

## Ab Initio Study of Complexation of Alkali Metal Ions with Alkyl Esters of *p*-*tert*-Butylcalix[4]arene

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The complexation characteristics of tetramethyl (**1**) and tetraethyl esters (**2**) of *p*-*tert*-butylcalix[4]arene with alkali metal cations have been investigated by *ab initio* calculation. The structures of *endo*- or *exo*-complexation of the hosts in cone conformation with alkali metal ions have been optimized using HF/6-31G method followed by B3LYP/6-31G(d) single point calculation. B3LYP/6-31G(d) calculations suggest that *exo*-complexation efficiencies of sodium ion to the cavity of lower rim of hosts **1** and **2** are 27.1 and 25.8 kcal/mol better than that of potassium ion, respectively. The *exo*-complexation efficiencies of potassium ion to the cavity of lower rim of hosts **1** and **2** are 33.3 and 31.5 kcal/mol better than the *endo*-complexation inside the upper rim (four aromatic rings) as expected from the experimental results. B3LYP/6-31G(d) calculation of the ethyl ester **2** shows 29.5 and 30.8 kcal/mol better *exo*-complexation efficiency for both sodium and potassium ions than the methyl ester **1**.

**Key Words** : Calix[4]aryl ester, Complexation, Alkali metal ion, *Ab initio* calculation, B3LYP/6-31G(d)

### Introduction

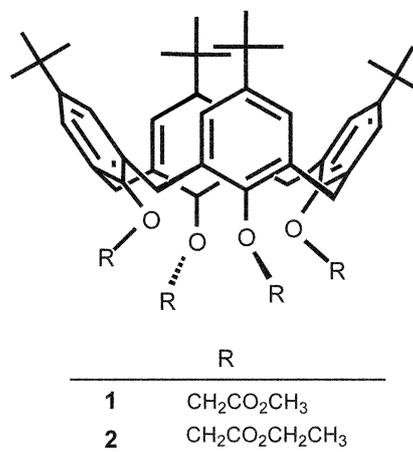
Recently, there has been much progress in the computational approaches in supramolecular chemistry, which may lead to the deeper microscopic insight into the structural and thermodynamical features involved in the processes of molecular recognition and supramolecular organization.<sup>1</sup> The calixarenes having well-defined molecular framework are particularly attractive as a basic skeleton for the construction of new supramolecular systems.<sup>2</sup> The most extensively studied properties of calixarenes are the recognition of metal ions in the hydrophilic and polar region created after functionalization of the lower rim, and the inclusion of neutral molecules in the apolar cavity by the interaction with the aromatic nuclei.<sup>3-5</sup> Earlier, Chang *et al.*<sup>6</sup> as well as McKervey group<sup>7</sup> were attracted to the possibility of introducing carbonyl containing substituents by the expectation that ester moiety might be able to act cooperatively as efficient ligating groups attached to the calixarene substructure in much the same way that ester carbonyl groups participate in cation binding in natural receptors such as valinomycin.<sup>8</sup> They reported the decisive peak selectivity of sodium ion among alkali metal cations by the calix[4]aryl esters. The functionalization of calixarenes with alkoxy carbomethyl functions like in **1** and **2** has been extensively employed in the design of numerous functional ionophores.<sup>6,7(c,d)</sup>

Wipff group has performed molecular dynamics studies on complexation characteristics of alkali metal cations with a series of important ionophores derived from calix[4]arenes.<sup>9</sup> Kinetics and mechanism of the sodium ion complexation by tetramethoxy derivative of *p*-*tert*-butylcalix[4]arene have

been reported experimentally.<sup>10</sup>

We have studied the structures and energies of the cone-shaped *p*-*tert*-butylcalix[4]crown-6-ether and its alkyl ammonium complexes using *ab initio* HF/6-31G method.<sup>11</sup> By a series of calculations the central part of the crown moiety is confirmed to be the primary binding site of *p*-*tert*-butylcalix[4]crown-6-ether for the recognition of alkyl ammonium guests in the cone conformation.

Hay *et al.* calculated the complexation behaviors of sodium and cesium cations with tetramethoxycalix[4]arene using a combined density-functional theory and second-order perturbation theory.<sup>12</sup> We have also studied the conformational characteristics of tetramethoxycalix[4]arene using HF/6-31G\*\* method, which reports that partial-cone conformer is 0.31 kcal/mol more stable than cone.<sup>13</sup> However, our conformational study of tetraethyl ester (**2**) of the *p*-*tert*-butylcalix[4]arene using B3LYP/6-311+G(d,p)//HF/6-31G calculations suggests that cone conformational



**Scheme 1.** Chemical structures of calix[4]aryl esters.

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isomer is slightly more stable than partial-cone analogue.<sup>14</sup> Recently, *endo*- or *exo*-complexation of calix[4]arene with alkali metal cations has been analyzed by HF, MP2 and DFT calculations,<sup>15</sup> and the impact of multiple cation- $\pi$  interactions upon dehydroxylated calix[4]arene substrate binding and specificity for alkali metal cations has been calculated using B3LYP/6-31G(d) method.<sup>16</sup>

Here, we have undertaken the relative binding affinity study of cone-shaped *tert*-butylcalix[4]aryl esters toward alkali metal cations focusing on the binding site of upper or lower-rim pocket of the host molecules **1** and **2** using the B3LYP/6-31G(d)//HF/6-31G calculation method.

### Computational Methods

The initial structures of *p-tert*-butylcalix[4]aryl esters were constructed by HyperChem.<sup>17</sup> In order to find optimized structures, we executed conformational search by simulated annealing method.<sup>18</sup> The alkali metal ion complexes of tetramethyl (**1**) and tetraethyl esters (**2**) of *p-tert*-butylcalix[4]arene obtained from MM/MD calculations were fully re-optimized using *ab initio* methods to estimate the absolute and relative energies for the different complexes after semi-empirical AM1 energy minimization. RHF/6-31G optimizations of the complexes of **1** and **2** by Gaussian 98 on supercomputer took more than 100 hours to reach an optimum structure with error limit of less than 0.01 kcal/mol ( $2 \times 10^{-6}$  atomic unit (A.U.)) for each complex. After optimization, B3LYP/6-31G(d) single point calculations of the final structures are done to include the effect of electron correlation and the basis set with polarization function as well as to reduce the basis sets superposition error (BSSE<sup>19</sup>). The large portions of the computations were carried out with the use of the computer facilities at the Research Center for Computational Science of The Okazaki National Research Institutes of Japan.

### Results and Discussion

The *ab initio* HF/6-31G full optimizations without any constraint followed by B3LYP/6-31G(d) calculations were carried out for the *exo/endo*-complexes<sup>20</sup> of sodium or potassium ion with the tetramethyl and tetraethyl esters of *p-tert*-butylcalix[4]arene. The HF/6-31G optimized energies are reported in Table 1, and B3LYP/6-31G(d) single point energies are listed in Table 2.

**Complexation characteristics of tetramethyl ester of *p-tert*-butylcalix[4]arene.** Figure 1 shows the calculated stable complexes of tetramethyl ester of *p-tert*-butylcalix[4]arene with alkali metal ions. *Exo*-complexation efficiency of sodium ion (Figure 1(a)) to the cavity of lower rim of host **1** is 31.8 (HF energy) or 27.1 (B3LYP) kcal/mol better than that of potassium ion (Figure 1(b)) that is in line with the experimental observations (see next section). And this *exo*-complexation efficiency of potassium ion inside the cavity of lower rim of host **1** is 45.7 (HF) or 33.3 (B3LYP) kcal/mol better than the *endo*-complexation of K<sup>+</sup> inside the upper rim

**Table 1.** HF/6-31G Optimized Energies<sup>a</sup> of the Host, Guest, and Complexes of *p-tert*-Butylcalix[4]aryl Esters with Alkali Ions

<i>Ab initio</i> HF/6-31G		Guest alkali ions		
		Na <sup>+</sup>	K <sup>+</sup>	
		-161.6593	-598.9700	
Host	Guest position	Complexes with host		
-3059.6079	<b>1</b>	( <i>exo</i> )	-3221.4591	-3658.7191
		( <i>endo</i> )	<sup>c</sup>	-3658.6463
-3215.7004	<b>2</b>	( <i>exo</i> )	-3377.5545	-3814.8182
		( <i>endo</i> )	<sup>c</sup>	-3814.7478
Host <b>1</b> + Guest ( <i>exo</i> ) complexation <sup>b</sup>			-120.4	-88.6
Host <b>1</b> + Guest ( <i>endo</i> ) complexation <sup>b</sup>			<sup>c</sup>	-42.9
Host <b>2</b> + Guest ( <i>exo</i> ) complexation <sup>b</sup>			-122.3	-92.7
Host <b>2</b> + Guest ( <i>endo</i> ) complexation <sup>b</sup>			<sup>c</sup>	-48.5

<sup>a</sup>Error limits in these calculations are about  $2 \times 10^{-5}$  A.U. Units for the *ab initio* total energies are in A.U., and units for complexation energies are in kcal/mol converted using conversion factor 1 A.U. = 627.50955 kcal/mol. <sup>b</sup>Complexation energies (kcal/mol) = E<sub>Complex</sub> - E<sub>Host</sub> - E<sub>Guest</sub>. <sup>c</sup>Spontaneously changed to *exo*-position during the geometry optimization.

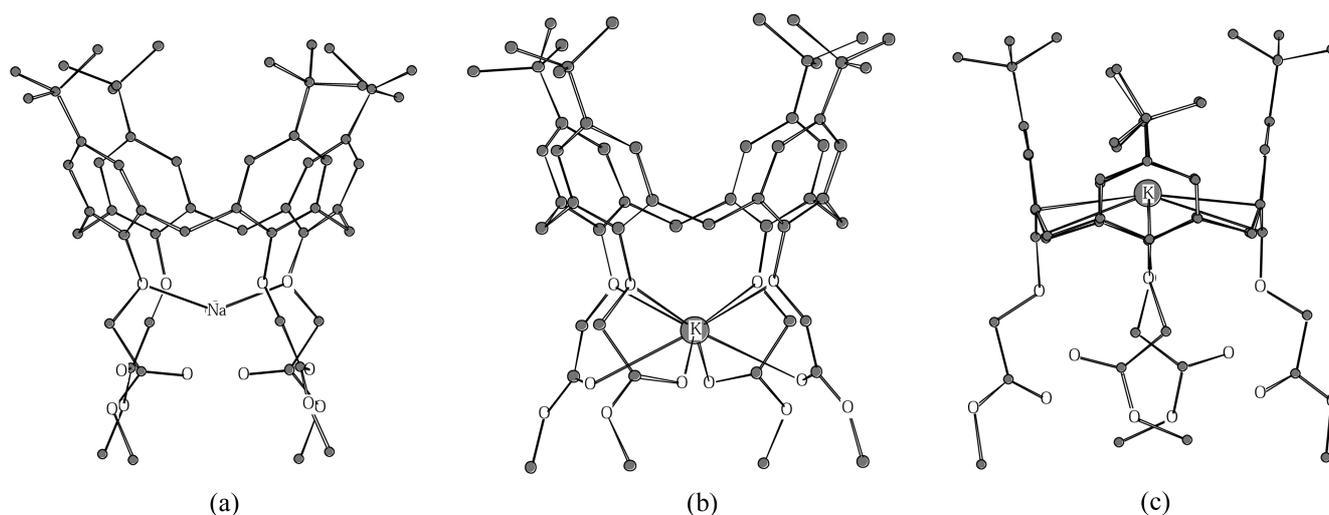
**Table 2.** DFT Energies<sup>a</sup> of the Host, Guest, and Complexes of *p-tert*-Butylcalix[4]aryl Esters with Alkali Ions

B3LYP/6-31G(d) calculation after HF/6- 31G optimization		Guest alkali ions		
		Na <sup>+</sup>	K <sup>+</sup>	
		-162.0812	-599.7250	
Host	Guest position	Complexes with host		
-3080.0934	<b>1</b>	( <i>exo</i> )	-3242.2687	-3679.8693
		( <i>endo</i> )	<sup>c</sup>	-3679.8162
-3237.3231	<b>2</b>	( <i>exo</i> )	-3399.5435	-3837.1461
		( <i>endo</i> )	<sup>c</sup>	-3837.0959
Host <b>1</b> + Guest ( <i>exo</i> ) complexation <sup>b</sup>			-110.9	-83.8
Host <b>1</b> + Guest ( <i>endo</i> ) complexation <sup>b</sup>			<sup>c</sup>	-50.5
Host <b>2</b> + Guest ( <i>exo</i> ) complexation <sup>b</sup>			-140.4	-114.6
Host <b>2</b> + Guest ( <i>endo</i> ) complexation <sup>b</sup>			<sup>c</sup>	-83.1

<sup>a,b,c</sup>See Table 1.

(four aromatic rings in Figure 1(c)) of **1**. This relative *exo/endo*-complexation efficiency is originated from the fact that the cation- $\pi$  interactions in the upper rim are different from the number and strength of electrostatic interactions of metal ionic guest with the efficient ligand site of ether and ester carbonyl functions in the lower rim. *Ab initio* calculated binding strengths are explained in detail below.

The cation-oxygen and cation- $\pi$  interaction energies of alkali metal ion with various conformers of tetramethoxy-calix[4]arene have been calculated using BLYP/6-31G\*\* method,<sup>12</sup> where the binding energy of Na<sup>+</sup> with the four oxygens of cone-type tetramethoxycalix[4]arene is reported -76.2 kcal/mol. The cation-oxygen binding energies are reported as -26.2 (Na<sup>+</sup>) and -18.1 (K<sup>+</sup>) kcal/mol when cation is binding to the O-H group of phenol from the HF/6-311G(d,p) calculation.<sup>15</sup> The cation- $\pi$  interaction energy of alkali metal ion with a benzene ring and debutylated calix[4]arene has been calculated using B3LYP/6-31G(d)



**Figure 1.** (a) *Ab initio* calculated structure of **1** *exo*-complexed with sodium ion and (b) structure of **1** *exo*-complexed with potassium ion. (c) structure of **1** *endo*-complexed with potassium ion. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.<sup>21</sup>

method,<sup>16</sup> in which Na<sup>+</sup>-benzene binding energy is reported -28.5 kcal/mol and Na<sup>+</sup>-cone-calix[4]arene binding energy in upper rim is -54.8 kcal/mol, and K<sup>+</sup>-benzene binding energy is reported -18.7 kcal/mol and K<sup>+</sup>-cone-calix[4]arene binding energy is -43.3 kcal/mol.

When we see *endo*-complexation of K<sup>+</sup> inside aromatic rings of **1** in Figure 1(c), the major portion of binding energy is coming from four (2 strong and 2 weak) K<sup>+</sup>- $\pi$  interactions. However, binding energy of alkali metal ion to the cavity of lower rim of host **1** is contributed from four ether-oxygens and four carbonyl oxygens of ester groups. Both factors of individual binding strength and the different number of electrostatic interactions may explain the better binding of *exo*-complexation than *endo*-analogue.

*Endo*-complexation of sodium ion inside the upper rim was so unstable that Na<sup>+</sup> ion (diameter = 1.90Å) in *endo*-position spontaneously moved down through the annulus of calix[4]arene backbone to more stable *exo*-position during the geometry optimization of the complex. However, *endo*-complexation of bigger K<sup>+</sup> ion (diameter = 2.66Å) inside the upper rim was stable enough to stay inside the pocket of four aromatic rings although this had weaker binding strength compared to *exo*-position. An interesting thing to mention about the *endo*-position structure (Figure 1(c)) of **1**+K<sup>+</sup> is that the planes of four benzene rings show significantly different dihedral angles for opposite rings. Two opposite rings are almost parallel and the other opposite planes are almost perpendicular, whereas *exo*-position structure (Figure 1(b)) of **1**+K<sup>+</sup> displays C<sub>4v</sub> symmetry. This result was also repeated in the tetraethyl ester **2**.

Table 3 reports the calculated distances between alkali metal ion and the ether-oxygens and carbonyl-oxygens of calix[4]aryl esters **1** and **2**. In Figures 1 and 2, the guest ion and the ligating atoms of the host in optimized structure, which are within a certain distance (the bond proximate distance) from one another, were automatically indicated as bonded.<sup>21</sup> However, these are not real coordinations or

**Table 3.** HF/6-31G Optimized Distances between Alkali Metal Ion and the Ether-oxygens and Carbonyl-oxygens of Calix[4]aryl Esters<sup>a</sup>

Distance from alkali ion	<i>Exo</i> -complex			
	<b>1</b> +Na <sup>+</sup>	<b>2</b> +Na <sup>+</sup>	<b>1</b> +K <sup>+</sup>	<b>2</b> +K <sup>+</sup>
Ether-Oxygen (1)	2.406	2.440	2.677	2.679
Ether-Oxygen (2)	2.369	2.434	2.680	2.680
Ether-Oxygen (3)	2.406	2.440	2.676	2.679
Ether-Oxygen (4)	2.367	2.434	2.677	2.678
Carbonyl-Oxygen (1)	3.042	2.681	2.825	2.826
Carbonyl-Oxygen (2)	2.448	2.624	2.825	2.829
Carbonyl-Oxygen (3)	3.050	2.682	2.829	2.822
Carbonyl-Oxygen (4)	2.451	2.619	2.829	2.827

<sup>a</sup>In the structures given in Figures 1 and 2, atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.<sup>21</sup> For Na<sup>+</sup> complex, the distances less than 2.400 Å were the cases. For K<sup>+</sup> complex, all cases are less than 2.830 Å and marked as bonded.

bonds. Alkali metal cations cannot have these many coordination numbers. For Na<sup>+</sup> complex, the distances less than 2.400 Å were the cases. For K<sup>+</sup> complex, all cases are less than 2.830 Å and marked as bonded. The potassium ion complexed at the *exo*-position of **1** (Figure 1(b)) shows electrostatic interactions with all of the ether- and the carbonyl-oxygens of four branches of host **1**. An interesting fact deduced from the Table 3 is that the distance (~2.678 Å) between K<sup>+</sup> and the ether-oxygens of both hosts **1** and **2** is always ~0.149 Å shorter than the value (~2.827 Å) between K<sup>+</sup> and the carbonyl-oxygens of hosts.

In order to analyze the electrostatic interactions of the alkali metal cation with ether- or carbonyl-oxygens of the host, we have tabulated the B3LYP/6-31G(d) calculated partial charges of the atoms of *exo*-complexes in consideration in Table 4. When we compared these values with the partial charges of oxygens obtained from other calculation methods such as HF or AM1 semi-empirical methods, they

**Table 4.** B3LYP/6-31G(d) Calculated Partial Charges of Ether-oxygens, Carbonyl-oxygens of Calix[4]aryl ester and Alkali Metal Cations in Complexes

Partial Charge <sup>a</sup>	Exo-complex			
	1+Na <sup>+</sup>	2+Na <sup>+</sup>	1+K <sup>+</sup>	2+K <sup>+</sup>
Ether-Oxygen (1)	-0.574	-0.571	-0.574	-0.574
Ether-Oxygen (2)	-0.582	-0.571	-0.574	-0.574
Ether-Oxygen (3)	-0.574	-0.571	-0.575	-0.574
Ether-Oxygen (4)	-0.582	-0.572	-0.575	-0.575
Average Ether-Oxygen	-0.578	-0.571	-0.575	-0.574
Carbonyl-Oxygen (1)	-0.486	-0.489	-0.494	-0.497
Carbonyl-Oxygen (2)	-0.489	-0.489	-0.494	-0.498
Carbonyl-Oxygen (3)	-0.486	-0.490	-0.494	-0.497
Carbonyl-Oxygen (4)	-0.489	-0.490	-0.494	-0.498
Average Carbonyl-Oxygen	-0.488	-0.490	-0.494	-0.498
Alkali Metal Cation	+0.362	+0.350	+0.507	+0.491

<sup>a</sup>The partial charges of oxygen and alkali metal ion obtained from other calculation methods were very much different.<sup>22</sup> Therefore a lot of care should be taken for the interpretation of electrostatic interactions in different situations.

were very much different.<sup>22</sup> Therefore a lot of care should be taken for the interpretation of electrostatic interactions in different situations. The average partial charge (-0.578) of the ether-oxygens of 1+Na<sup>+</sup> complex is more negative than that (-0.488) of carbonyl-oxygens of the complex, which may suggest stronger interactions of the cation with ether-oxygens of the hosts. A similar kind of characteristic behavior is also observed in tetraethyl ester (2) of *p-tert*-butylcalix[4]arene.

**Complexation characteristics of tetraethyl ester of *p-tert*-butylcalix[4]arene.** Experimental results<sup>6,7</sup> reported that the ethyl ester 2 provides better extraction of alkali metal ions than the methyl ester 1 from the fact that longer chains of the bottom of lower rim will improve the captivity of guest ion. So, we have also calculated the complexation

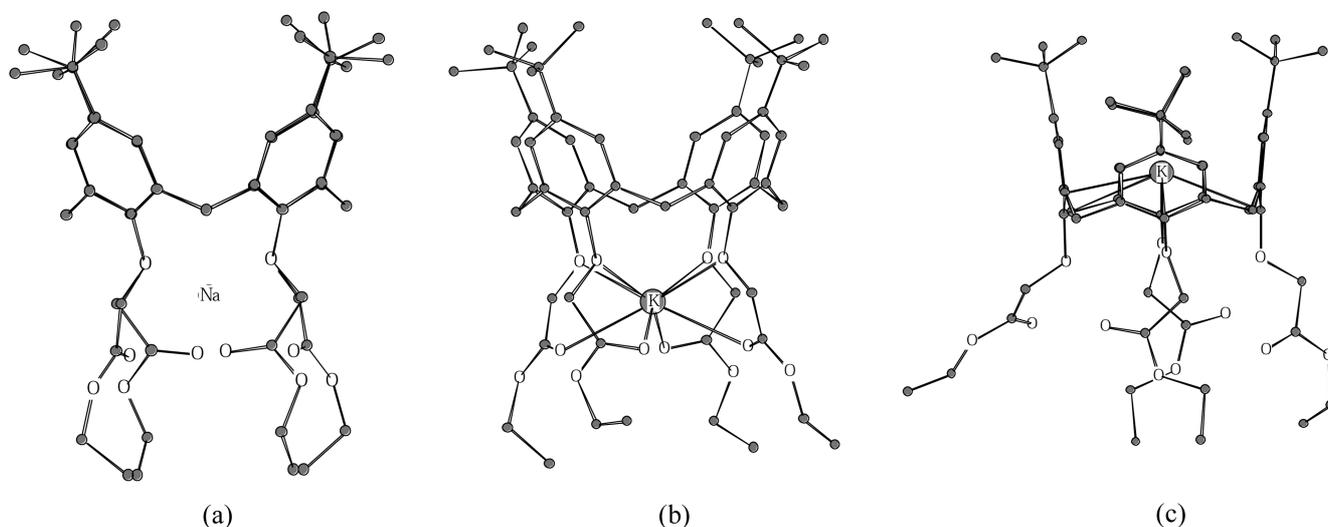
efficiency of host 2 with the alkali metal cations. Figure 2 shows the calculated stable complexes of tetraethyl ester of *tert*-butylcalix[4]arene.

*Exo*-complexation efficiency of sodium ion inside the cavity of lower rim of host 2 is 26.2 (HF energy) or 25.8 (B3LYP) kcal/mol better than that of potassium ion inside lower rim as expected from experiments.<sup>6,7</sup> The extractions of alkali picrates from basic aqueous solution into dichloromethane have shown that Na<sup>+</sup> = 95% and K<sup>+</sup> 49%.<sup>7b</sup> Thermodynamic stability constant measurements of host 2 showed that complexation selectivity ( $\beta(\text{Na}^+)/\beta(\text{K}^+) = 400$ ).<sup>7b</sup> Another experiment<sup>7c</sup> of stability constant reported that ( $\beta(\text{Na}^+)/\beta(\text{K}^+)$ ) was about 100 for both methyl and ethyl esters of *p-tert*-butylcalix[4]arene.

*Exo*-complexation efficiency of potassium ion by host 2 is 44.2 (HF) or 31.5 (B3LYP) kcal/mol better than the *endo*-complexation inside the upper rim with aromatic rings of 2. B3LYP calculation also suggests that the ethyl ester 2 exhibited 29.5 kcal/mol better *exo*-complexation efficiency than the methyl ester 1 toward sodium ion, and 2 showed 30.8 kcal/mol better than 1 for the bigger potassium ion.

## Conclusion

Using the *ab initio* method we have calculated the absolute and complexation energies of the different complexes of the tetramethyl (1) and tetraethyl (2) esters of *p-tert*-butylcalix[4]arene with alkali metal cation. The structures of *endo*- or *exo*-complexation of alkali metal cation with the cone-type hosts have been optimized using RHF/6-31G method followed by B3LYP/6-31G(d) single point calculation. *Exo*-complexation efficiency of sodium ion inside the cavity of lower rim of hosts 1 and 2 are 27.0 and 23.0 kcal/mol, respectively, better than that of potassium ion. And this *exo*-complexation efficiency of potassium ion inside the cavity of lower rim of hosts 1 and 2 are 33.0 and 31.5 kcal/mol better than the *endo*-complexation inside the upper rim (four



**Figure 2.** (a) *Ab initio* calculated structure of 2 *exo*-complexed with sodium ion and (b) structure of 2 *exo*-complexed with potassium ion. (c) structure of 2 *endo*-complexed with potassium ion.

aromatic rings) as expected from experiment. B3LYP/6-31G(d) single point calculations show that the ethyl ester **2** has better *exo*-complexation efficiency than the methyl ester **1** for both sodium and potassium ions.

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