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A B3LYP and MP2 theoretical investigation into host-guest interaction between calix[4]arene and Li$^+$ or Na$^+$

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Abstract The DFT-B3LYP and MP2 methods with 6-311G** and 6-311++G** basis sets have been applied to study the complexation energies of the host-guest complexes between the cone calix[4]arene and Li$^+$ or Na$^+$ on the B3LYP optimized geometries. A comparison of the complexation energies obtained from the MP2(full) with those from MP2(fc) method is also carried out. The result shows that it is essential to introduce the diffuse basis set into the geometry optimizations and complexation energy calculations of the alkali-metal cation-π interaction complexes of calix[4]arene, and the D_e values show a maximum of 21.13 kJ mol^{-1} (14.45% of relative error) between the MP2(full)/6-311++G** and MP2(fc)/6-311++G** method. For Li$^+$ cation, the complexation is mainly energetically stabilized by the lower rim/cation (namely O–Li$^+$) interaction. However, binding energies and NBO analyses confirm that Na$^+$ cation prefers to enter the calix[4]arene cavity and the cation-π interaction is predominant, which contradicts the previous low-level theoretical studies. Furthermore, the complexation with Li$^+$ is preferred over that with Na$^+$ by at least 12.70 kJ mol^{-1} at MP2(full)/6-311++G**//B3LYP/6-311++G** level.

Introduction

Host-guest interaction plays an extremely important role in chemistry and biochemistry, especially in the fast growing field of supramolecular host-guest chemistry [1, 2]. As one of the effective hosts, the macrocyclic calixarene has been of great chemical interest for a long time [3]. Indeed, since the 1,3-alternate calix[4]arene crown ether derivatives were found as the most effective hosts for the selective extraction of cesium from liquid nuclear wastes [4], this property of the calixarene has led to an urgent attempt to provide a theoretical explanation of the selectivity for the binding to alkali metal cation [4-6]. Thereby, recently the host-guest interactions between the calixarenes and alkali-metal cations have received much attention in experimental studies and theoretical calculations [7-11].

Calixarenes are one of the most important molecular scaffolds in the host–guest supramolecular chemistry. The original calix[n]arenes are macrocyclic compounds, and can include small molecules in the hydrophobic cavity formed by the phenol aromatic rings. Furthermore, considering possible up-down arrangements to build up new materials that simultaneously can present a hydrophobic pocket for host-guest recognition and functionalities for the selective binding, many groups have been involved in the investigations on the self-assembly of calixarenes [11, 12]. Thus, a novel kind of host-guest chemistry is now expanding in

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scope [4]. Up to now, the calixarenes have been extensively explored in the context of host-guest complexation, including self-assemble [13-15], calixarene-based anion receptors [2, 16-18], recognition of neutral molecules [7, 9, 16, 19], complexation of fullerenes [20-22], luminescent probes [23] and nuclear waste treatment [24], etc.

Very interestingly, due to the potential to establish the host-guest interactions with the cations, the calixarene frame can "hold" the metal center and the substrate (metalloenzyme) at a certain distance from one another in the catalytic process [25-27]. Furthermore, the ability of calixarenes to simultaneously bind a number of potentially catalytic centers is leading to useful cooperatives effects [25]. Particularly in view of the ability to tune either their sterics or electronics (or both) of either the lower or the upper rim, combined with the availability of the "pockets"/ cavities which could provide subtle substrate specificities and multiple host-guest interactions, the mixed-metal system for the calixarene-based catalysis has been developed [28]. So it becomes very essential to investigate the host-guest interactions between the calixarenes and cations.

The reliable prediction of the host-guest interaction is an important goal in supramolecular chemistry. It is well established that the high-level quantum chemical calculations with electron correlation and large basis set including both diffuse and polarization functions are crucial to adequately describe the host-guest interactions [6]. In particular, as one of the strong host-guest interactions, cation-π interaction contributes significantly to the overall binding strength in most cases [29-32], and it is necessary to reveal the nature of the cation-π interaction using the high-level calculations. Most of the theoretical investigations were performed at the Hartree–Fock method with relative small basis sets, using the semi-empirical methods or molecular mechanics or Monte-Carlo simulations [33, 34]. It was not until 2003 that, at 6-31G(d) level, a DFT-B3LYP investigation on host-guest interaction between calix[4]arene and the alkali-metal cation was published [35]. In 2005, the RI-BP86/SV(P) approximation was employed for studying the conformational features of calix[4]arenes with alkali-metal cations [6]. Recently, the energetic and structural properties of the calix[4]arenes with alkali-metal cations were presented with performance of various quantum chemical methods without the diffuse functions included in the basis sets [36].

It has been shown that, without the diffuse functions included in the basis sets, geometric parameters and energies obtained by using HF and DFT are in relatively poor agreement with the experimental values for the calixarenes and their complexes [37]. For example, in the investigation on the pinched cone-pinched cone transition equilibrium of tetraethoxythiacalix[4]arene, Matousek et al. have found that the transition energy barrier in the gas phase is 7.13 kcal mol^{-1} (B3LYP/6-31G**), whereas NMR studies of this transition in chloroform gave the value 11.9 kcal mol^{-1}. As a possible explanation for the failure of HF and DFT calculations, the authors suggested lack of treatment of the dispersion interaction between aromatic rings of the calixarenes [38]. On the other hand, in most cases, the semiempirical methods (such as AM1, PM3) are known to suffer from a bad description of the intermolecular interactions [39]. Furthermore, recently Liliya et al. have highlighted the weakness of the Monte-Carlo and molecular mechanics simulations in the prediction of the alkali metal complexes with the calixarenes. In the conformers obtained through Monte-Carlo searches procedure, the low values of preorganization, complexation, and binding energies indicated the wrong geometry of the potassium complexes of thiacalix[4]arene [37]. Moreover, HF bond distances are often shorter than the experimental results due to the neglect of the electron correlation, also leading to the relatively poor agreement with the experimental values for the geometric parameters [40]. Now the ever-increasing power of computers has allowed extended theoretical calculations of the structure, conformational equilibrium and intermolecular interaction of the big molecules calixarenes and their derivatives.

For the calix[4]arene monomer, the cone conformer was found to be the most stable in the gas and aqueous phases due to hydrogen bonding among the four hydroxyl groups [4]. The experimental structures of [p-tert-butylmethoxycalix[4]arene-sodium-toluene]$^+$ and the complex of tert-butylcalix[4]arene with Li$^+$ indicated that the calix[4]arene macrocycle adopted the cone conformation [41, 42]. NMR spectra of alkali-metal salt of monoanionic calix[4]arene also showed that the calix[4]arene formed the cone conformation in solution [43]. Therefore, the quantum chemical study will be carried out considering only cone calix[4]arene in the present study. This paper will, applying the high-level calculations, provide a thorough investigation on the host-guest interaction between cone calix[4]arene and Li$^+$ or Na$^+$ to clarify the structural and energetic characteristics of this kind of host-guest complexes. We believe that our theoretical results must be essential for better understanding of interactions of cations with various types of organic ligands possessing π-electrons.
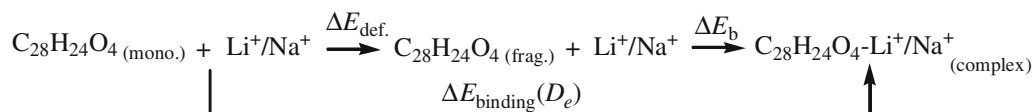
Computational methods

As a cost-effective approach, in most cases, geometry optimizations by the DFT methodology are feasible and being applied successfully to investigate the complexes of calix[4]arene with the charged species [44]. However, for the investigation on complexation energies of the host-guest complexes, the MP2(full) method is reliable [45-47]. In

order to establish the validity of the 6-311++G** basis set for evaluating the host-guest interactions between the calixarenes and alkali-metal cations, we employed both 6-311G** and 6-311++G** basis sets for the purposes of comparison. On the other hand, for many users of Gaussian 03, the global minima searches and the calculations of energies using MP2(full) method are now still very prohibitively expensive for the large molecules calixarenes and their complexes with Li$^+$ or Na$^+$. Can the interaction energies be estimated using the MP2(fc) approach instead of the MP2(full) method for the large molecules and their complexes? To answer this question, a comparison of the complexation energies obtained from the MP2(full) with those from MP2(fc) method is carried out.

All calculations have been performed using GAUSSIAN 03 programs [48] with the Becke 3-parameter hybrid exchange functionals and Lee-Yang-Parr correlation functionals

(B3LYP) [49-51] and second-order MØller–Plesset approximation (MP2) methods [45]. Six complexes have been found at the B3LYP/6-311G** and B3LYP/6-311++G** levels, and vibrational frequency calculations have also been performed. However, only four complexes corresponding to the minimum energy points (NImag=0) at the molecular energy hypersurface have been obtained. Single point energy calculations have been carried out using B3LYP, MP2(fc) and MP2(full) methods with 6-311G** and 6-311++G** basis sets. The D_e corrected for the basis set superposition error (BSSE) [52, 53] and zero-point energy correction (ZPEC) (only for the B3LYP method) was evaluated.   NBO analysis has been carried out at B3LYP/6-311++G** level [54].

The binding energy (D_e) has been calculated as the difference between the total energy of the complex and the sum of the total energies of the metal cation and the isolated cone calix[4]arene. It is defined as:

$$C_{28}H_{24}O_{4\,(mono.)} + Li^+/Na^+ \xrightarrow{\Delta E_{def.}} C_{28}H_{24}O_{4\,(frag.)} + Li^+/Na^+ \xrightarrow{\Delta E_b} C_{28}H_{24}O_4\text{-}Li^+/Na^+{}_{(complex)}$$

$$\Delta E_{binding}(D_e)$$

The deformation energy ($\Delta E_{def.}$) is defined as the energy difference between the calix[4]arene molecular framework at the geometry of the complex and the isolated calix[4] arene. It could not be negligible for the host-guest interactions between calixarenes and alkali-metal cations because the reverse of the order of the interactions is often attributed to geometry deformation contribution [6]. On the other hand, ΔE_b is obtained by subtracting the energies of the cation and the molecular framework of calix[4]arene in complex from the energy of the complex. Thus, in this paper the binding energy (D_e) is divided into the deformation energy ($\Delta E_{def.}$) and ΔE_b. It can be expressed as follows:

$$D_e = \Delta E_{def} + \Delta E_b.$$

Results and discussion

Six complexes (a)–(f) are obtained and their fully optimized geometries and atomic labels are shown in Fig. 1. The geometric parameters and their interaction energies are listed in Tables 1 and 2, respectively.

Geometry of the complex

From Fig. 1, the C_4 symmetrical Li$^+$ complex of calix[4] arene (a) appears as a minimum at the potential energy

surfaces at B3LYP/6-311++G** level. In this complex, the Li$^+$ cation is laid in the plane containing four oxygen atoms, and it is coordinated toward the oxygen atoms. The distance between Li$^+$ and the oxygen atom is 1.99 Å. This value is in excellent agreement with X-ray data (1.920–2.089 Å) for the tetralithium derivative of p-tertbutylcalix[4] arene [41], showing that our calculated result is reliable at B3LYP/6-311++G** level. On the other hand, a considerable increase of the O…H hydrogen bonding (more than 0.88 Å) is observed upon complexation, perhaps due to the repulsive interaction between Li$^+$ and the hydrogen of the hydroxyl groups. Furthermore, this repulsive interaction also causes the enlargement of the cavity of the calix[4] arene lower rim. However, no obvious variation of the C-C bonds or bond angles of calix[4]arene is found.

Allowing Li$^+$ cation moving along the C_4 axis into the cavity of the calix[4]arene, the complex is subsequently reoptimized at B3LYP/6-311++G** level. Unfortunately, another C_4 complex was not found to be the true minimum, but the cation shifted automatically from the C_4 axis to the position between the rings A and B (see C_1 symmetrical complex (b)). Similar to the calculated results from the complex between the dehydroxylated calix[4]arene and Li$^+$ [35], the complex (b) might be stabilized by the cation-π interaction between Li$^+$ and the ring A or B. Here, key structural changes are defined in Fig. 2. The greatest variation occurs in the position of the rings, which bend inward toward the center and the cation when the R$_Y$-C$_Y$-P$_C$ angle decreases, and outward when the angle increases. For

Fig. 1 The six optimized structures of the host-guest complexes between the cone calix[4] arene and the cations Li$^+$ or Na$^+$ at B3LYP/6-311++G** level. (**a**) Li$^+$ complex of calix[4] arene, C_4 symmetry (coordination with four oxygen atoms); (**b**) Li$^+$ complex of calix[4] arene, C_1 symmetry (coordination with A and B aromatic rings); (**c**) Na$^+$ complex of calix [4]arene, C_4 symmetry (coordination with four oxygen atoms, the Na$^+$ cation is at 1.815Å above the plane including the four oxygen atoms); (**d**) Na$^+$ complex of calix[4]arene, C_4 symmetry (coordination with four oxygen atoms, the four hydrogen bonds in the calix[4] arene lower rim are broken, the Na$^+$ cation is in the plane including the four oxygen atoms) (**e**) Na$^+$ complex of calix[4] arene, C_4 symmetry (coordination with four oxygen atoms, the Na$^+$ cation is at 1.12Å below the plane including the four oxygen atoms) (**f**) Na$^+$ complex of calix [4]arene, C_2 symmetry (mainly coordination with A and C aromatic rings)
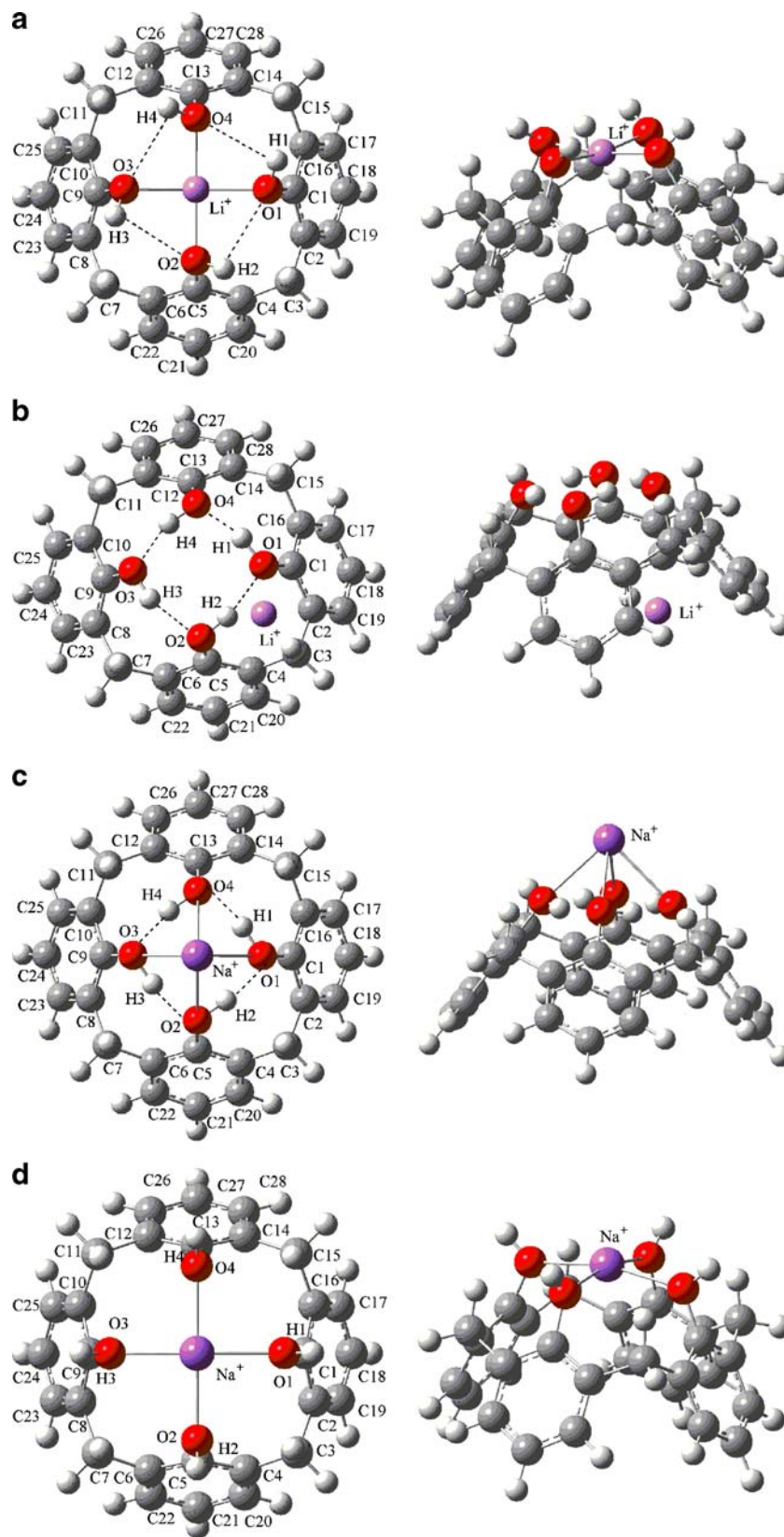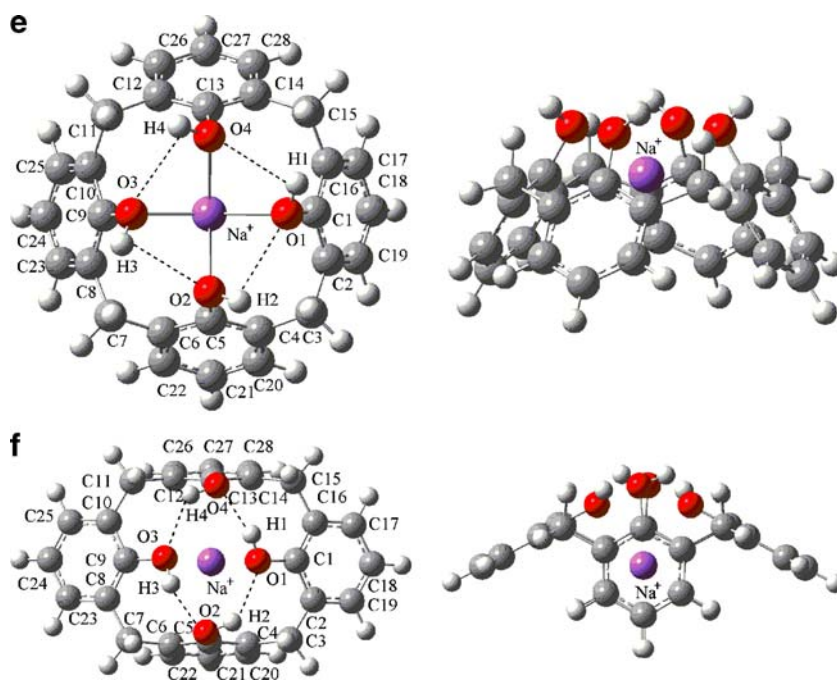
Fig. 1 (continued)

this complex, the rings A and B move closer to each other and bend inward: $R_{A...}R_B$ changes from 4.88 to 4.63 Å, and $R_A\text{-}C_A\text{-}P_C$ decreases from 125.7° to 118.6°. These changes are not in agreement with the study on the complex between the dehydroxylated calix[4]arene and Li$^+$ at B3LYP/6-31G(d) level, where the C_2 symmetrical complex was found and rings A and C moved closer and bent inward: $R_{A...}R_C$ changed from 5.51 to 4.66 Å, and $R_A\text{-}C_A\text{-}P_C$ decreased from 98.3° to 82.2° [35]. Then, we repeated the optimization of the complex between the dehydroxylated calix[4]arene and Li$^+$ at B3LYP/6-311++G** level. The result shows that this C_2 symmetrical complex of the dehydroxylated calix[4]arene is indeed a true minimum, suggesting indirectly that the hydrogen bonds among the hydroxyl act as an important part in determining the conformer of the complex (b).

Similar to the Li$^+$ complex (a), Na$^+$ is also coordinated to the oxygen atoms in the C_4 symmetrical complex (c). However, the Na$^+$ cation is not in the plane including the four oxygen atoms but at 1.82 Å above. Furthermore, in the Li$^+$ complex (a), the distance of the O…H hydrogen bonding is lengthened from 1.71 to 2.60 Å, however a contraction of 0.06 Å is found in the Na$^+$ complex (c) accompanied by the constriction of the cavity of the calix[4]arene lower rim. This is possibly due to the strong attractive interactions between the Na$^+$ cation and the four oxygen atoms.

Although complex (d) also adopts the same C_4 symmetry as the complex (c), the Na$^+$ cation is laid in the plane including the four oxygen atoms. The distance between the Na$^+$ and oxygen atom is 2.27 Å at B3LYP/6-311++G**

level. In the previous investigations, the HF/3-21G(d,p), B3LYP/6-31G(d,p) and RHF/6-311G(d,p) results also predicted that the C_4 symmetric conformation was a stable conformer when the Na$^+$ was laid in the plane including the four oxygen atoms [55, 56]. However, different from the low-level calculations, this complex is not the true minimum at B3LYP/6-311++G** level, where the four hydrogen bonds among the hydroxy groups are broken and vibrational analysis gives three imaginary frequencies corresponding to the wagging of the O-H bonds. In order to search for a true minimum at B3LYP/6-311++G** level, this complex is reoptimized with tighter SCF convergence criteria of 10^{-9} and disabled symmetry instead of 10^{-8}. The same energy and imaginary frequency are found.

In the C_4 symmetrical complex (e), the Na$^+$ cation enters into the cavity of the calix[4]arene and stays at 1.12 Å below the plane including the four oxygen atoms. It is also not the true minimum at B3LYP/6-311++G** level, where the four hydrogen bonds among the hydroxy groups are also broken badly and one imaginary frequency is found. The distance of the O…H hydrogen bonding and O…Na$^+$ is 2.44 and 2.35 Å, respectively. The decrement of the $R_{A...}R_C$ distance is decreased slightly by only 0.09 Å, suggesting that the cation-π interaction might be weak in this complex and the O…Na$^+$ interaction is predominant.

Subsequently, allowing Na$^+$ movement along the C_4 or C_2 axis into the cavity of the calix[4]arene, the complex is optimized at B3LYP/6-311++G** level. Only the C_2 symmetrical complex (f) is found to be a true minimum. Similar to complex (b), this complex might also be stabilized by the cation-π interaction between Na$^+$ and ring

Table 1 Principal geometric parameters of calix[4]arene and complexes at B3LYP/6-311++G** level (Distances are in Å and angles are in degree, $M^+=Li^+$ and Na^+)

parameter	calix[4]arene	(a)	(b)	(c)	(d)	(e)	(f)
R(C1–C2)	1.40	1.40	1.41	1.40	1.40	1.41	1.40
R(C1–C16)	1.40	1.40	1.41	1.40	1.40	1.41	1.40
R(C2–C3)	1.53	1.53	1.52	1.53	1.53	1.53	1.52
R(C2–C19)	1.40	1.40	1.40	1.40	1.40	1.40	1.40
R(C3–C4)	1.53	1.53	1.53	1.53	1.53	1.53	1.53
R(C4–C5)	1.40	1.40	1.41	1.40	1.40	1.41	1.41
R(C4–C20)	1.40	1.40	1.41	1.40	1.40	1.40	1.40
R(C5–C6)	1.40	1.40	1.41	1.40	1.40	1.41	1.41
R(R_A–R_B)	4.88		4.63	4.92		4.82	4.84
R(R_A–R_C)	6.91		7.00	6.96		6.81	5.53
R(M^+-O1)		2.00[a]		2.59	2.27[b]	2.35	
R(M^+…R_A)			2.53[c]			3.62	2.77[d]
R(M^+…R_C)			5.51			3.62	3.96
R(O1…H2)	1.71	2.60	1.86	1.66	3.78	2.44	2.36
R(O2…H3)	1.71	2.60	1.85	1.66	3.78	2.44	1.92
R(O3…H4)	1.71	2.60	1.71	1.66	3.78	2.44	2.36
R(O4…H1)	1.71	2.60	1.65	1.66	3.78	2.44	1.92
A(C2–C3–C4)	113.9	112.8	108.9	114.7	111.2	112.9	113.6
A(C6–C7–C8)	113.9	112.8	112.9	114.7	111.2	112.9	113.0
A(C10-C11-C12)	113.9	112.8	113.0	114.7	111.2	112.9	113.6
A(R_A-C_A-P_C)	125.7		118.6				98.4
A($R_{C/B}$-$C_{C/B}$-$P_{C/B}$)[e]	125.7		130.9				149.5

[a] the experimental values were in the 1.920–2.089 Å range (Ref. [41]) and 1.924 Å (Ref. [43]), and the calculated results were 1.90 Å at the HF/3–21G level (Ref. [55]) and 1.99 Å at the B3LYP/6-311G** level (in this study)

[b] the experimental values were in the 2.284–2.337 Å range (Ref. [43]) and 2.3 Å (Ref. [42]), and the calculated results were 2.25 Å at the HF/3–21G level (Ref. [55]) and 2.26 Å at the B3LYP/6-311G** level (in this study)

[c] the experimental value was 2.535 Å (Ref. [43]), and the calculated result was 2.21 at the B3LYP/6-311G** level (in this study)

[d] the experimental value was in the 2.792–2.900 Å range (Ref. [43]), the calculated result was 2.60 Å at the B3LYP/6-311G** level (in this study)

[e] The A(R_C-C_C-P_C) angle for complex (b) and the A(R_B-C_B-P_C) angle for complex (d)

A or C. Rings A and C move closer to each other and bend inward: $R_{A…}R_C$ changs from 6.91 to 5.53 Å, and R_A-C_A-P_C decreases from 125.7° to 98.4°. In the study on the complex between the dehydroxylated calix[4]arene and Na^+ at B3LYP/6-31G(d) level, $R_{A…}R_C$ changes from 6.893 to 6.507 Å, with a 9.8° decrease for the R_A-C_A-P_C angle [35].

From Table 1 it can be seen that HF bond distances are indeed shorter than the experimental results. This fact might be due to the neglect of the electron correlation, as is in accordance with our previous study [40]. From our calculations, geometric parameters of the M^+-O bonds obtained by using HF are in poor agreement with the experimental values. Although the B3LYP/6-311++G** level also underestimates the distance between the six-membered ring and the metal ion compared to the experimental values, it reproduces the experimental values most satisfactorily compared to the other methods. For example, for the Li^+-O distance in complex (a), the

experimental value is in the 1.920–2.089 Å range [41] and 1.924 Å [43], and the calculated result is 1.90 Å at the HF/3–21G level [55] and 1.99 Å at the B3LYP/6-311++G** level. Similarly, for the Na^+-O distance in complex (d), the experimental value is in the 2.284–2.337 Å range [43] and 2.3 Å [42], and the calculated result is 2.25 Å and 2.27 Å at the HF/3–21G [55] and B3LYP/6-311++G** levels, respectively.

It is worth mentioning that for the B3LYP method, the diffuse basis set has an effect on the geometry optimization of the cation-π interaction complexes (b) and (f). From Table 1, at the 6-311++G** basis set, the geometry optimization predicts the distance of 2.53 or 2.77 Å between the Li^+ or Na^+ and the centroid of the phenolic ring, whereas that is only 2.21 or 2.60 Å using the 6-311G** basis set. Furthermore, the results from the 6-311++G** basis set are close to the experimental values (2.535 or 2.792–2.900 Å) while those obtained from 6-311G** are

Table 2 Energetic information for the complexes

Method		Total energy (a.u.)	$\Delta E_{\text{def.}}$ (kJ/mol)	ΔE_{b} (kJ/mol)	D_{e} (kJ/mol)
(a)	B3LYP/6-311G**	−1390.11791	147.91	−431.87	−283.96 (−266.36)[a]
	MP2(fc)/6-311G**//B3LYP/6-311G**	−1386.11562	148.51	−440.50	−291.98 (−245.59)
	MP2(full)/6-311G**//B3LYP/6-311G**	−1386.73841	148.30	−447.21	−298.91 (−249.23)
	B3LYP/6-311++G**	−1390.12976	140.95	−411.26	−270.31 (−260.67)[b]
	MP2(fc)/6-311++G**//B3LYP/6-311++G**	−1386.16179	139.45	−413.17	−273.72 (−242.33)
	MP2(full)/6-311++G**//B3LYP/6-311++G**	−1386.78911	140.46	−422.38	−281.93 (−246.35)
(b)	B3LYP/6-311G**	−1390.09156	13.61	−228.39	−214.78 (−207.70)
	MP2(fc)/6-311G**//B3LYP/6-311G**	−1386.09084	8.41	−235.36	−226.95 (−201.60)
	MP2(full)/6-311G**//B3LYP/6-311G**	−1386.71348	7.12	−240.59	−233.47 (−207.23)
	B3LYP/6-311++G**	−1390.10558	12.11	−218.95	−206.84 (−203.90)
	MP2(fc)/6-311++G**//B3LYP/6-311++G**	−1386.13919	6.09	−220.47	−214.38 (−198.22)
	MP2(full)/6-311++G**//B3LYP/6-311++G**	−1386.76623	6.17	−228.04	−221.87 (−201.84)
(c)	B3LYP/6-311G**	−1544.85335	31.87	−139.62	−107.75 (−98.46)
	MP2(fc)/6-311G**//B3LYP/6-311G**	−1540.47376	29.80	−137.37	−107.57 (−88.19)
	MP2(full)/6-311G**//B3LYP/6-311G**	−1541.21351	22.75	−144.11	−113.62 (−97.61)
	B3LYP/6-311++G**	−1544.86716	28.54	−127.55	−99.01 (−95.13)
	MP2(fc)/6-311++G**//B3LYP/6-311++G**	−1540.52228	26.99	−122.31	−95.32 (−85.72)
	MP2(full)/6-311++G**//B3LYP/6-311++G**	−1541.26709	28.95	−132.86	−103.91 (−88.70)
(d)	B3LYP/6-311G**	−1544.86951	217.88	−368.06	−150.18 (−136.75)
	MP2(fc)/6-311G**//B3LYP/6-311G**	−1540.48342	219.89	−352.82	−132.93 (−98.70)
	MP2(full)/6-311G**//B3LYP/6-311G**	−1541.22796	219.11	−370.68	−151.57 (−298.74)
	B3LYP/6-311++G**	−1544.88350	207.80	−349.70	−141.90 (−131.23)
	MP2(fc)/6-311++G**//B3LYP/6-311++G**	−1540.53361	205.65	−330.72	−125.06 (−99.60)
	MP2(full)/6-311++G**//B3LYP/6-311++G**	−1541.28320	207.14	−353.33	−146.19 (−113.24)
(e)	B3LYP/6-311G**	−1544.87294	14.43	−173.62	−159.18 (−144.75)
	MP2(fc)/6-311G**//B3LYP/6-311G**	−1540.54076	15.25	−167.58	−152.33 (−121.26)
	MP2(full)/6-311G**//B3LYP/6-311G**	−1541.23664	49.70	−224.04	−174.34 (−124.63)
	B3LYP/6-311++G**	−1544.88544	7.33	−154.38	−147.05 (−139.72)
	MP2(fc)/6-311++G**//B3LYP/6-311++G**	−1540.58620	8.85	−151.01	−142.16 (−129.15)
	MP2(full)/6-311++G**//B3LYP/6-311++G**	−1541.28712	38.06	−194.55	−156.49 (−134.37)
(f)	B3LYP/6-311G**	−1544.88722	52.53	−249.20	−196.67 (−185.84)
	MP2(fc)/6-311G**//B3LYP/6-311G**	−1540.51575	42.55	−260.34	−217.78 (−182.43)
	MP2(full)/6-311G**//B3LYP/6-311G**	−1541.25866	43.50	−280.39	−232.16 (−193.38)
	B3LYP/6-311++G**	−1544.90000	55.66	−240.89	−185.23 (−179.30)
	MP2(fc)/6-311++G**//B3LYP/6-311++G**	−1540.56316	40.30	−242.94	−202.64 (−180.75)
	MP2(full)/6-311++G**//B3LYP/6-311++G**	−1541.31143	40.67	−260.95	−220.28 (−189.14)

[a] The values in parenthesis are corrected for BSSE

[b] For the complexes (a) –(f), De after correction of the ZPE amount to −249.32, −193.55, −90.03, −122.28, −117.69 and −162.88 kJ mol^{-1} at B3LYP/6-311++G** level, respectively

lower than the experimental results [43]. This suggests the necessity of the diffuse basis set on the geometry optimization of the alkali-metal cation-π interaction complexes of calix[4]arene. However, for the lower rim/cation interaction complexes, the above two basis sets predict the similar Li$^+$-O or Na$^+$-O distance (1.99 vs. 1.99 Å or 2.27 vs. 2.26 Å).

Binding energies and stabilities

Table 2 gives both uncorrected and corrected interaction energies after correction of the BSSE by means of the counterpoise method. For complexes (b) and (f), the cation-π interaction energies D_{e} after correction of the BSSE amount to −201.84 and −189.14 kJ mol^{-1} with the MP2
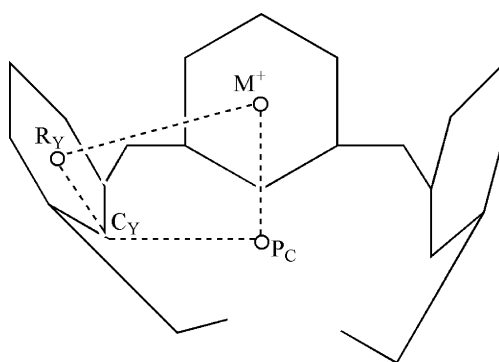
Fig. 2 A schematic view of the calixarene core and geometric parameters used for analysis

(full)/6-311++G** method, respectively. There is no direct measure of the cation-π interaction energy for the system, but there is value reported in the literature of −265.10 or −228.94 kJ mol^{-1} after correction of the BSSE for the cation-π interaction between the dehydroxylated calix[4] arene and Li$^+$ or Na$^+$ at B3LYP/6-31G(d) level [35]. Furthermore, many investigations on the cation-π interactions between alkali-metal cations and calix[4]arenes reveal that, in general, the cation-π interaction energies are in the range of 120–360 kJ mol^{-1} [6, 55]. Compared to the results mentioned above with the data listed in Table 2, it can be seen that our calculated results are reliable.

From Table 2, the BSSEs are in the range of 10.03–35.58 kJ mol^{-1} at MP2(full)/6-311++G** level. Even if the BSSEs are included, they do not change the ordering of the interaction energies since the binding energies differ by at least 42.28 kJ mol^{-1} employing MP2(full)/6-311++G** method in the discussed complexes. Indeed, the proportion of the BSSE correlated interaction energies for the complexes to their total binding energies, defined as $[(-D_e)-(-D_{e(BSSE)})]/(-D_e)$, is only up to 7.52% at B3LYP/6-311++G** level. This result suggests that it is not necessary to check the BSSE corrections for the host-guest interactions between calix[4]arenes and alkali-metal cations at B3LYP/6-311++G** level, as is consistent with the previous investigations [10]. However, the proportion of the BSSE is up to 20.36 or 22.54% employing the MP2(fc)/6-311++G** or MP2(full)/6-311++G** method, indicating that it must be considered for the MP2/6-311++G** method. Similarly, the ZPE correction, which is only up to 19.97 % for the B3LYP/6-311++G** method, might not be negligible, too.

As can also be seen from Table 2, the BSSE-corrected interaction energies D_e obtained by using B3LYP are always more than those obtained from the MP2 method except for those in the complex (f). This result is unexpected: in general, the interaction energy from B3LYP should be less than that from MP2 since dispersion

interaction is not accounted at B3LYP but given at MP2 level. Garau C. et al. also found that, for the complexes of benzene with cations, the interaction energies were also more favorable from B3LYP than MP2 method [57, 58].

It is worth mentioning that the deformation energies ($\Delta E_{def.}$), binding energies (ΔE_b) and interaction energies (D_e) are overestimated at 6-311G** basis set compared to those from 6-311++G**. For example for the complex (a), $\Delta E_{def.}$, ΔE_b and D_e are 148.30, −447.21 and −298.91 kJ mol^{-1} at MP2(full)/6-311G** level, respectively, whereas they are 140.46, −422.38 and −281.93 kJ mol^{-1} using the MP2(full)/6-311++G** level. In the same way, they amount to 147.91, −431.87 and −283.96 kJ mol^{-1} at B3LYP/6-311G** level, respectively, higher than those from the B3LYP/6-311++G** method by 6.96, 20.61 and 13.65 kJ mol^{-1}, respectively. These results show that the complexation energy depends on the quality of the basis set. In fact, it has been extensively shown from many theoretical results that the diffuse basis set is essential for describing delocalized electrons and electron correlation [59, 60]. On the other hand, we have found that the D_e values for the complexes show a maximum of 21.13 kJ mol^{-1} (14.45% of relative error) between the expensive MP2(full)/6-311++G** and MP2(fc)/6-311++G** method, indicating that D_e might be estimated using the MP2(fc)/6-311++G** approach instead of the more expensive MP2(full)/6-311++G** method.

The stability of the certain calixarene complexed with a specific cation has attracted considerable attention since, when not taking into account the environmental effect, it can provide information on the cation selectivity of the certain calixarene [24, 25]. As can be seen from the interaction energy D_e after correction of the BSSE, the complexation with Li$^+$ is preferred over that with Na$^+$ by at least 12.70 kJ mol^{-1} at MP2(full)/6-311++G**//B3LYP/6-311++G** level (the energy difference between the poorest interaction energy D_e in the Li$^+$ complexes and that of the strongest in the Na$^+$ complexes). This suggests that the cation selectivities of the calix[4]arene might follow the electrostatic series Li$^+$ >Na$^+$, as is in agreement with the result from the investigation on the similar complex between the dehydroxylated calix[4]arene and alkali-metal cations [35]. However, the solvation effect could not be negligible for cation selectivities because the selectivity ordering obtained from interaction energies can be easy reversed after taking into account the environmental effects, and it is well known in the case of crown ethers-cation inclusion complexes [4].

In fact, the stability ordering can also be easily reversed due to the geometry deformation for the host-guest complexes between calixarenes and alkali-metal cations. So in this paper the binding energy (D_e) is divided into the deformation energy ($\Delta E_{def.}$) and ΔE_b. Indeed, for the Na$^+$

complexes the ordering of ΔE_b is (d) > (f) while that of D_e turns into (f) > (d) when the deformation energy $\Delta E_{def.}$ is considered.

As can be seen from Table 2, for Li$^+$ cation the stability of the cation-π interaction complex (b) is poorer than that of the complex (a) stabilized by electrostatic interaction at all levels. However, for Na$^+$ cation the stability of the cation-π interaction complex (f) is stronger than that of the complex (c), (d) or (e) which is mainly energetically stabilized by electrostatic interaction. For example, the complex (f) is lower in energy by 116.40, 74.11 and 63.82 kJ mol^{-1} than complexes (c), (d) and (e) at MP2(full)/6-311++G**// B3LYP/6-311++G** level, respectively. Furthermore, inter-action energy (D_e) amounts to −220.28 kJ mol^{-1} at MP2 (full)/6-311++G**//B3LYP/6-311++G** level for the com-plex (f), while it is only −103.91, −146.19 or −156.49 kJ mol^{-1} for the complex (c), (d) or (e). These results contradict the previous low-level theoretical studies in which the Na$^+$ cation prefers to be bound closely to the oxygen rather than the aromatic cavity of the calix[4]arene [55, 56].

NBO analysis

To explain the origin that the cation-π interaction is stronger than electrostatic interaction for the Na$^+$ cation complex, NBO analysis has been carried out. The net charge transfer is evaluated to be from calix[4]arene to Li$^+$ cation by 95.0 and 66.2 me for the complexes (a) and (b), respectively. This result indicates that for Li$^+$ complexes, the charge transfer component in π-electron/cation complex (b) is less than that in the lower rim/cation complex (a). However, for Na$^+$ complexes, the charge transfer compo-nent in π-electron/cation complex (f) is more than that in the lower rim/cation complex (c), (d) or (e): it is evaluated to be from calix[4]arene to Na$^+$ cation by 100.3, 22.3, 48.7, and 66.73 me for the complexes (f), (c), (d) and (e), respectively. This result indicates that the Na$^+$ cation might prefer to enter the calix[4]arene cavity and the cation-π interaction is predominant, as is consistent with the binding energies analysis.

Conclusions

The DFT-B3LYP and MP2 methods with 6-311G** and 6-311++G** basis sets have been applied to study the structures and complexation energies of the host-guest complexes between calix[4]arene and Li$^+$ or Na$^+$ cation. NBO and binding energy analyses confirm that Na$^+$ cation prefers to enter the calix[4]arene cavity and the cation-π interaction is predominant, while for Li$^+$ cation the complexation is mainly energetically stabilized by the

lower rim/cation interaction. The complexation with Li$^+$ is preferred over that with Na$^+$ by at least 12.70 kJ mol^{-1} at MP2(full)/6-311++G**//B3LYP/6-311++G** level. Fur-thermore, it is necessary to introduce the diffuse basis set into the geometry optimizations and complexation energy calculations of the alkali-metal cation-π interaction com-plexes of calix[4]arene. These results must be useful for a better understanding of the factors governing the specificity of metal cations and further study of ion carriers and model structures for biomimetic research in calixarene and the other macrocyclic biological systems.

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