Articles

DFT Study for Azobenzene Crown Ether *p-tert*-Butylcalix[4]arene Complexed with Alkali Metal Ion

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Stable molecular isomers were calculated for the azobenzene crown ether *p-tert*-butylcalix[4]arene (**1**) in the host and their alkali-metal-ion complexes. The structures of two distinct isomers (*cis* and *trans*) have been optimized using *DFT* B3LYP/6-31G(d,p) method. *Trans* isomer of **1** is found to be 11.69 kcal/mol more stable than *cis* analogue. For two different kinds of complexation mode, the alkali-metal-cation in the crown-ether moiety (*exo*) has much better complexation efficiency than in the benzene-rings (*endo*) pocket for both isomers of **1**. Sodium ion has much better complexation efficiency than potassium ion in all kinds of complexation mode with host **1**. The Na^+ complexation efficiency of the *trans*-complex (**1**) in the *exo*-binding mode is 8.24 kcal/mol better than *cis-exo* analogue.

Key Words : Azobenzene calix[4]crown-ether, Complexation, Alkali metal ion, *DFT* B3LYP/6-31G(d,p)

Introduction

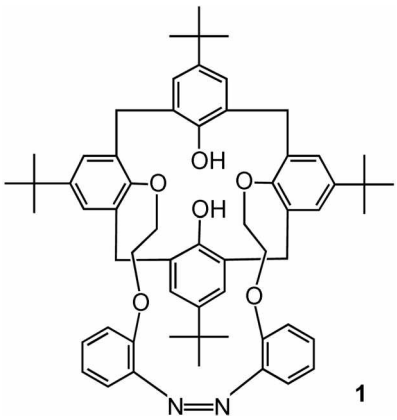
Calix[4]crown ethers and related derivatives that have calix[4]arene[1] moiety as a subcyclic unit of crown ether are well studied, and their ion-binding properties toward alkali and alkaline earth metal cations have been characterized.[2] Several different host compounds based on the calix-crown framework, including selective chromoionophores for alkali metal ion[3] and double-calix-crowns,[4] have been prepared and their interesting ionophoric properties were investigated.

1,3-Dimethyl ether of *p-tert*-butylcalix[4]crown-5-ether has shown a surprisingly high K^-/Na^+ selectivity in extraction.[5] Recently, *endo*- or *exo*-complexation of calix[4]arene with alkali metal cations has been analyzed by HF, MP2 and DFT calculations.[6]

Azobenzenes have been incorporated into a number of supramolecular frameworks to produce ionophores for transports and photo-switchable receptors.[7] They are interested in constructing a switchable molecular system which can selectively bind Na^+ or K^- mimicking the biological Na^-/K^+ pump.[7(b),(c)]

We have undertaken the relative binding affinity study of cone-shaped *p-tert*-butylcalix[4]aryl esters toward alkali metal cations focusing on the binding site of upper or lower-rim pocket of the host molecule using *DFT* calculation method.[8] The B3LYP/6-31G(d) calculation suggested that *exo*-complexation efficiency of alkali metal ion inside the cavity of lower rim of *p-tert*-butylcalix[4]aryl esters was much better than the *endo*-complexation inside the upper rim (four aromatic rings).

Recently, we have calculated the relative stabilities and stable structures of three different (cone, partial cone and 1,3-alternate) conformers for the 1,3-dialkyl ether of *p-tert*-butylcalix[4]crown-5-ether[9(a),(b)] and their potassium-cation complexes using the B3LYP/6-31G(d,p) method, and also for the conformers of 1,3-dimethyl ether of *p-tert*-butylcalix[4]arene crown ether bridged at the lower rim with pyridyl unit[9(c)] and their K^- complexes. In their *DFT* calculations, *exo*-complexes in crown cavity were 20-30 kcal/mol more stable than *endo*-analogues.



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Scheme 1. Chemical drawing of the *cis* isomer of azobenzene crown ether *p-tert*-butylcalix[4]arene (**1**).

The first objective of this research is to determine the relative stability of *cis*/*trans* isomers for the azobenzene crown ether *p-tert*-butylcalix[4]arene (**1**)[7(c)] by using *DFT* B3LYP/6-31G(d,p) calculations. The second objective is to compare the relative complexation efficiencies of their *endo*/*exo* alkali-metal-ion complexes of **1**. And the third objective is to investigate the characteristics of cation-oxygen (nitrogen) and cation-π interactions in the various complexes.

Computational Methods

The initial isomers of azobenzene crown ether *p-tert*-butylcalix[4]crown-ether (**1**) were constructed by HyperChem.[10] In order to find optimized structures, we executed conformational search by simulated annealing method.[11] The alkali-metal-ion complexes of **1** were fully re-optimized using *DFT* B3LYP/6-31G(d,p) methods to estimate the absolute and relative energies for the different complexes after semi-empirical AM1 energy minimization. The *DFT* optimizations of *cis*/*trans* isomers of host **1** and their alkali-metal-ion complexes of **1** by Gaussian 98[12] were done with error limit of less than 0.01 kcal/mol (2×10^{-6} atomic unit (A.U.)) for each structure.

Results and Discussion

The *DFT* B3LYP/6-31G(d,p) calculations without any constraint were carried out for two isomers of the host **1**. The *DFT* optimizations were also carried out for two kinds of complexation mode for each isomer: combining *cis* or *trans* isomer of **1** with an alkali metal ion in two different locations (the crown-ether (*exo*) or benzene-rings (*endo*) pocket) of **1**. Table 1 reports the B3LYP/6-31G(d,p) optimized energies of the *cis* and *trans* isomers of host (**1**) and four different complexes in two different binding modes.

The calculations suggest that *trans* isomer of **1** is found to be 11.69 kcal/mol more stable than *cis* analogue due to the steric hinderance of benzene rings.

When one compares the relative binding efficiencies of the complexes for the two different alkali metal ions in Table 1, the sodium ion has much better (~10-50 kcal/mol) complexation efficiency than potassium ion in all four kinds of complexation mode with host **1**. Particularly, the *exo*-complexes show more prominent differences. For examples, the sodium $\mathbf{1}_{cis}$-*exo*-complex ($\mathbf{1}_{cis}$•Na^-_{exo}) is 56.96 kcal/mol more efficient than the potassium analogue ($\mathbf{1}_{cis}$•K^+_{exo}), and the sodium $\mathbf{1}_{trans}$-*exo*-complex ($\mathbf{1}_{trans}$•Na^-_{exo}) is 47.77 kcal/mol better than the K^+ analogue ($\mathbf{1}_{trans}$•K^+_{exo}). Primary reason of these huge differences in the binding efficiencies is the difference between the binding energies of Na^- and K^+ per cation-oxygen interaction (The cation-oxygen binding energies are reported as −26.2 (Na^-) and −18.1 (K^-) kcal/mol when a cation is binding to the O-H group of phenol from the HF/6-311G(d,p) calculation.).[14] Also, the conditions between calculation (in vacuum) and experimental environment[7(c)] (in solution) are different. One should note that in the gas phase it is natural that smaller cationic species such as Na^- should have higher binding energy than larger K^- cation. However, in the presence of aqueous or polar solvents, a specific size of cations (rather than a smaller ion) would more selectively bind receptors.[19]

When one compares the relative stabilities of the complexes for the different guest positions in Table 1, the sodium ion in the crown-ether moiety (*exo*) has better (~20 kcal/mol) complexation efficiencies than in the benzene-rings (*endo*) pocket for both isomers of **1**. For example, the *trans exo*-complex ($\mathbf{1}_{trans}$•Na^+_{exo}) is 22.07 kcal/mol more stable than the *trans endo*-complex ($\mathbf{1}_{trans}$•Na^-_{endo}), and the *cis exo*-complex ($\mathbf{1}_{cis}$•Na^-_{exo}) is 25.29 kcal/mol more stable than the *cis endo*-complex ($\mathbf{1}_{cis}$•Na^+_{endo}). The weaker *endo*-complexation efficiencies are originated from the fewer number of electrostatic interactions of the sodium cation with ligand sites of oxygen and nitrogen atoms. However, the potassium ion in the benzene-rings (*endo*) pocket has better (8-21 kcal/mol) complexation efficiencies than in the crown-ether moiety (*exo*) for the isomers of **1**, due to the fewer number of electrostatic interactions of the potassium ion in the *exo*-position.

The *trans* complexes of **1** are found to be more stable (about 8-17 kcal/mol) than the *cis* analogues of **1** toward alkali metal ions. For example, the *trans*-complex ($\mathbf{1}_{trans}$+Na^-_{exo}) is 8.14 kcal/mol more stable than the *cis*-complex ($\mathbf{1}_{cis}$•Na^-_{exo}), and the *trans*-complex ($\mathbf{1}_{trans}$+K^+_{exo}) is 17.33 kcal/mol more stable than the *cis*-complex ($\mathbf{1}_{cis}$•K^+_{exo}).

Figures 1(a) and 1(b) show the *trans* and *cis* isomers of the free host **1**, respectively. Figures 1(c) and 1(d) display their (*trans* and *cis*) sodium complexes in *exo*-mode, and Figures 1(e) and 1(f) display their sodium complexes in *endo*-mode, respectively. When one sees the Figure 1(d) of the *cis*-complex ($\mathbf{1}_{cis}$•Na^+_{exo}), all of the nitrogen and oxygen atoms in the crown-ether moiety are symmetrically converged to the center of the crown-ether ring due to the strong electrostatic attraction from sodium cation. The Figure 1(e) of the *trans endo*-complex ($\mathbf{1}_{trans}$•Na^-_{endo}) displays the cation-π interactions from sodium cation to the π electrons of two benzene rings whose planes are almost parallel to each other. When one sees the Figure 1(f) of the *cis endo*-complex

Table 1. *DFT* B3LYP/6-31G(d,p) Energies[a] of Host (**1**) and Different Complexes with Alkali Metal Ions

B3LYP/6-31G(d,p) Calculated		Alkali metal guest	
		Na^-	K^-
		−162.0812	−599.7250
Host Energy	Binding mode[b]	Complex Energy	
−2889.4454	Host($\mathbf{1}_{cis}$)•Guest (*exo*)	−3051.6620	−3489.2150
	Host($\mathbf{1}_{cis}$)•Guest (*endo*)	−3051.6217	−3489.2491
−2889.4640	Host($\mathbf{1}_{trans}$)•Guest (*exo*)	−3051.6936	−3489.2612
	Host($\mathbf{1}_{trans}$)•Guest (*endo*)	−3051.6584	−3489.2749
		Complexation Energy ($\Delta E_{complex}$)[c]	
Host($\mathbf{1}_{cis}$)•Guest (*exo*) complexation		−84.91	−27.95
Host($\mathbf{1}_{cis}$)•Guest (*endo*) complexation		−59.62	−49.35
Host($\mathbf{1}_{trans}$)•Guest (*exo*) complexation		−93.05	−45.28
Host($\mathbf{1}_{trans}$)•Guest (*endo*) complexation		−70.98	−53.86

[a]Error limits in these calculations are about 2×10^{-5} a.u. Units for the *DFT* energies of hosts, guests and complexes are reported in hartrees (a.u.), and units for the complexation energies are shown in kcal/mol, converted using conversion factor 1 a.u. = 627.50955 kcal/mol. [b]*exo* indicates crown-ether pocket binding, and *endo* means benzene-rings pocket mode. Host($\mathbf{1}_{cis}$) means the *cis* isomer of 1. Host($\mathbf{1}_{trans}$) denotes the *trans* isomer of 1. [c]$\Delta E_{complex}$ is defined as the energy of the complex minus the sum of the energies of the cation and the free ligand isomer.

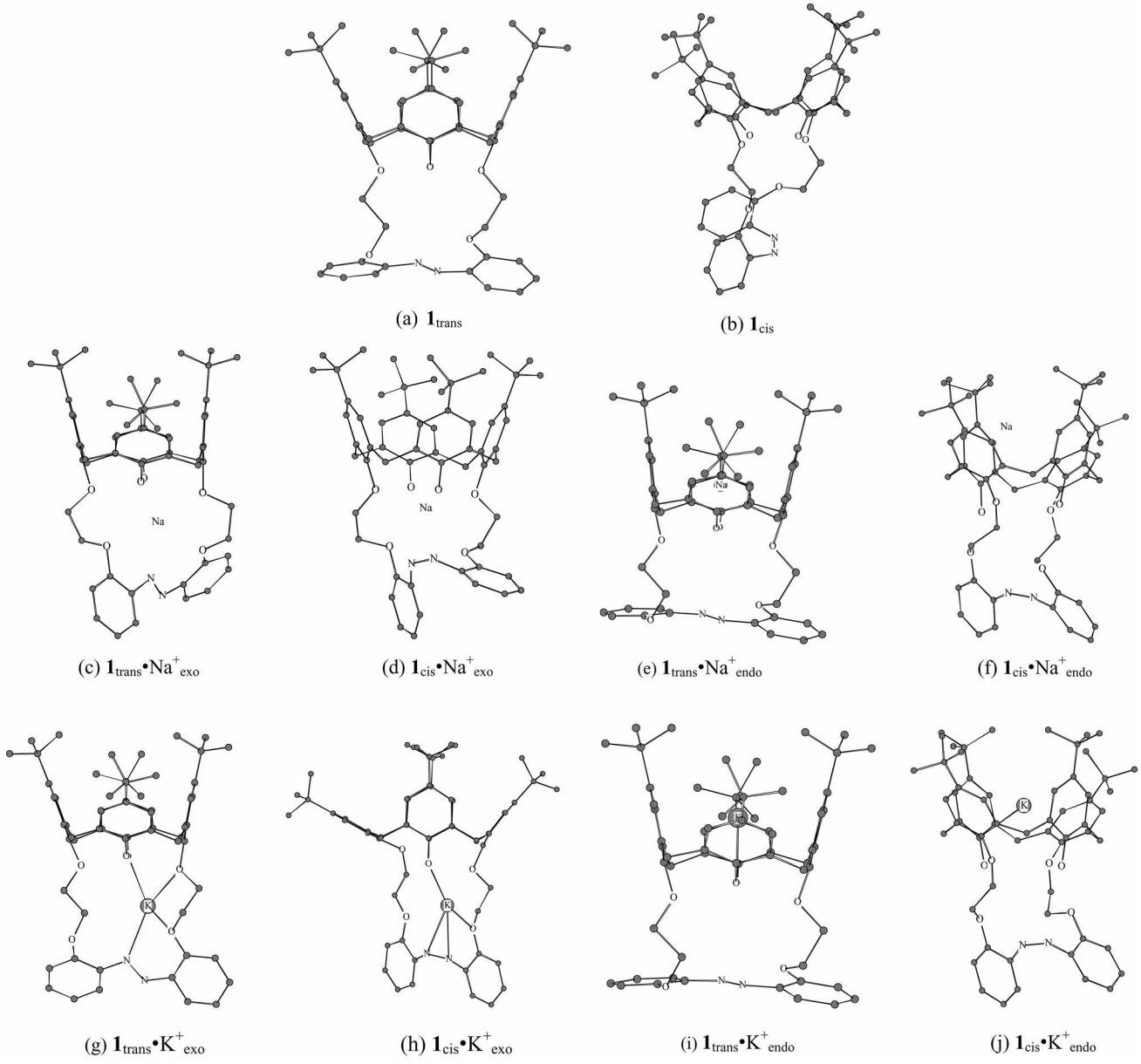

Figure 1. *DFT* calculated structures of *trans* and *cis* isomers of host **1** and their alkali-metal-ion complexes: (a) *trans* and (b) *cis* isomers of the free host **1**, (c) *trans exo*-complex ($\mathbf{1}_{trans}$•Na^-_{exo}), (d) *cis exo*-complex ($\mathbf{1}_{cis}$•Na^+_{exo}), (e) *trans endo*-complex ($\mathbf{1}_{trans}$•Na^-_{endo}), (f) *cis endo*-complex ($\mathbf{1}_{cis}$•Na^+_{endo}), (g) *trans exo*-complex ($\mathbf{1}_{trans}$•K^-_{exo}), (h) *cis exo*-complex ($\mathbf{1}_{cis}$•K^+_{exo}), (i) *trans endo*-complex ($\mathbf{1}_{trans}$•K^+_{endo}) (j) *cis endo*-complex ($\mathbf{1}_{cis}$•K^+_{endo}). Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.[13]

($\mathbf{1}_{cis}$•Na^-_{endo}), the sodium cation is shifted and more closely coordinated with two *tert*-butylbenzyl groups in the calix[4]-arene moiety of the host due to the cation-π interactions.

When one sees the Figure 1(g) of the *trans*-complex ($\mathbf{1}_{trans}$•K^+_{exo}), one of the nitrogen atoms and three of the oxygen atoms in the crown-ether moiety are converged to potassium cation due to the electrostatic attractions. When one sees the Figure 1(h) of the *cis*-complex ($\mathbf{1}_{cis}$•K^+_{exo}), both of the nitrogen and some of oxygen atoms in the crown-ether moiety are converged to the center of the crown-ether ring due to the electrostatic attraction from potassium cation. The Figure 1(i) of the *trans endo*-complex ($\mathbf{1}_{trans}$•K^-_{endo}) displays the cation-π interactions from potassium cation to the π electrons of two benzene rings. where planes are not parallel as much as the Figure 1(e) of the sodium-complex ($\mathbf{1}_{trans}$•Na^-_{endo}). When one sees the Fig. 1(j) of the *cis endo*-complex ($\mathbf{1}_{cis}$•K^+_{endo}). the potassium cation is coordinated with all four *tert*-butylbenzyl groups in the calix[4]arene moiety of the host due to the bigger diameter of K^- (2.66 Å) than Na^+ (1.90 Å).

The binding energies in the complexations of alkali metal cations with the host **1** are coming from cation-π interactions in benzene rings and cation-oxygen(nitrogen) interactions in crown-ether. The B3LYP/6-31G(d) calculations suggest that cation-π binding energy is −27.4 kcal/mol when Na^- is binding to a benzene ring, and that cation-π interaction

Table 2. *DFT* Calculated Distances (Å) between Alkali Metal Cation and the Oxygen and Nitrogen Atoms of Host(**1**) in the *exo*-Complex

	Na^+-Complex		K^--Complex	
Distance from Cation	$\mathbf{1}_{trans}$•Na^+	$\mathbf{1}_{cis}$•Na^-	$\mathbf{1}_{trans}$•K^+	$\mathbf{1}_{cis}$•K^-
Ether-Oxygen (1)	2.437	2.951	2.660	2.719
Ether-Oxygen (2)	2.490	2.920	2.914	
Ether-Oxygen (3)	2.700	2.774		
Ether-Oxygen (4)		2.865		
Ave. Ether-Oxygen	2.542	2.878	2.787	2.719
Hydroxy Oxygen (1)	2.388	2.234	2.580	2.667
Hydroxy Oxygen (2)	2.589	2.277		
Ave. Hydroxy Oxygen	2.489	2.256	2.580	2.667
Nitrogen (1)	2.622		2.883	2.872
Nitrogen (2)				2.889

energy is −17.3 kcal/mol for K^- with the benzene.[15] The MP2/6-311+G(d) calculations suggest that cation-π interaction energy is −18.7 kcal/mol for K^+ with the benzene ring of anisole, and that cation-oxygen binding energy is −19.4 kcal/mol when K^- is binding to the anisole oxygen.[16,17]

To understand the cation-oxygen (nitrogen) interactions of the complexes of **1**, we have measured the distances from the alkali-metal-cation to the nitrogen and oxygen atoms of the host **1**. (See Table 2).

An interesting fact deduced from the Table 2 is that the average distance (2.256 Å) between Na^+ and the hydroxy oxygen atoms of *cis*-isomer of **1** in *exo*-binding mode is much (0.622 Å) shorter than the average value (2.878 Å) between Na^+ and the crown-ether-oxygen atoms of the host. This suggest that the electrostatic attraction between Na^+ and the methoxy oxygen is much stronger, since the movement of hydroxy-oxygen atom is relatively free compared to the oxygen atoms of the crown-ether framework. BLYP/6-31G(d,p) calculation suggests that the optimized binding distance between Na^+ and the oxygen atom of dimethylether is 2.197 Å.[18]

Conclusion

DFT B3LYP/6-31G(d,p) calculations suggest that *trans* isomer of **1** is found to be 11.69 kcal/mol more stable than *cis* analogue. The alkali-metal-cation in the crown-ether moiety (*exo*) has much better (~20 kcal/mol) complexation efficiency than in the benzene-rings (*endo*) pocket for both isomers of **1**. Sodium ion has much better (~10-50 kcal/mol) complexation efficiency than potassium ion in all kinds of complexation mode with host **1**. The Na^+ complexation efficiency of the *trans*-complex (**1**) in the *exo*-binding mode is 8.25 kcal/mol better than *cis-exo* analogue. The number of cation-oxygen(nitrogen) interactions in crown-ether ring and hydroxy groups with alkali-metal-cation was crucial to the stability of the *cis*/*trans* isomers of **1**•Na^+ or **1**•K^+ complex.

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