Articles

DFT Study for Azobenzene Crown Ether \( p\text{-}t\text{ert}-\text{Butylcalix[4]arene} \) Complexed with Alkali Metal Ion

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Stable molecular isomers were calculated for the azobenzene crown ether \( p\text{-}t\text{ert}-\text{butylcalix[4]arene} \) in the host and their alkali-metal-ion complexes. The structures of two distinct isomers (cis and trans) have been optimized using \( \text{DFT B3LYP/6-31G(d,p)} \) 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, \( \text{DFT B3LYP/6-31G(d,p)} \)

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 \( p\text{-}t\text{ert}-\text{butylcalix[4]arene} \) 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.\(^7\) We have undertaken the relative binding affinity study of cone-shaped \( p\text{-}t\text{ert}-\text{butylcalix[4]arene} \)aryl esters toward alkali metal cations focusing on the binding site of upper or lower-rim pocket of the host molecule using \( \text{DFT calculation method.} \) The B3LYP/6-31G(d) calculation suggested that exo-complexation efficiency of alkali metal ion inside the cavity of lower rim of \( p\text{-}t\text{ert}-\text{butylcalix[4]arene} \)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 \( p\text{-}t\text{ert}-\text{butylcalix[4]arene} \) crown ether bridged at the lower rim with pyridyl unit\(^9\) and their potassium-cation complexes using the B3LYP/6-31G(d,p) method, and also for the conformers of 1,3-dimethyl ether of \( p\text{-}t\text{ert}-\text{butylcalix[4]arene} \) crown ether bridged at the lower rim with pyridyl unit\(^9\) and their K\(^+\) complexes. In their \( \text{DFT calculations, exo-complexes in crown cavity were 20-30 kcal/mol more stable than endo-analogues.} \)

The first objective of this research is to determine the relative stability of cis/trans isomers for the azobenzene crown ether \( p\text{-}t\text{ert}-\text{butylcalix[4]arene} \) (1).
Computational Methods

The initial isomers of azobenzene crown ether, p-tert-butylicalix[4]crown-ether (1) were constructed by HyperChem. In order to find optimized structures, we executed conformational search by simulated annealing method. The alkali-metal-ion complexes of I 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 I and their alkali-metal-ion complexes of I by Gaussian 98 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 I. The DFT optimizations were also carried out for two kinds of complexation mode for each isomer: combining cis or trans isomer of I with an alkali metal ion in two different locations (the crown-ether (exo) or benzene-rings (endo) pocket) of I. Table 1 reports the B3LYP/6-31G(d,p) optimized energies of the cis and trans isomers of host I and four different complexes in two different binding modes.

The calculations suggest that trans isomer of I 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 I. Particularly, the exo-complexes show more prominent differences. For examples, the sodium I_cis-exo-complex (I_cis\_Na evolution) is 56.96 kcal/mol more efficient than the potassium analogue (I_cis\_K evolution), and the sodium I_cis-exo-complex (I_cis\_Na evolution) is 47.77 kcal/mol better than the K' analogue (I_cis\_K' evolution). 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.).

Also, the conditions between calculation (in vacuum) and experimental environment (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.

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 I. For example, the trans exo-complex (I_trans\_Na evolution) is 22.07 kcal/mol more stable than the trans endo-complex (I_trans\_Na' evolution), and the cis exo-complex (I_cis\_Na evolution) is 25.29 kcal/mol more stable than the cis endo-complex (I_cis\_Na' evolution). 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 I, due to the fewer number of electrostatic interactions of the potassium ion in the exo-position.

The trans complexes of I are found to be more stable (about 8-17 kcal/mol) than the cis analogues of I toward alkali metal ions. For example, the trans-complex (I_trans\_Na evolution) is 8.14 kcal/mol more stable than the cis-complex (I_cis\_Na evolution), and the trans-complex (I_trans\_K' evolution) is 17.33 kcal/mol more stable than the cis-complex (I_cis\_K' evolution).

Figures 1(a) and 1(b) show the trans and cis isomers of the free host I, 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 (I_cis\_Na evolution), 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 (I_trans\_Na evolution) 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...
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When one sees the Figure 1(g) of the trans-complex (I\textsubscript{trans}•Na\textsuperscript{+}endo), one of the nitrogen atoms and three of the oxygen atoms in the crown-ether moiety are converged to the potassium cation due to the electrostatic attractions. When one sees the Figure 1(h) of the cis-complex (I\textsubscript{cis}•K\textsuperscript{+}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 (I\textsubscript{trans}•K\textsuperscript{+}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 (I\textsubscript{trans}•Na\textsuperscript{+}endo). When one sees the Fig. 1(j) of the cis endo-complex (I\textsubscript{cis}•K\textsuperscript{+}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\textsuperscript{+} (2.66 Å) than Na\textsuperscript{+} (1.90 Å).

The binding energies in the complexations of alkali metal cations with the host I 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\textsuperscript{+} is binding to a benzene ring, and that cation-π interaction

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**Figure 1.** DFT calculated structures of trans and cis isomers of host I and their alkali-metal-ion complexes: (a) trans and (b) cis isomers of the free host I, (c) trans exo-complex (I\textsubscript{trans}•Na\textsuperscript{+}exo), (d) cis exo-complex (I\textsubscript{cis}•Na\textsuperscript{+}exo), (e) trans endo-complex (I\textsubscript{trans}•Na\textsuperscript{+}endo), (f) cis endo-complex (I\textsubscript{cis}•Na\textsuperscript{+}endo), (g) trans exo-complex (I\textsubscript{trans}•K\textsuperscript{+}exo), (h) cis exo-complex (I\textsubscript{cis}•K\textsuperscript{+}exo), (i) trans endo-complex (I\textsubscript{trans}•K\textsuperscript{+}endo) (j) cis endo-complex (I\textsubscript{cis}•K\textsuperscript{+}endo). Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.13
energy is ~17.3 kcal/mol for K + with the benzene. 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.

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 the crown-ether framework is 2.256 Å. The Na + cation was crucial to the stability of the cis-exo analogue. The alkali-metal-cation in the crown-ether ring and hydroxy groups with alkali-metal-cation was crucial to the stability of the cis/trans isomers of 1.

### 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 +'s 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.

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### References


