Complexation of alkali metal ions with di and tri-propyl ether of P-tert-butyl-calix[4]arenes: ab initio approach

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ABSTRACT

The binding selectivity of di- and tri-propyl ether of p-tert-butyl-calix[4]arenes (1 and 2) with alkali metal ion have been investigated and the structure and complexation energies of a simplified host with alkali metal ions also have been optimized by ab initio HF/6-31G quantum mechanics method.

The binding selectivity of di- and tri-propyl ether of P-tert-butyl-calix[4]arenes (**1** and **2**) towards alkali cations, based on the stability constant values of the formed complexes, is in the order of $Cs^+ > Li^+ > Na^+ > Rb^+ > K^+$ and $Cs^+ > Li^+ > Rb^+ > Na^+ > K^+$, respectively. On the basis of the complex's enthalpy $\Delta H_{Complex}$, complexation efficiencies of Cs^+ and Li^+ are favored towards (**1** and **2**). The result suggests the electron-donating tendency of the hydroxyl group is effective especially on the smaller cations.

INTRODUCTION

Calixarenes are basket-shaped compounds of potential interest for host–guest complexation and biomimics /1-5/ and have received considerable attention as an interesting class of ionic and molecular binding hosts /2,4,6/.

Calixarenes are comformationally flexible compounds; depending upon the relative orientation of the para and phenolic sites, the tetramer can adopt four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate. But due to the strong intermolecular H bonding the etheric derivatives definitely favor the cone conformation /7/.

Since one of the main driving forces for studies of this class of compounds is their ability to coordinate metal ions, it is important in some cases to estimate the degree of selectivity of the calixarene hosts toward metal ions guests /8/.

Considerable researches indicate the ability of calixarene systems to interact with alkali metal ions /9-13/. It has been shown that most of the widely available molecular mechanics force fields could be used to give

very reasonable molecular structures for the various conformations available to calixarenes /14/, but the methods are rather less successful in predicting the energy ordering of the conformations which can be adopted by any given molecule /15,16/.

In this study we have used ab initio HF/6-31G quantum mechanical methods /17/ for computer simulation of the complexation behaviors of di- and tri-propyl ether of tertbutyl- calix[4]arenes toward alkali metal ions and the main emphasis of this research study is determining the selectivity of the calixarene host toward different alkali metal ion guests. We have tried to change the cavity size by using two different numbers of propoxy substituents in the lower rim of the calixarene molecules and also using alkali metal ions with different ionic radius and comparing the effect of the cavity size of the host with the ionic radius of the guests in the complexation Gibbs free energies.

The complexes typically contain more than 120 atoms, so that *ab-initio* methods are prohibitively expensive studies.

COMPUTATIONAL METHODS

We have chosen 25, 27, dipropoxy-26, 28, di hydroxy 5, 11, 17, 23, tetra-tert-butyl calix[4]arene, **1**, and 25, 26, 27, tripropoxy-28 hydroxy 5, 11, 17, 23, tetra-tert-butyl-calix[4]arene, **2**, for the ligand framework study, due to the existence of very few experimental and theoretical reports on its chelating abilities towards metal ions /13/. The structure of the studied calixarenes is shown in Figure 1.

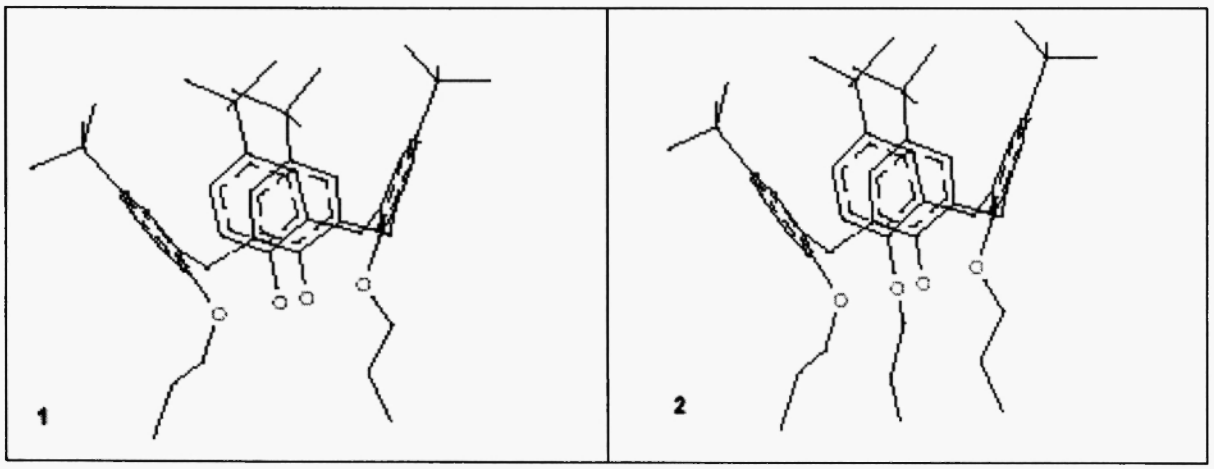

Fig. 1: Chemical structure of cone, di-propyl ether of p-tert-butyl-calix[4]ares (1) and tri-pr ·pyl ether of p-tert-butyl-calix[4]ares (2) in which hydrogen atoms are omitted for clarity

The experimental results have been shown that both ligands form exclusively 1:1 (ratio of metal ion to ligand) complexes with alkali metal anion /18/, so in all calculations we suppose that only one alkali metal ion is complexed with calixarenes ligands in each complex molecule.

The initial structures of host molecule and host–guest complexes for *ab initio* calculations were

constructed and studied with semi-empirical methods by Hyper Chem program /19/. Although it was already shown that due to the strong intermolecular H bonding these etheric derivatives definitely prefer the cone conformation /7/, the semi-empirical AM1 method /20/ in Hyper Chem /19/ was used to confirm that the most stable conformation is the Cone-type conformer /23/. Initially we tried to calculate the host together with guest ions, but this complex was too big to be optimized by the *ab initio* HF/6-31G method; therefore we had to change the tert-butyl group in the upper rim of the calix[4]arene to hydrogen atom To confirm that the final structure is in the local minimum point we have calculated the normal mode frequency of the optimized complex. Each vibrational spectrum shows no negative value of frequency, which suggests that the optimized structure is really at the minimum point.

Since the binding energy and enthalpy of formation are directly connected to the calculation of complex's energy ($E_{Complex}$ is exactly the same as the complexation enthalpy $\Delta H_{Complex}$), we report only the value of the calculated enthalpy.

Ab initio HF/6-31G took more than 160 hours to reach an optimized structure of host or its complexes by Gaussian 98.

All systems have been optimized in the Hartree-Fock level and were carried out using the Gaussian 98[8] program.

RESULTS AND DISCUSSION

We have performed *ab initio* quantum mechanical calculations for the complexation of di- and tri-propyl ether of tert-butyl-calix[4]arenes toward alkali metal ions.

As mentioned in the "Computational Methods" section, we could not calculate the whole structure of the host due to the memory size, but fortunately the smaller calix[4]aryl ether could be optimized using the HF/6-31G method.

Also, as the experimental results have shown that both ligands form exclusively 1:1 (ratio of metal ion to ligand) complexes with alkali metal anion /18/, in all calculations we use it as an initial assumption.

The selectivity ability of di and tri-propyl ether of P-tert-butyl-calix[4]arenes derivatives (**1**,**2**) of alkali metal ion was determined (Figure 2).

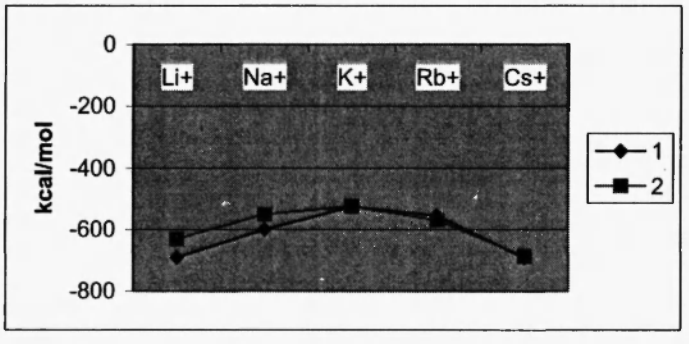

Fig. 2: Ab initio HF/6-31G energies of propoxy calix[4]arene complexes with alkali metal ion.

The calixarenes in this study all consist of four benzene rings which are arranged conically, so that hydroxyl and the propoxy groups form a coordination sphere where metal cations can be bound. The different substituents in the lower rim of the ligands change the ability of these molecules to tailor to different cavity sizes and rigidities and prepare them to have various preferences towards alkali cations complexation. Table-2 indicate the distances between the alkali metal ion and the mean plane of etheric-oxygen atoms of host (**1**, **2**).

Table 1

Ab initio HF/6-31G energies (kcal/mol) of propoxy calix[4]arene and the complexes with alkali metal ions

	Li^+	Na^+	K^+	K^+	Cs^+
Host 1	-690.01	-599.57	-525.43	-553.56	-568.03
Host 2	-630.39	-550.38	-523.61	-568.03	-686.24
Host 1	-508.89 (kcal/mol)		Host 2	-541.32 (kcal/mol)	

Table 2

Distances (A°) between the alkali metal ion and the mean plane of etheric-oxygen atoms of host (**1**, **2**)

	Li^+	Na^+	K^+	Rb^+	Cs^+
Host -1	63.12 A°	63.29 A°	63.49 A°	63.57 A°	63.80 A°
Host -2	61.12 A	61.33 A°	61.53 A°	61.76 A°	61.20 A°

From this, two different propoxy derivatives of calix[4]arene (**1**,**2**) show different affinities for small cations (Li^+ and Na^+) and large cations (Rb^+ and Cs^+).and it appears that host **1** is more efficient for chelating alkali metal ions and that the most stable complexes of **1** and **2** are formed with Cs^+.

The results of *ab initio* HF/6-31G energies for the 1:1 complexes of Host **1**,**2** and each metal ion are listed in Table 1. The results are in agreement with the experimental results /18/.

Between the two calixarenes, **1** appears to be more efficient for chelating alkali metal ions. The most stable complexes of **1** and **2** are formed with Cs^+.

The introduction of hydroxyl group in the ligands, from one to two, leads to an increase in the stability of the complexes formed by the smaller cations, Li^+ and Na^+, and practically no change in the stability of K^+, Rb^+, and Cs^+ complexes. This result suggests the electron-donating tendency of the hydroxyl group is effective especially on the smaller cations. The binding selectivity of **1** and **2** towards alkali cations on the stability constant values of the formed complexes, Table 1, is in the order of $Cs^+ > Li^+ > Na^+ > Rb^+ > K^+$ and $Cs^+ > Li^+ > Rb^+ > Na^+ > K^+$, respectively. The results suggest that K^+ could be possibly located near the cavity of **1** and hence be more shielded than the other ions, which better fit the cavity size of the ligand. Similar discussion can be stated for **2**. The binding selectivity of **1** and **2** towards Li^+, could be possibly due to the cavity sizes of the ligands and the stability constant values obtained in this work confirm that Li^+ should well encaged and protected by the ligands **1** and **2**, resulting in a higher formation constant and more

stable complexes.

Figure 3 shows the linear relationship of the distances between the alkali metal ions and the mean plane of etheric-oxygen atoms of host **1** , **2** in cone conformation.

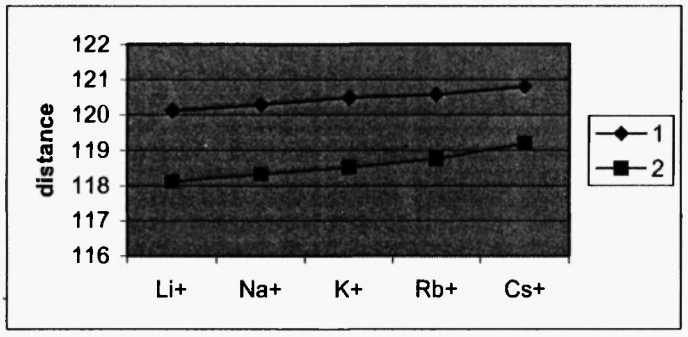

Fig. 3: Plot of distances between the alkali metal ion and the mean plane of etheric-oxygen atoms of host (**1, 2**) in cone conformation

It is shown that with increasing the alkali metal radius, it is located relatively farther away from the oxygen atoms of the ether groups, which causes it to be pushed into the aromatic rings of the calix[4]- arene framework.

However, in both cases Cs^+ appears to have a good tendency to chelate with the ligands. The results obtained in this work suggest Cs^+ possibly binds with the ligands and forms endo complexes, due to the participation of phenyl ɔelectrons with soft dispersion and induction interaction of a large soft cation.

Although the calculations are performed under quite different conditions of vacuum from the experimental results obtained, we believe that the present simulations provide a general and useful explanation for the molecular recognition behavior of the calix[4]arene derivatives toward alkali metal ions.

REFERENCES

1. V. Bohmer, *Angew. Chem., Int. Ed. Engl.*, **34**, 713 (1995).
2. C. D. Gutsche, In *Calixarenes*; Stoddard, F. J., Ed.; Supramolecular Chemistry, Royal Society of Chemistry: Cambridge, UK, 1989.
3. C. D. Gutsche, J. S. D. Rogers, D. Stewart and K.A. See, *Pure Appl.Chem.*, **62**, 485 (1990).
4. J. Vicens and V. Bohmer, *Calixarenes: a Versatile Class of Macrocyclic Compounds*, Kluwer, Dordrecht, 1990
5. M. A. Mckervey and V. Bohmer, Chem. Ber., **28**, 724 (1992)
6. X. Hu, Y. Chen, Z. Tian and Z. Xue, *J. Chem. Research (S)*, **1999**, 332-333.
7. S. Stumpf, G. Goretzki, Kerstin Gloe and Karsten Gloe. *J. Inclusion Phenomena Macrocycl. Chem.* **45**: 225–233 (2003).
8. J. Rebek, *Chem. Commun.*, **2000**, 637–643.

9.. I-P.Muhl and K Gloe, *Chem Tech.*, **41**, 457 (1989).

10. H.J.Bart, *Reactive Extraction*, Springer, Berlin, 2001.

11. J. Wickens, R.A.W. Dryfe, F.S. Mair, R. G. Pritchard, R.Hayes and D.W. M. Arrigan, *New J. Chem.*, **24**, 149-154 (2000).

12. A.F. Danil de Namor, A. Pugliese, A.R. Casal, M.B. Llerena, P.J. Aymonino and F.J.S. Velarde, *Phys. Chem. Chem. Phys.*, **2**, 4355-4360 (2000).

13. A.F. Danil de Namor, D. Kowalska, E.E. Castellano, O.E. Piro, F.J.S. Velarde and J.V. Salas, *Phys. Chem. Chem. Phys.*, **3**, 4010-4021 (2001).

14. V. Lamare, D. Haubertin, J. Golebiowski and J.F. Dozol, *J. Chem. Soc., Perkin Trans. 2*, **2001**, 121–127

15. F. Gharib, K. Zare and A. Taghvamanesh, *Main Group Met. Chem.* **25**, 647 (2002).

16. S.E.J. Bell, M.A. McKervey, D. Fayne, P. Kane and D. Diamond, *J. Mol. Model.* **4**, 44-52 (1998).

17. J.In Choe, S. Kyu Chang, M. Satoshi and S. Nanbu, *Bull. Korean Chem. Soc.* **24**, No. 1 (2003).

18. F. Gharib, K. Zare, S. Taghvaei, M. Monajjemi and A. Amiri, *Main Group Metal Chemistry*, **26**, 255 (2003).

19. *HyperChem Release 4.5*; Hypercube, Inc.: Waterloo, Ontario, Canada, 1995.

20. J.In Choe, K. Kim, S.Kyu Chang, *Bull. Korean Chem. Soc.* **21**, No. 2 (2000).