Ab initio Study of the Complexes of Trimethyl Ether of Monodeoxycalix[4]arene with Potassium Ion: Cation-π Interactions

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In this study, we have performed *ab initio* computer simulations to investigate the conformational and complexation characteristics of the trimethyl ether of *p-tert*-butylmonodeoxycalix[4]arene (**6**) with a potassium ion. The structures of different conformers of **6** and their potassium complexes were optimized by using *ab initio* RHF/6-31G and B3LYP/6-31G(d,p) methods. The relative stability of the various conformers of the uncomplexed **6** is in following order: cone (most stable) > 1-partial-cone ~ 2i-partial-cone > 2-partial-cone ~ 1,3-alternate > 3i-partial-cone. However, the relative stability of the conformational complexes of **6** with K^+ is in the following order: 2-partial cone ~ 1,3-alternate > cone > 3-partial cone > 1-partial cone (least stable). The highest binding strengths of 2-partial-cone and 1,3-alternate complexes originate from two strong cation-π interactions and two strong cation-oxygen interactions in the complex of **6**+K^+. Due to the cation-π interactions, the calculated C-C bond distances in the arenes of the K^+-complexes are about 0.0048 Å longer than the values of their isolated hosts.

Key Words : *Ab initio*, B3LYP/6-31G, Monodeoxycalix[4]arene, Conformer, Cation-π interaction

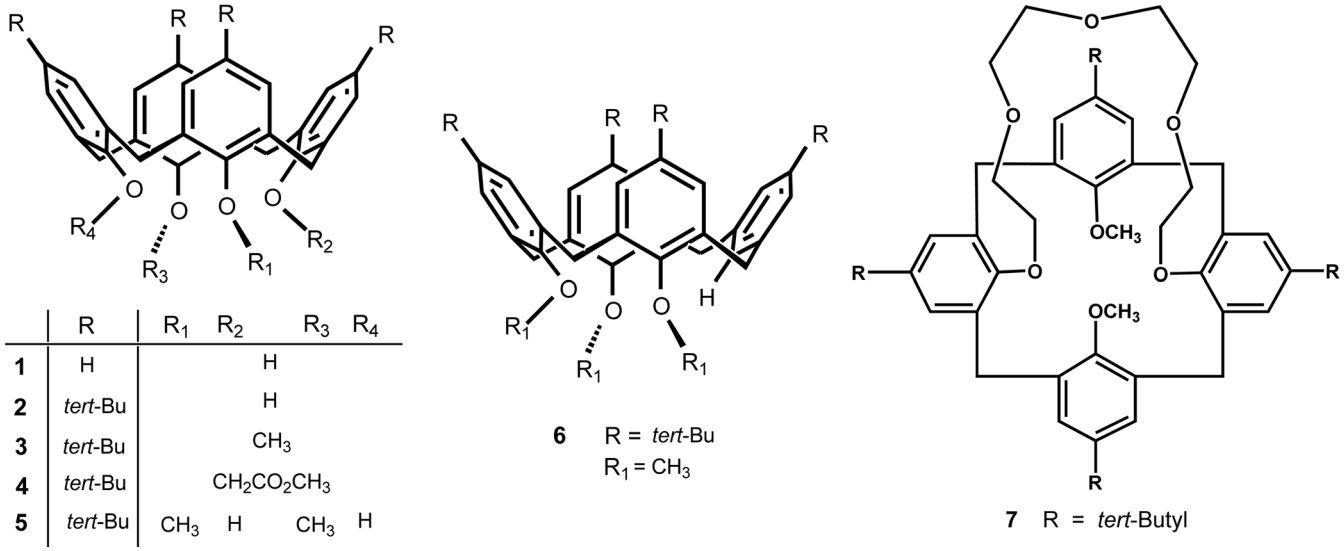
Introduction

The calixarenes are particularly attractive as a basic skeleton for new supramolecular systems due to their well-defined molecular framework.[1] The Wipff group has performed molecular dynamics studies on complexation characteristics of alkali metal cations with a series of important ionophores derived from calixarenes.[2]

The relative stabilities of the various conformations of calix[4]aryl derivatives are determined by experimental and theoretical methods.[3-10] Four different conformations of the tetramethoxycalix[4]arene (**3**) have been calculated, and the trend (in the order of partial cone (most stable) > cone > 1,2-alternate ~ 1,3-alternate) is consistent with the relative free energies obtained from the NMR spectroscopic data.[5] Reinhoudt *et al.* have also reported both the calculated and the experimental results of conformational distributions of **3**.[6] The kinetic results and mechanistic features of the complexation process of **3** with sodium ions have been reported experimentally.[7] We have studied the conformational characteristics of **3** by using the HF/6-31G** method, which reveals that the partial-cone conformer is 0.31 kcal/mol more stable than the cone.[8] However, our conformational studies of the tetraethyl ester of the *p-tert*-butylcalix[4]arene by using B3LYP/6-311+G(d,p)//HF/6-31G calculations suggest that the cone conformational isomer is slightly more stable than the partial-cone analogue.[9] The relative stability of different conformational isomers for the trimethyl ethers of the monodeoxycalix[4]arene (**6**) was investigated by performing a ^{1}H NMR experiment as well as by MM3 molecular mechanics calculation.[10]

Due to their suitable molecular pre-organizations with aromatic units concentrated in a relatively small space, calix[n]arenes have been recognized as interesting compounds exhibiting an enhanced ability for cation-π interactions.[11] Their π-rich cavities favor charged guest molecules that are stabilized by noncovalent binding forces related to cation-π interactions.[12-16] Nicholas *et al.* reported a high level *ab initio* molecular orbital study of cation-π binding between the alkali-metal cations and benzene[17] as well as anisole.[18] These researchers also calculated the complexation behaviors of sodium and cesium cations with tetramethoxycalix[4]arene by using the combination of density-functional and second-order perturbation theories.[19] Recently, *endo*-[20] or *exo*-complexation of calix[4]arene with alkali-metal cations was analyzed by using HF, MP2 and DFT calculations,[21] and the impact of multiple cation-π interactions upon dehydroxylated calix[4]arene substrate binding and specificity for alkali metal cations was calculated by using the B3LYP/6-31G(d) method.[22] We have also performed the relative binding affinity studies of cone-shaped *tert*-butylcalix[4]aryl esters (**4**) with alkali metal cations, focusing on the binding site of the upper or lower-rim pocket of the host molecule **4** by using the B3LYP/6-31G(d)//HF/6-31G calculation method.[23]

The first objective of this research is to determine the relative stability of different conformational isomers for the trimethyl ethers of the monodeoxycalix[4]arene (**6**)[10] and their potassium complexes by using *ab initio* calculations. Another objective is the investigation of potassium cation-π interactions in a series of the calix[4]aryl complexes **1**-**7**. The calculation results might provide a basis for the utili-



	R	R_1	R_2	R_3	R_4
1	H	H			
2	*tert*-Bu	H			
3	*tert*-Bu	CH_3			
4	*tert*-Bu	$CH_2CO_2CH_3$			
5	*tert*-Bu	CH_3	H	CH_3	H

Scheme 1. Structures of calix[4]aryl derivatives. **1** = Calix[4]arene, **2** = *p-tert*-Butylcalix[4]arene, **3** = Tetramethyl ether of *p-tert*-butylcalix[4]arene, **4** = Tetramethyl ester of *p-tert*-butylcalix[4]arene, **5** = 1,3-dimethyl ether of *p-tert*-butylcalix[4]arene, **6** = Trimethyl ether of *p-tert*-butylmonodeoxycalix[4]arene, **7** = 1,3-dimethyl ether of *p-tert*-butylcalix[4]crown-5-ether.

zation of the unique molecular frameworks of calix[4]arenes in the designing of other functional ionophores having various conformational isomers and supramolecular functions. Moreover, calix[4]quinone and calix[4]hydroquinone recently have been reported as being very useful chemical substances for synthesizing organic nanotubes and silver nanowires,[24] so it would be interesting to investigate the conformations of calix[4]arenes as building blocks of nano-materials.

Computational Methods

The initial structures of *p-tert*-butylcalix[4]arene derivatives were constructed by using HyperChem.[25] In order to find optimized conformations, we executed a conformational search by using a simulated annealing method, which has been described in a previous publication.[26] The structures of the trimethyl ether of *t*-butylmonodeoxycalix[4]arene (**6**) obtained from MM/MD calculations were fully re-optimized by using the *ab initio* methods to estimate the absolute and relative energies of the different conformations of the host and their potassium complexes. RHF/6-31G followed by B3LYP/6-31G(d,p) optimizations of the calix[4]aryl derivatives by using Gaussian 98 on the supercomputer took more than several days to reach an optimum conformation with an error limit of less than 0.01 kcal/mol (2×10^{-6} atomic unit (A.U.)) for each conformer. The normal mode frequencies of the final structures also have been calculated by the RHF/6-31G method. Each vibrational spectrum shows no negative value of frequency, which suggests that the optimized structure exists in the minimum point. The B3LYP/6-31G(d,p) optimizations of the final structures are done to include the effect of electron correlation and the basis set with polarization function.

Results and Discussion

Conformational characteristics of trimethyl ether of *p-tert*-butylmonodeoxycalix[4]arene. It is well known that the calix[4]arene-25,26,27,28-tetraols **1** and **2** form strong intramolecular hydrogen bonds among OH groups and represent the cone conformer as the most stable structure.[1(d)] Substitution of all the phenolic protons of a calix[4]arene by a bulky alkyl group generally leads to conformationally rigid structures like **4**.[23] However, when the substituent is small enough such as a methyl group, the resulting methyl ether **3** is no longer rigid, and any anisole ring can rotate *via* oxygen-through-the-annulus to give a mixture of the four possible conformers.[5-8]

It is interesting to investigate what kind of influence on the relative stabilities for the different conformers of tetramethoxy-*p-tert*-butylcalix[4]arene (**3**) will be made by the substitution of one of the four *p-tert*-butylanisole rings in **3** with a *p-tert*-butylbenzene. Although all four rings of **6** are able to move through the annulus of the lower rim, the deoxylated ring can freely rotate through the annulus. Various conformations of **6** can be generated by the different orientation of the three methyl groups. As a result, six distinct conformers (cone, 1-partial-cone, 2-partial-cone, 3-partial-cone, 1,2-alternate, and 1,3-alternate) can be exist.

The *ab initio* optimizations without any constraint were carried out for the various conformers of the trimethyl ether of *p-tert*-butylmonodeoxycalix[4]arene (**6**). Table 1 shows the absolute and relative energies (in kcal/mol) of the stable conformers of **6** obtained by the RHF/6-31G and B3LYP/6-31G(d,p) calculations. Although the relative stabilities of the various conformers do not show much difference, the calculation results suggest that a cone conformer is the most

Table 1. *Ab Initio* RHF/6-31G and B3LYP/6-31G(d,p) Calculated Energies (kcal/mol)[a] of the Various Conformers of **6**

Method \ Conformation	Cone	1-Paco[b]	2i-Paco[c]	2-Paco[d]	3i-Paco[e]	1,3-Alt[f]
Notation in Ref. 10	uuuu	uuud	uudiu	uudu	udiuu	uidud
Figures	1(a) and 1(b)	2(a) and 2(b)	3(a) and 3(b)	4(a) and 4(b)	5(a) and 5(b)	6(a) and 6(b)
HF/6-31G Optimized	−1279921.61	−1279918.64	−1279918.80	−1279917.80	−1279916.19	−1279917.81
HF/6-31G (relative)	0.00	2.97	2.81	3.81	5.42	3.80
B3LYP/6-31G(d,p) Optimized	−1288923.60	−1288921.72	−1288920.63	−1288920.78	−1288917.74	−1288919.44
B3LYP/6-31G(d,p) (relative)	0.00	1.89	2.97	2.83	5.87	4.17

[a]Error limits in these calculations are about 2×10^{-5} A.U. Conversion factor: 1 A.U. = 627.50955 kcal/mol. [b]Partial-cone conformer of **6** with an inverted deoxy-ring. [c]Partial cone of **6** with an inverted anisole ring which is next to the deoxy-ring. The methyl group of the inverted second-ring is inside the upper rim. [d]Partial cone of **6** with an inverted anisole ring which is next to the deoxy-ring. [e]Partial cone of **6** with an inverted anisole ring which is at the opposite side of the deoxy-ring. The methyl group of the inverted third-ring is inside the upper rim. [f]1,3-Alternate conformer of **6** with an inverted anisole ring as well as a horizontal deoxy-ring

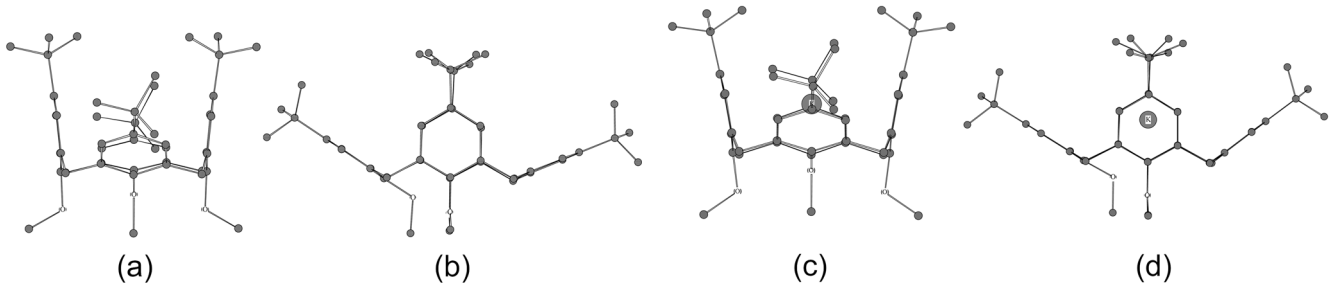


Figure 1. *Ab initio* calculated structures of the cone conformer of **6**: (a) front view of cone (uuuu) host, (b) side view of cone (uuuu) host, (c) front view of cone (uuuu) complex, (d) side view of cone (uuuu) complex: 2A+1O. Hydrogen atoms are omitted for clarity. The notation (uuuu) is from reference 10.

stable one among the conformers of **6** in the following order: cone (most stable) > 1-partial-cone > 2-partial-cone ~ 2i-partial-cone > 1,3-alternate > 3i-partial-cone. 1,2-alternate conformer was omitted in the list due to high instability. The notations of 2i- and 3i- partial-cones are explained in the footnotes of Table 1. This trend is similar to the outcome of the triethyl ester of *p-tert*-butylcalix[4]arene.[9] The *ab initio* calculated ordering of the conformers of **6** is a little different from that of the ^{1}H NMR analysis, where 2-partial-cone conformation shows the highest population.[10] One reason for this discrepancy between the calculated values and the experimental data might be the different conditions between the calculation (in vacuum without any solvent molecule) and the experimental environment (in solvent).

Cation-π and cation-oxygen interactions in the complexes of 6 with potassium ion. Two kinds of complexation modes for the cation in the calix[4]aryl host **6** are possible. The primary binding site is located in the upper rim of the calix[4]arene cup (*endo*[20]), and the second site is located in the lower rim (*exo*). The preference between the *endo*- and the *exo*-binding modes could be determined by the number of the cation-π and cation-oxygen interactions of potassium ion with the various conformations of the trimethyl ether of *p-tert*-butylmonodeoxycalix[4]arene. In order to show the binding modes, we have identified the stable complexes with an abbreviation such as 2A+1O to explain the number of cation-π interactions and the number of cation-oxygen interactions of potassium ion with the host **6**.

Table 2 shows the RHF/6-31G and B3LYP/6-31G(d,p) absolute and relative energies (in kcal/mol) of five stable K^+-complexes of **6**. The calculation results suggest the following order of stability: 2-partial cone (2A+2O) ~ 1,3-alternate (2A+2O) > cone (2A+1O) > 3-partial cone (2A+1O) > 1-partial cone (2A+1O : least stable). B3LYP/6-31G(d,p) calculations display smaller differences in the relative energies between the most stable conformer and less stable ones. The highest binding strengths of 2-partial-cone (Figures 4(c) and 4(d)) and 1,3-alternate (Figures 6(c) and 6(d)) complexes originate from two strong cation-π interactions and two strong cation-oxygen interactions (2A+2O) in the complex of **6**+K^+.

The planes of four arenes in the *endo*-cone complex show significantly different dihedral angles for opposite rings. Two opposite rings (Figures 1(c)) are almost parallel, and the other opposite rings (Figures 1(d)) are almost perpendicular, whereas the *exo*-cone complex (Figures 1(b) in reference 23 of **4**+K^+) displays C_{4v} symmetry. For the *endo*-complexation of K^+ inside the aromatic rings of **6** in Figure 1(c), the major portion of binding energy is from the result of two strong K^+-π interactions. However, additional binding energy of the potassium ion to the cavity of the lower rim is also contributed by one strong cation-oxygen interaction (2.750 Å) with the ether-oxygen of host **6**. Those cation-π plus cation-oxygen interactions may explain the better binding behavior of *endo*-complexation than *exo*-analogue. Since the *exo*-complexation of potassium ions inside the lower rim is less stable than the *endo*-position, K^+ in *exo*-position spontaneously moves up through the annulus of the

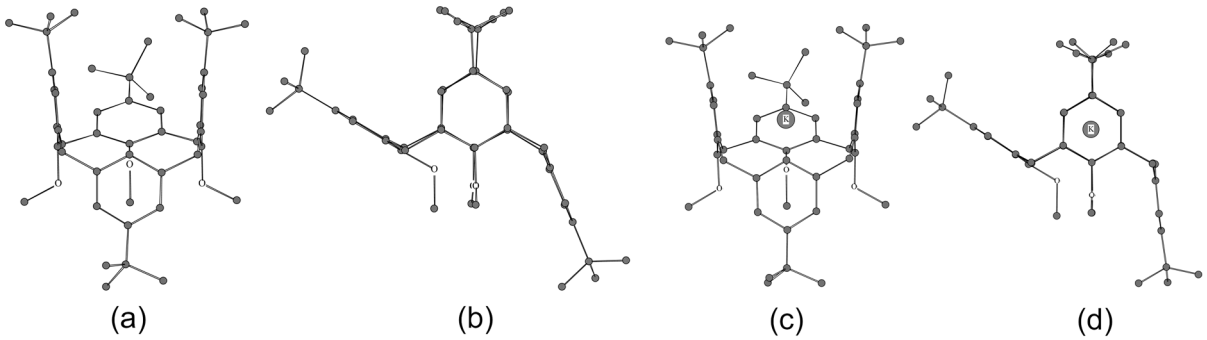


Figure 2. *Ab initio* calculated structures of the 1-partial cone conformer of **6**: (a) front view of 1-PACO (uuu<u>d</u>) host, (b) side view of 1-PACO (uuu<u>d</u>) host, (c) front view of 1-PACO (uuu<u>d</u>) complex, (d) side view of 1-PACO (uuu<u>d</u>) complex: 2A+1O.

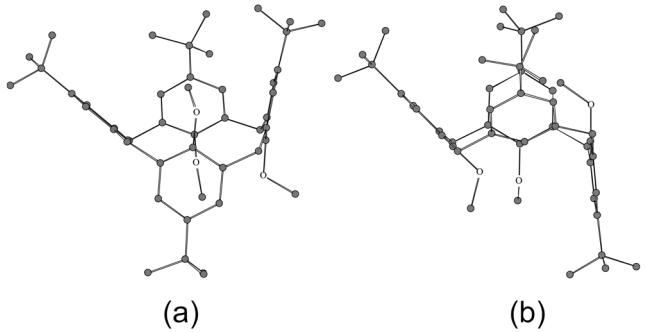


Figure 3. *Ab initio* calculated structures of the 2i-partial cone conformer of **6**: (a) front view of 2i-PACO (uudi<u>u</u>) host, (b) side view of 2i-PACO (uudi<u>u</u>) host.

monodeoxycalix[4]arene backbone to reach the more stable *endo*-position during the molecular dynamics and geometry optimizations.

In order to observe the effect of the cation-π interactions in the various calix[4]aryl complexes with potassium ion, we have compared the calculated C-C bond distances in the arenes of the host with those values in the arenes of the complexes. Table 3 shows the average values of six C-C distances (Å) in the arenes of the uncomplexed host and the complexes in a series of calix[4]aryl derivatives **1** through **7**.[27] The calculated C-C bond distances in the arenes of K^+-complexes are about 0.0048 Å longer than the values of their hosts, since the donation of electron density from the ring to the potassium cation makes the C-C bonds weaker.

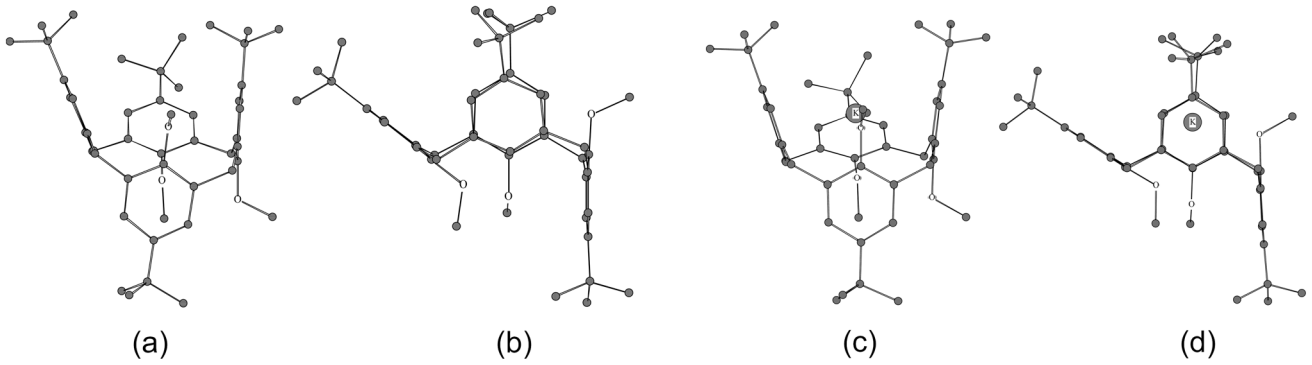


Figure 4. *Ab initio* calculated structures of the 2-partial cone conformer of **6**: (a) front view of 2-PACO (uud<u>u</u>) host, (b) side view of 2-PACO (uud<u>u</u>) host, (c) front view of 2-PACO (uud<u>u</u>) complex, (d) side view of 2-PACO (uud<u>u</u>) complex: 2A+2O.

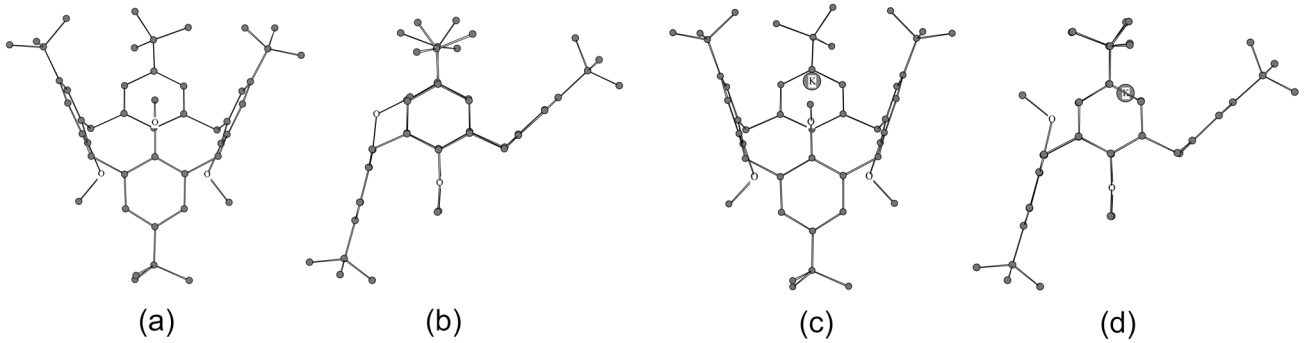


Figure 5. *Ab initio* calculated structures of the 3i-partial cone conformer of **6**: (a) front view of 3i-PACO (udiu<u>u</u>) host, (b) side view of 3i-PACO (udiu<u>u</u>) host, (c) front view of 3-PACO (udu<u>u</u>) complex, (d) side view of 3-PACO (udu<u>u</u>) complex: $2A_{weak}$+1O.

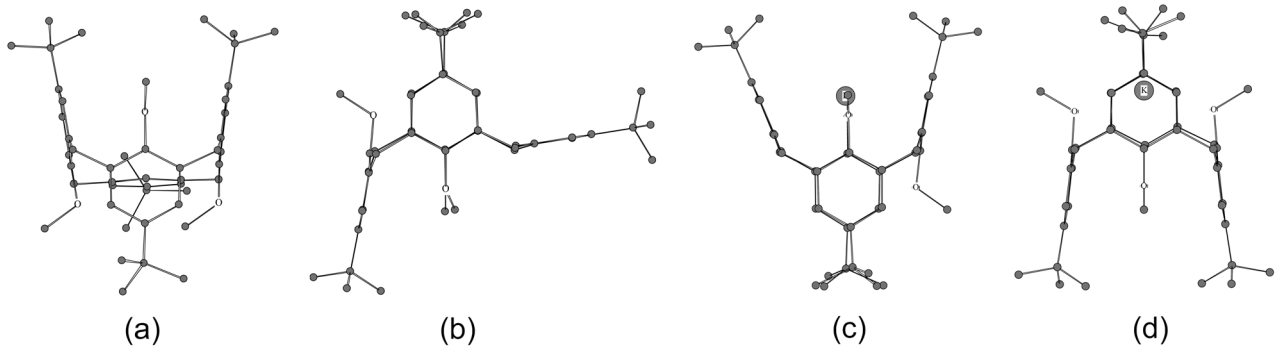


Figure 6. *Ab initio* calculated structure of the 1,3-alternate conformer of **6**: (a) front view of 13-ALT (uidud) host, (b) side view of 13-ALT (uidud) host, (c) front view of 13-ALT (dudu) complex, (d) side view of 13-ALT (dudu) complex: 2A+2O.

Table 2. *Ab Initio* RHF/6-31G and B3LYP/6-31G(d,p) Calculated Energies (kcal/mol) of **6**+K^+ Complexes

Method \ Conformation	Cone	1-Paco	2-Paco	3-Paco	1,3-Alt
Notation in Ref. 10	uuuu	uuud	uudu	uduu	dudu
Figures	1(c) and 1(d)	2(c) and 2(d)	4(c) and 4(d)	5(c) and 5(d)	6(c) and 6(d)
Binding Modes	2A+1O[a]	2A+1O[b]	2A+2O[c]	$2A_{weak}$+1O[d]	2A+2O[e]
HF/6-31G Optimized	−1655835.79	−1655828.36	−1655841.13	−1655832.18	−1655842.19
HF/6-31G (relative)	6.40	13.83	1.06	10.01	0.00
B3LYP/6-31G(d,p) Optimized	−1665313.12	−1665309.10	−1665316.24	−1665312.14	−1665316.17
B3LYP/6-31G(d,p) (relative)	3.12	7.14	0.00	4.10	0.07

[a]Cone complex of **6**+K^+ with two strong cation-π interactions and one strong cation-oxygen interaction. [b]1-Partial-cone complex of **6**+K^+ with two strong cation-π interactions and one strong cation-oxygen interaction. [c]2-Partial-cone complex of **6**+K^+ with two strong cation-π interactions and two strong cation-oxygen interactions. [d]3-Partial-cone complex of **6**+K^+ with two weak cation-π interactions and one strong cation-oxygen interaction. [e]1,3-Alternate complex of **6**+K^+ with two strong cation-π interactions and two strong cation-oxygen interactions.

Table 3. RHF/6-31G Optimized C-C Bond Distances (Å)[a] in the Arenes of Calix[4]arene Derivatives and Their Complexes with Potassium Cation, and the Distances (Å) of K^+-Arene Centroid

Compound	Reference	C-C Bond Distance			K^+…Centroid
		Host	*Endo*-K^+-Complex	Difference	
1	Recalc.	1.3895			
2	Recalc.	1.3907			
3	10	1.3908			
4	23	1.3910	1.3960	0.0050	2.9300
6	This study	1.3907	1.3952	0.0045	3.0423
7	27	1.3910	1.3958	0.0048	3.0040
Average		1.3906	1.3957	0.0048	2.9921

[a]Error limits in these calculations are about 0.0005 Å

Table 4. Optimized C-C Bond Distances (Å) in Benzene and its K^+-Complex, and the Distances (Å) of K^+-Benzene Centroid

Calculation Method[17]	C-C Bond Distance			K^+…Centroid
	Benzene	Benzene+K^+ Complex	Difference	
RHF/6-311G*	1.386	1.390	0.004	2.992
MP2/6-311+G*	1.400	1.404	0.004	2.890
SVWN/ TZ94p	1.394	1.398	0.004	2.769
BP86/TZ94p	1.407	1.411	0.004	2.972

Table 4 shows the similar data including higher-level *ab initio* calculations for benzene and its K^+-complex.[17] The C-C bond distance in the K^+-benzene complex is always 0.0040 Å longer than the values of the isolated benzene, which is very similar to the average value (0.0048 Å) of calix[4]aryl derivatives **1** through **7**. Table 4 also suggests that the C-C bond distances of both the uncomplexed and the complexed benzenes obtained from the HF calculation are

Table 5. Experimental C-C Bond Distances (Å) in the Arenes of Calix[4]aryl Derivatives

Compound	CSD[31] entry			C-C Bond Distance
	Refcode	Ref.	Guest	Host Only
1	DACMAV	29(a)	none	1.3909
2	CUPWAL	29(b)	none	1.3854
4	SEKBEP	29(c)	none	1.3891
Host Average				1.3885
				Endo-Complexes
2+K^+	HOSVOA	30(a)	K^+(*endo*)/W(exo)	1.3973
2+Na^+	MODYIN	30(b)	Na^+(*endo*)	1.4013
5+Na^+	RIRNAH	30(c)	Na^+(*endo*)	1.3937

Table 6. RHF/6-31G Optimized C-C Bond Distances (Å) in the Arene *vs.* Distance between K^+ and the Arene Centroid of *endo*-Complex

Compound	K^+... Arene Centroid	C-C Bond Distance in Arene
4+K^+(cone)	2.929	1.3958
4+K^+(cone)	2.931	1.3960
6+K^+(cone)	2.980	1.3952
6+K^+(cone)	2.982	1.3950
6+K^+(1-paco)	2.875	1.3963
6+K^+(1-paco)	2.870	1.3966
6+K^+(2-paco)	3.014	1.3941
6+K^+(2-paco)	2.987	1.3944
6+K^+(3-paco)	3.269	1.3923
6+K^+(3-paco)	3.169	1.3922
6+K^+(1,3-alt)	3.076	1.3959
6+K^+(1,3-alt)	3.019	1.3960
6+K^+(1,3-alt,*exo*)	3.089	1.3941
6+K^+(1,3-alt,*exo*)	3.081	1.3942
7+K^+(cone)	2.957	1.3958
7+K^+(cone)	2.963	1.3958
7+K^+(paco)	2.974	1.3953
7+K^+(paco)	2.955	1.3952
7+K^+(1,3-alt)	3.089	1.3952
7+K^+(1,3-alt)	3.086	1.3952

normally 0.014 Å shorter than the values obtained from a MP2 method.

Experimental data on the structures of calix[4]aryl complexes with potassium cation are scarce.[28] Table 5 shows some experimental C-C bond distances (Å) in the arenes of calix[4]aryl hosts[29] and their complexes[30] with alkali metal ions obtained from the Cambridge Structure Database.[31] The average (1.3885 Å) of the experimental C-C distances in the arenes of hosts is very close to the calculated value (1.3906 Å) in Table 3. Although the calix[4]aryl complexes with alkali metal ions in Tables 3 (calculation) and Table 5 (experiment) do not have the same cations, the trend of the elongated distances in the calix[4]aryl complexes from the uncomplexed derivatives is clearly identified in the values obtained from both the calculation and the experimental data.

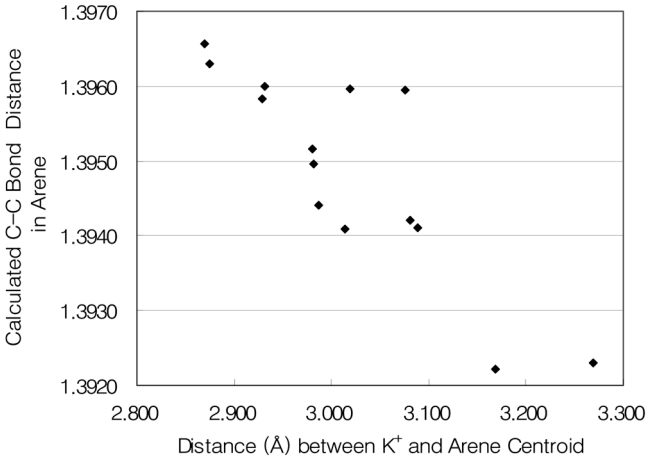


Figure 7. Plotting patterns of the C-C bond distance in the arene versus the K^+-centroid distance in calix[4]aryl derivatives **4**, **6** and **7** obtained from the RHF/6-31G calculations.

To display the dependence of the strength of the cation-π interactions on the distance between the cation and the arene centroid, we have tabulated the calculated C-C bond distance versus the K^+-centroid distance in calix[4]aryl derivatives **4**, **6** and **7** in Table 6 along with the plotting patterns in Figure 7 by using the RHF/6-31G calculations. These relationships clearly reveal that the shorter K^+-centroid distance makes the C-C bond distance longer with stronger cation-π interaction. The calculated and experimental C-C bond distances of the calix[4]aryl hosts and their K^+-complexes very clearly suggest that strong cation-π interactions exist between the potassium cation and the arenes.

Conclusion

Ab initio computer simulations were carried out to investigate the conformational and complexation characteristics of the trimethyl ether of *p-tert*-butylmonodeoxycalix[4]arene (**6**) with a potassium ion. The structures of different conformers of **6** and their potassium complexes were optimized by using RHF/6-31G and B3LYP/6-31G(d,p) methods. The relative stability of the various conformers of **6** is in the following order: cone (most stable) > 1-partial-

cone ~ 2i-partial-cone > 2-partial-cone ~ 1,3-alternate > 3i-partial-cone. However, cation-π interactions and cation-oxygen interactions make the relative stability of the conformational complexes of **6**+K^+ different from those of the host, in the following order: 2-partial cone ~ 1,3-alternate > cone > 3-partial cone > 1-partial cone (least stable). The calculated C-C bond distances in the arenes of K^+-complexes are about 0.0048 Å longer than the values of their hosts. The calculated and experimental C-C bond distances of the calix[4]aryl hosts and their K^+-complexes very clearly suggest that strong cation-π interactions exist between the potassium cation and the arenes of the host.

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