduced the ΔE values for all the conformers, especially *1,3-alt* of **1**. However, this effect does not modify any energetic ordering.

Table 2 Relative energy (ΔE, in kcal mol^{-1}) of the main conformers of **1** and **2** at different DFT levels (the energy of the most stable conformer was taken as reference)

		Cone **I**	*Cone* **II**	*Paco*	*1,2-alt*	*1,3-alt*
Dibromo-dipropoxythiacalix[4]arene (**1**)						
B3LYP/6-31G(d)^{a}	*Vacuum*	0.00	2.19	3.05	1.25	6.53
PBE1PBE/6-31G(d)^{a}	*Vacuum*	0.00	2.09	2.13	0.94	5.61
B3LYP/6-31+G(d,p)^{b}	*Vacuum*	0.00	1.85	1.95	0.71	2.42
B3LYP/6-31G(d)^{c}	*Chloroform*	0.00	1.32	3.03	1.07	6.88
PBE1PBE/6-31G(d)^{c}	*Chloroform*	0.00	1.15	1.86	0.35	5.75
Dipropoxythiacalix[4]arene (**2**)						
B3LYP/6-31G(d)^{a}	*Vacuum*	0.00	2.02	3.78	1.06	6.79
PBE1PBE/6-31G(d)^{a}	*Vacuum*	0.00	1.92	3.40	0.63	6.34
B3LYP/6-31+G(d,p)^{b}	*Vacuum*	0.00	1.44	2.60	0.92	5.12
B3LYP/6-31G(d)^{c}	*Chloroform*	0.00	1.25	3.19	0.35	5.78
PBE1PBE/6-31G(d)^{c}	*Chloroform*	0.75	1.85	3.61	0.00	6.11
Thiacalix[4]arene						
B3LYP/6-31G(d)^{a,d}	*Vacuum*	0.00		10.66	14.75	14.71
PBE1PBE/6-31G(d)^{a,d}	*Vacuum*	0.00		9.78	14.04	13.58

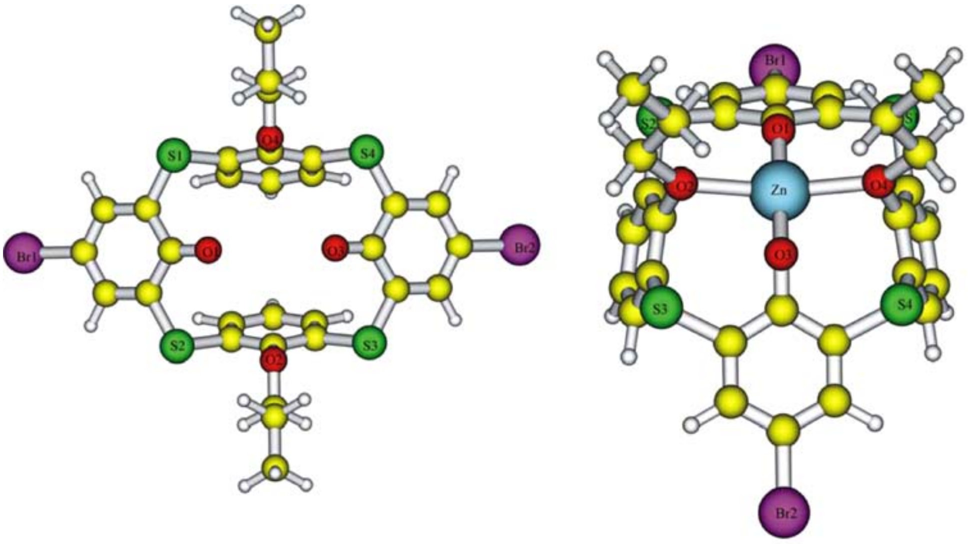
^{a} Geometries were optimized at this level of theory
^{b} Geometries were optimized at B3LYP/6-31G(d)
^{c} Solvation free energy difference ($\Delta\Delta G_{\text{sol}}$, in kcal mol^{-1}) in chloroform
^{d} See [15]

In order to study the solvent effect on the conformation equilibrium, a mean electrostatic potential effect of the bulk chloroform solvent was taken into account using the IEF-PCM solvation model [20–22]. The ΔG_{sol} is the sum of the electronic components and all the non-electrostatic terms such as cavitation, dispersion and repulsion energy. Due to the big size of the molecular systems, it was not possible to perform geometry optimizations or to include the explicit solvent molecules in the first solvation shell within the PCM model. However, it is expected that solvent molecules do not establish short-range interactions with the atoms of the solute that could eventually induce a change in their optimized structures. Therefore, the solvent effect study was carried out through single-point calculations on the previous optimized structures in vacuum. The predicted solvation free energy of the conformational conversion between the most stable conformer and the other conformers in chloroform ($\Delta\Delta G_{\text{sol}}$) is also reported in Table 2. The electrostatic influence of chloroform does not modify the vacuum energetic ordering of both **1** and **2**, except a reversion between the *1,2-alt* and *cone* **I** in **2** at PBE1PBE level. The solvent effect leads to a reduction in the energy gap between different conformers of both compounds obtained from either B3LYP and PBE1PBE functionals except *1,3-alt* of **1** and *paco* of **2**. It is interesting to note that the energy difference between *cone* **I** and *1,2-alt* is less than 1.0 kcal mol^{-1} in chloroform, which suggests an easy conformational exchange in solution. This is supported by a previous ^{1}H NMR study [38] in trimethoxythiacalix[4]arene and distally dimethoxythiacalix[4]arene where it was shown a conformational exchange in CDCl$_3$ solution. In fact, the dimethoxythiacalix[4]arene adopts *cone* conformation as the major isomer in solution, whereas in solid state it prefers *1,2-alt* conformer [38]. This is one example of unusual thiacalix[4]arene behavior in the distally dialkoxy derivatives, which differs from the corresponding substituted classical calix[4]arene where only *cone* conformation is found in both solution and solid state [39,40].

3.3 Structure and energy analysis of Zn^{2+} complexes

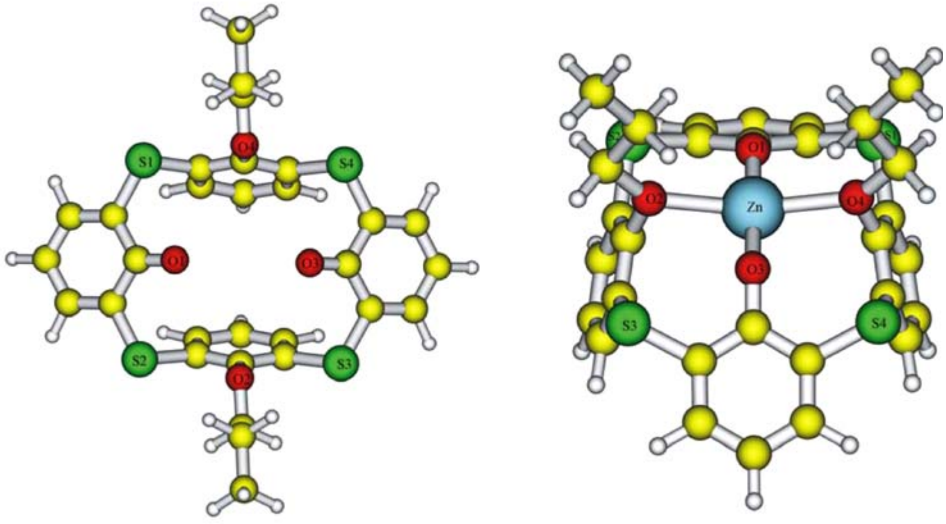
Unfortunately, no supporting experimental data on both dipropoxythiacalix[4]arene derivatives complexes have been achieved yet. The study considers only 1:1 neutral complex [M^{2+} L^{2-}], where M^{2+} and L^{2-} denote separately the metal ion and the twofold deprotonated form of the ligand in its *cone* conformation. This stoichiometry is the same as found in previous solvent extraction [41,42] and NMR [41] studies on the metal complexes of *p-tert*-butylthiacalix[4]arene. Although this type of molecular systems possesses many local minima, our interest is restricted to the binding modes in which phenolate and propoxy oxygens and sulfur atoms at lower rim coordinated to the metal ion in different ways. Only an opposite phenolate isomer was found in the twofold deprotonated forms of **1** and **2**, which differs from a previous study on thiacalix[4]arene obtained where both adjacent and opposite phenolate patterns were found [15]. Therefore, only two different possibilities of metal ion binding modes were considered in this work as starting points for the full geometry optimization procedures. The former one involves the metal coordinated to one phenolate oxygen, one propoxy oxygen and one sulfur atom forming two five-membered chelated rings, whereas the latter one presents the metal interacting to all the four oxygen atoms at lower rim. However, only the latter type of coordination was found as final local minimum for Zn^{2+} complexes of both **1** and **2**. The structures of the twofold deprotonated forms and the corresponding Zn^{2+} complexes are shown in Fig. 3.

It is interesting to emphasize that the position of the deprotonated phenols might determine the binding pattern of metal complexes because this binding mode is in a good agreement with an earlier study on the binding mode of thiacalix[4]arene with opposite phenolates to Zn^{2+} [15]. Although this binding mode completely conflicts with the contribution of sulfur and two adjacent phenolate oxygen atoms to coordinate the metal found in a previous study of thiacalix[4]arene complexes [15], a previous study of the reaction between diethylzinc and a distally dipropoxycalix[4]arene proposed that one Zn^{2+}



Two fold deprotonated species of **1**

Zn2+ complex of **1**



Two fold deprotonated species of **2**

Zn2+ complex of **2**

Fig. 3 Two fold deprotonated species of dibromo-dipropoxythiacalix[4]arene (**1**) and dipropoxythiacalix[4]arene (**2**) and the corresponding Zn^{2+} complexes. Optimized structures obtained at B3LYP/DFT level using the cc-pVTZ basis set for C,H,O,S and aug-cc-pVTZ for Br and CEP-31G for Zn^{2+}

is coordinated to four oxygen atoms at lower rim and one ethyl [43]. Another example is the X-ray crystal structure of the Zn^{2+} complex from the reaction between a bimetallic alkylzinc calix[4]arene complex and boron trifuoride [44]. This complex presents the Zn^{2+} coordinated to four oxygen atoms at lower rim in the equatorial plane and two aqua ligands in axial positions [44].

Binding energies, E_{bind}, of Zn^{2+} complexes obtained at B3LYP level, using several basis sets for the twofold deprotonated form of each ligand and the effective core pseudo potential CEP-31G for Zn^{2+} in all the calculations are summarized in Table 3. The results show a stronger Zn^{2+} complex with **2** when compared with a previous thiacalix[4]arene complex obtained at the same 6-31G(d) basis set [15]. This might suggest that the introduction of two opposite propyl groups at lower rim induces stronger binding to metal ions. However, the values of the E_{bind} seem to be overestimated. A variety of basis set was employed in a comparative study between the Zn^{2+} complex of **1** and **2**. Adding diffuse functions only to Br atoms, as B3LYP/6-31G+(d), resulted in a slightly reduction of E_{bind}. The Zn^{2+} complex of **1** is weaker than of **2** at this basis set. This is good corresponding to the principle theory because the Br atom in *para* position usually acts as electron-withdrawing group which reduces the charge of phenolate oxygens. Accordingly, a weaker electrostatic interaction between ligand and Zn^{2+} should be observed.

The moderate basis set as MIDI! [24,25] was selected and employed for all atoms in the calculations. MIDI! is designated as a hetero atom polarized valence-double-zeta basis set because it adds a set of *d* functions to the MIDI basis set [45,46] for all the atoms with occupied valence *p* orbitals except C, whereas for C and H atoms unpolarized MIDI basis are used. For Br atom, MIDI! is developed by adding a single set of *d* polarization functions to the 3-21G basis set [25]. The binding energy of Zn^{2+} complex with **2** is stronger than with **1** at this basis set, but the E_{bind} values seem to be overestimated when compared with the previous values obtained from 6-31G(d) or 6-31G+(d) basis sets. The cc-pVTZ basis set [26–30] was then considered as an alternative one and it was used for C, H, O and S atoms, while diffuse functions were added to Br atoms as aug-cc-pVTZ. It seems that this basis set can be applied successfully for the comparison between Zn^{2+} complexes of **2** and **1**. These results show that inclusion of high angular momentum polarization and diffuse functions in the correlation consistent basis set for Br atoms, such as *f* functions, can improve the quality of the binding energy results.

Some relevant structural parameters for twofold deprotonated species of *cone* conformer obtained from different basis set at B3LYP/DFT level is presented in supplementary material. The majority of the geometric parameters seem to remain unchanged upon the deprotonation process except for the C–O and O–O bond distances and the C–C–O bond angles. The C–O bond distance of the phenolate in twofold deprotonated is shortened by about 0.10 Å, whereas the C–C–O bond angles are increased by *ca* 6.0 when compared with neutral species. Some relevant geometric parameters of complexes obtained at different basis set are presented in Table 4. All the results point out that bond lengths of the two oxygen atoms (O_2, O_4) of the coordinated propoxy to Zn are always longer than the other ones of two phenolate (O_1, O_3) connected to Zn, which reveals the importance of the electrostatic component in the interaction with the metal ion. On the other hand, these values correspond well to Zn–O distances between the phenolate and the benzyl ether in the ethylzinc complexes, with the lengths about 2.0 and 2.4 Å, respectively [43]. The Zn^{2+} complex for both **1** and **2** adopt almost a

Table 3 Energetic analysis for the Zn^{2+} complexes with both dipropoxythiacalix[4]arene derivatives obtained from different basis sets at B3LYP level

Basis set	Total energy of twofold deprotonated species [a] (au)	Total energy of complex (au)	ΔE (kcal/mol)
Dibromo-dipropoxythiacalix[4]arene (**1**)			
6-31G(d)	−8194.061483	−8420.205461	−658.29
6-31+G(d)[b]	−8194.075536	−8420.214862	−655.37
MIDI!	−8159.197952	−8385.387402	−686.82
cc-pVTZ[c]	−8200.414045	−8426.525079	−637.61
Dipropoxythiacalix[4]arene (**2**)			
6-31G(d)	−3052.428286	−3278.599802	−675.57
MIDI!	−3036.352063	−3262.565676	−701.98
cc-pVTZ	−3053.136398	−3279.274723	−654.74

[a] Zn^{2+} complexes were optimized using different basis sets for twofold deprotonated species of each ligand and the CEP-31G for Zn^{2+} in all calculations. Total energy (au) of Zn^{2+} is −225.094932 at B3LYP/CEP-31G

[b] 6-31+G(d) was used for Br atom, and 6-31G(d) was used for the other atoms (C,H,O,S)

[c] cc-pVTZ was used for the C,H,O,S atoms, and the aug-cc-pVTZ was used for Br atom

Table 4 Structural parameters for the Zn^{2+} complexes with both dipropoxythiacalix[4]arene derivatives obtained from different basis sets at B3LYP level (atom numbering corresponding to Fig. 3)

	Compound **1**				Compound **2**		
Parameter	6-31G(d)	6-31+G(d)[a]	MIDI!	cc-pVTZ[b]	6-31G(d)	MIDI!	cc-pVTZ
Zn–O_1	1.83	1.83	1.86	1.82	1.83	1.85	1.82
Zn–O_2	2.31	2.31	2.19	2.32	2.33	2.20	2.34
Zn–O_3	1.83	1.83	1.86	1.82	1.83	1.85	1.82
Zn–O_4	2.31	2.30	2.19	2.32	2.33	2.20	2.34
O_1–Zn–O_2	90.0	90.1	89.9	90.1	90.1	90.0	90.1
O_2–Zn–O_3	90.0	90.1	89.9	90.1	90.0	89.9	90.1
O_3–Zn–O_4	90.1	90.1	90.0	90.2	90.1	90.0	90.1
O_4–Zn–O_1	90.1	90.1	90.0	90.2	90.0	89.9	90.1
O_1–Zn–O_3	178.8	178.6	178.5	177.9	179.3	178.3	178.3
O_2–Zn–O_4	164.3	164.4	169.7	164.0	163.5	168.9	163.2

Zn^{2+} complexes were optimized using the different basis set for twofold deprotonated species of each ligand, and the CEP-31G were used for Zn^{2+} in all calculations

[a] 6-31+G(d) was used for Br atom, and 6-31G(d) was used for the other atoms (C,H,O,S)

[b] cc-pVTZ was used for the C,H,O,S atoms, and the aug-cc-pVTZ was used for Br atom

square planar coordination as shown in Fig. 3, whereas the previous thiacalix[4]arene complex possesses a distorted square planar structure [15]. This is confirmed by the O–Zn–O bond angles which are closer to the standard values of this structure (90, 180). However, the O–Zn–O bond angles between propoxy oxygen are smaller than those between phenolic oxygen. It is interesting to note that the bromination at upper rim does not seem to modify the structural parameters for the twofold deprotonated species and the corresponding Zn^{2+} complexes. The changing of the basis set does not affect these structural parameters significantly, but it plays an important role for improving the binding energy results.

4 Conclusion

The structural and energetic aspects of the four main conformers of dibromo-dipropoxythiacalix[4]arene (**1**) and dipropoxythiacalix[4]arene (**2**) were investigated by B3LYP and PBE1PBE methods. All the results point out *cone* to be the most stable conformer for both compounds. However, the smaller energy gaps between conformers when compared with the parent thiacalix[4]arene suggest higher flexibilities and easier interconversions. Interestingly, the bromination at the upper rim does not affect the energetic ordering when compared with an unsubstituted dipropoxythiacalix[4]arene compound. The intramolecular hydrogen bonding at lower rims seems to play a dominant contribution for the stabilization of the different conformers. The presence of the chloroform was taken into account by means of a combination of the IEF-PCM and DFT methodologies. That solvent effect did not modify the energy ordering of the conformers, but a reduction of the energy gaps were observed. The modern PBE1PBE functional produced almost the same results as B3LYP, although a slight discrepancy in the energetic ordering of the conformers was observed in solution. Therefore, PBE1PBE can be also applied for the structural and energetic study of these molecular systems.

The complexation features of both **1**and **2** towards Zn^{2+} were investigated in detail at B3LYP level. Only one binding mode was found in 1:1 Zn^{2+} complex, which adopted a square planar coordination using two propoxy oxygens and two phenolate groups in opposite pattern. Although this binding mode conflicts with the expectation of sulfur contribution to metal coordination as in thiacalix[4]arene complex, it aggress well with the previous study on metal complexes of modified thiacalix[4]arene with phenolate oxygen atoms in opposite pattern. This might support our previous idea that the position of the deprotonated phenols seems to be an important factor to determine the structural pattern of binding modes. As expected, the electrostatic interaction between a positive metal ion and a negative ligand seems to be determinant, the preferred metal coordination modes always include both phenolate oxygen atoms. The size of the basis set affects the binding energies of Zn^{2+} complexes, whereas the structures remain almost unchanged. The bromination at upper rim leads to a weaker metal complex when compared with the unsubstituted dipropoxythiacalix[4]arene. Understanding the host–guest properties in coordination ability of both compounds toward Zn^{2+} will provide a new progress for the design and development of novel molecular receptors in supramolecular chemistry field.

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