Ab Initio Study of the Complexation Behavior of Calix[6](aza)cryptand with Alkyl Ammonium Cations

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Received January 31, 2005

The structures and complexation energies of *p-tert*-butylcalix[6](aza)cryptand **1** with a series of alkylammonium cations have been calculated by using *ab initio* HF/6-31G method. After geometry optimizations, B3LYP/6-31G(d) single point calculations of the final structures are carried out including the effect of an electron correlation and the basis set with a polarization function. The calculated complexation efficiencies of **1** for alkylammonium guests are better than those of the previously reported calix[5]arenes, and much better than those of the calix[4]crown-6-ether. The calculation results show that calix[6](aza)cryptand also has much better complexation ability with smaller ammonium cations than with bulky alkylammonium guests. The structural characterizations of the calculated complexes are described as the function of the nature of the alkyl substituents of the ammonium guests.

Key Words : Calix[6](aza)cryptand, Alkylammonium ion, Complex, *ab initio* HF/6-31G, B3LYP/6-31G(d)

Introduction

Recently, calixarenes[1] have been receiving much attention as one of the most widely employed molecular frameworks for the construction of many versatile supramolecular systems.[2] The molecular recognition of organic ammonium guests is very important in view of the many functional biogenic ammonium ions, and a number of sophisticated host systems are derived from crown ethers and calixarenes.[3,4] Most of the previous studies showed that, whereas calix[4]arenes suffer from the smallness of their cavities, the larger calix[6]arenes are too flexible to provide a proper recognition for the alkylammonium cations.[1,5,6] Selective *endo*-calix complexation with alkylammonium cations by functionalized (1,3)-*p-tert*-butylcalix[5]crown ether[7] and by calix[5]arene-based molecular vessels **2**[8] has been reported. 1,3-Bridged calix[5]crown-6-ether was investigated as a tool for the shape recognition of alkylammonium ions in focusing the *endo*- versus *exo*-cavity complexation.[9] The cavity of calix[6]arene could not be exploited unless their flexibilities were restricted. Recently, Reinaud and Jabin have reported the three-step synthesis of the calix[6]arene capped with the TAC unit to immobilize the arms of the lower rim of calix[6]arene.[10,11] The *p-tert*-butylcalix[6]-(aza)cryptand, namely, calix[6]TAC **1** (TAC: 1,3,5-triazacyclohexane) showed an exceptionally high affinity for small alkylammonium ions.[11]

We have reported the *ab initio* calculation results for the molecular recognition behaviors of **2** (*tert*-butyl *p-tert*-butylcalix[5]aryl ester)[12] and its simplified structure **3** with a series of alkylammonium cations.[13] We have also studied the structures of **4** (*p-tert*-butylcalix[4]crown-6-ether) and their alkylammonium complexes by using the HF/6-31G method.[14] In this paper, we report the *ab initio* calculation results for the energies and structures of *p-tert*-butylcalix[6](aza)-cryptand and its alkylammonium complexes. The objective

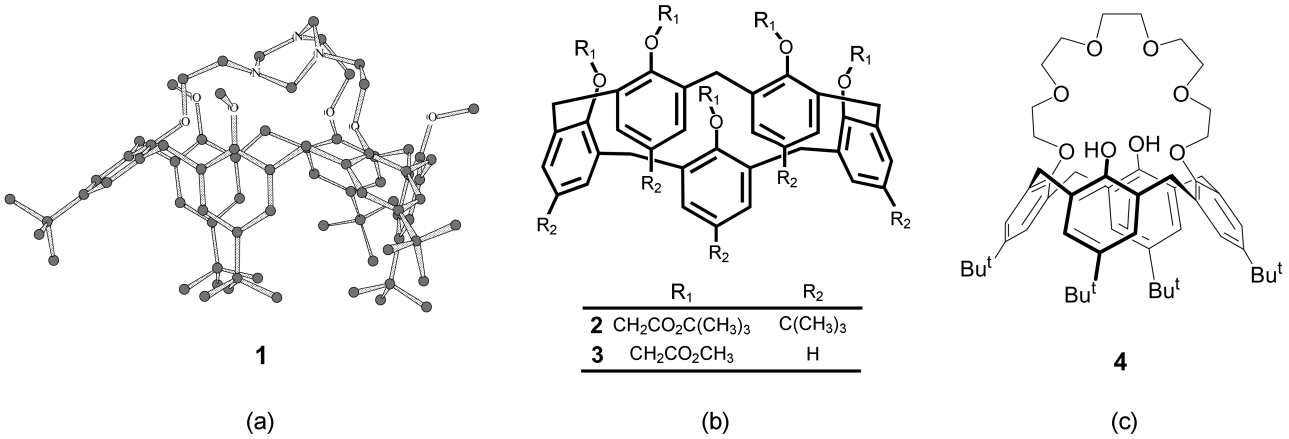


Figure 1. Chemical structures of (a) *p-tert*-butylcalix[6](aza)cryptand **1**, (b) calix[5]arene derivatives **2** and **3**, and (c) *p-tert*-butylcalix[4]crown-6-ether **4**. Hydrogen atoms are omitted except for the hydroxyl groups in Figure 1(c).

of this study is to determine the relative binding affinity of a cone-shaped host **1** with various alkylammonium guests and to compare the complexation efficiency of **1** with the previously calculated calixaryl derivatives **2-4** by using the *ab initio* HF/6-31G method.

Computational Methods

The initial structures of host and guest molecules were created by using HyperChem.[15] In order to find optimized conformations, we executed conformational searches by using the simulated annealing method described in previous research.[16] The *ab initio* HF/6-31G optimization, without any constraint of host **1** or its alkylammonium complexes, by using Gaussian 98[17] on a supercomputer (NEC SX-7) at the Okazaki National Research Institute of Japan took more than 3 days to reach the optimum conformation for each complex. After geometry optimizations, B3LYP/6-31G(d) single point calculations of the final structures were performed. Although we tried to use the bigger basis sets, the computational limits of the supercomputer did not allow us to calculate the higher quality data. The normal mode frequencies of the final structures also have been calculated. Each vibrational spectrum shows no negative value of frequency, which suggests that the optimized structure exists in the minimum point. The frequency analysis was a quite time and cost-consuming procedure because the host **1** has 192 nuclei and 570 ($192 \times 3 - 6$) vibrational modes. By using a supercomputer with the parallel processing of four CPU's, we could determine the vibrational frequencies after 10 days of non-stop calculation.

Results and Discussion

As we discussed in previous reports,[12,13] we have focused on explaining of the energetics and structural characteristics of the most stable *endo*-cone-shaped complexes of **1** with various alkylammonium ions. Our calculations might improve the understanding of the selective recognition behaviors of calixarene-based hosts for the recognition of a variety of important biogenic amines.

Table 1 summarizes the *ab initio* minimized energies and the complexation efficiencies of **1** with the alkylammonium cations. The trend of the complexation efficiencies for host **1** when using the HF/6-31G method is in the order of NH_4^+ > $MeNH_3^+$ > $EtNH_3^+$ > *n*-$PrNH_3^+$ > *n*-$BuNH_3^+$ ~ *iso*-$BuNH_3^+$ ~ *sec*-$BuNH_3^+$ > *tert*-$BuNH_3^+$. We can generalize that the complexation efficiency decreases gradually as the length of the alkyl chain increases. The trend of *ab initio* calculated binding affinities of **1** for linear alkylammoniums is a little different from the experimental data, where ethylammonium ion shows the highest "percent extraction" values.[11] Previous *ab initio* calculations for different kinds of host (**2-4**) also displayed that the ammonium ion having no alkyl group always had the highest complexation efficiencies among the alkylammonium ions.[12-14] One of the reasons of this discrepancy between the calculated values and the experimental data might be caused by the different conditions between the calculation (in vacuum without any solvent molecule) and the experimental environment (in solution). Another reason could be the underestimation of the CH-π interactions between the alkylammonium and the aromatic walls of the host in the HF/6-31G calculations.

The *ab initio* optimized structure for the cone conformation of host **1** is described in Figure 2. The covalent capping restricts both the TAC and the calix core mobilities, leading to a rigidified calix-cryptand. However, the unliganded host **1** shows the distorted structure of the TAC (1,3,5-triazacyclohexane) with respect to the central pseudo-cavity of the host.

Figures 3 through 8 show the *ab initio* optimized structures of the *endo*-cone-type complex of **1** with alkylammonium cations, for example, Figure 3(a) created by POSMOL[18] shows all atoms including hydrogen bondings, and Figure 3(b) created by Chem3D[19] is drawn without hydrogen atoms for clarity. Figure 3(c) presents the top view to show the TAC cap of calix[6]TAC. The structures of host **1** in Figures 4-8 became more C_{3v}-symmetric upon complexation with alkylammonium ions, due to (i) hydrogen bondings to both the aza cap and the phenolic units of the calixarene and to (ii) cationic and CH-π interactions between the alkylammoniums and the aromatic walls of the host. ^{1}H NMR measurement shows that the protons in β-positions of the charged nitrogen atom of alkylammonium display higher

Table 1. *Ab initio* RHF/6-31G Optimized Energies (A.U.)[a] of Various Complexes of Calix[6](aza)cryptand with Alkylammonium Cations

Ab initio RHF/6-31G Method	Alkylammonium guest[b]							
	NH_4^+	Me	Et	*n*-Pr	*n*-Bu	*iso*-Bu	*sec*-Bu	*tert*-Bu
	–56.51590	–95.53880	–134.56576	–173.58622	–212.60529	–212.60627	–212.61113	–212.61725
Host	Complexes with host							
–3625.82637	–3682.49033	–3721.50313	–3760.52111	–3799.53056	–3838.53657	–3838.54174	–3838.54023	–3838.53809
Complexation energy (kcal/mol)								
ΔE^c	–92.91	–86.57	–80.94	–74.03	–65.83	–68.46	–64.47	–59.28
$\Delta\Delta E^d$	0.00	6.34	11.97	18.88	27.08	24.45	28.45	33.63

[a]Error limits in these calculations are about 2×10^{-5} A.U. Units for the *ab initio* total energies are in A.U., and units for complexation energies are in kcal/mol converted by using conversion factor 1 A.U. = 627.50955 kcal/mol. [b]Me = methylammonium, Et = ethylammonium, *n*-Pr = *n*-propylammonium, *n*-Bu = *n*-butylammonium cation, *etc*. [c]Complexation energy (ΔE) = $E_{Complex} - E_{Host} - E_{Guest}$. [d]$\Delta\Delta E = \Delta E - \Delta E\ (NH_4^+)$

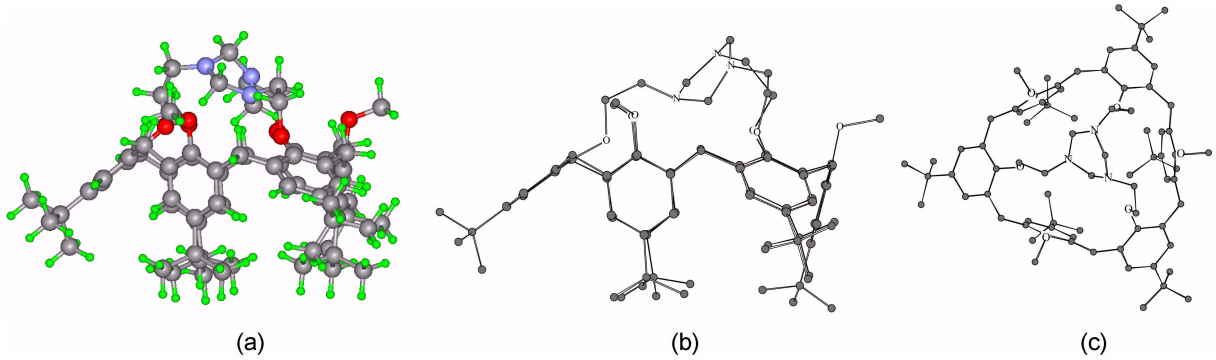


Figure 2. *Ab initio* calculated cone conformation of free host **1**. (a) shows all atoms, (b) is drawn without hydrogen atoms for clarity, and Figure 2(c) presents the top view to show the TAC cap.

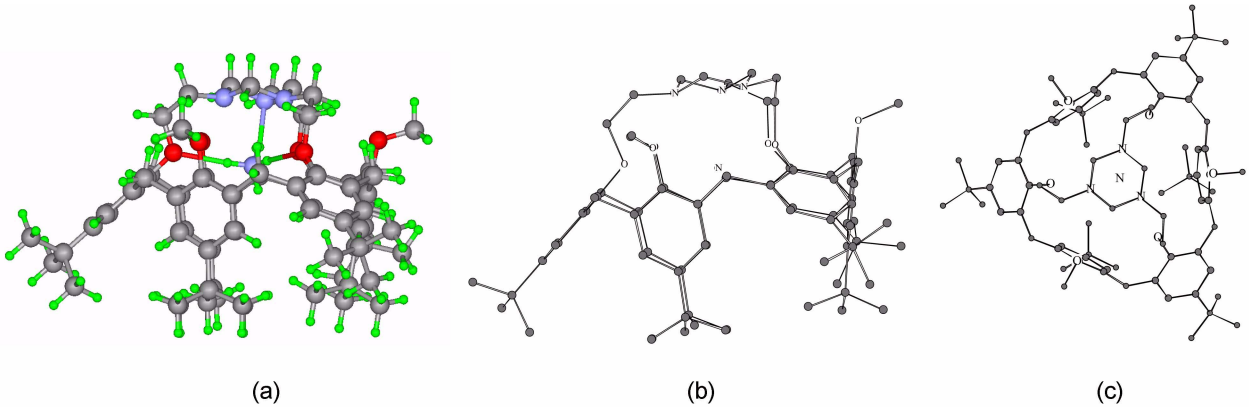


Figure 3. *Ab initio* calculated structure of *endo*-cone-type ammonium complex (**1**+NH_4^+). (a) shows all atoms including the hydrogen bondings. (b) and (c) are drawn without hydrogen atoms for clarity.

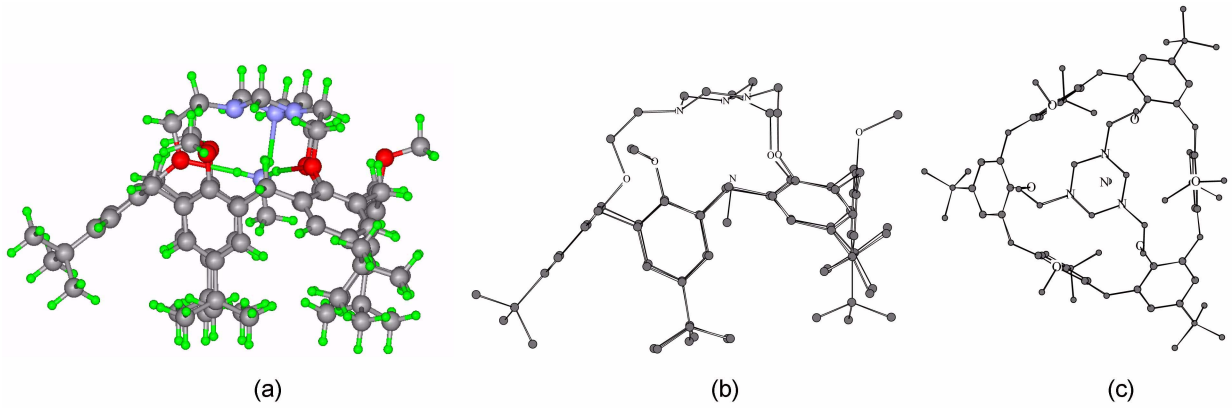


Figure 4. Calculated structure of the methylammonium complex (**1**+$CH_3NH_3^+$).

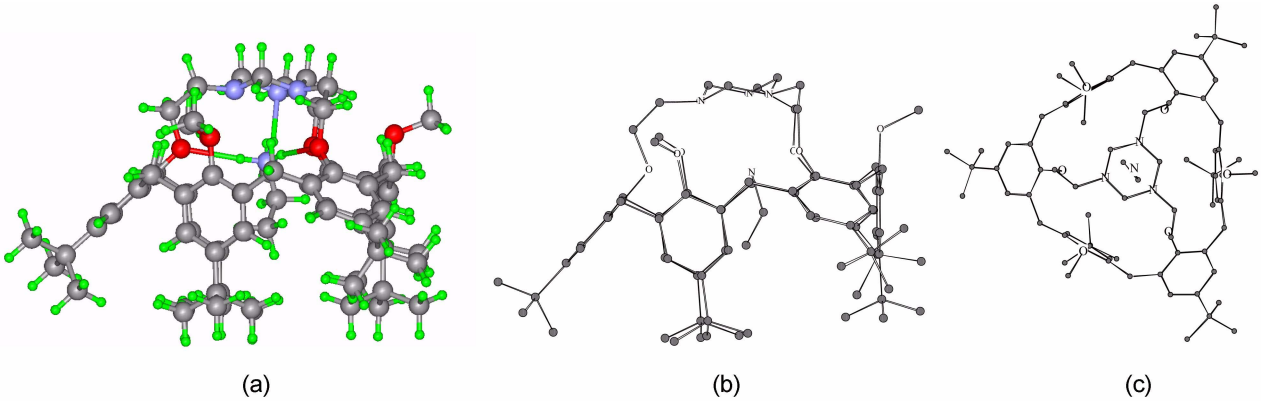


Figure 5. Calculated structure of the ethylammonium complex (**1**+$CH_3CH_2NH_3^+$).

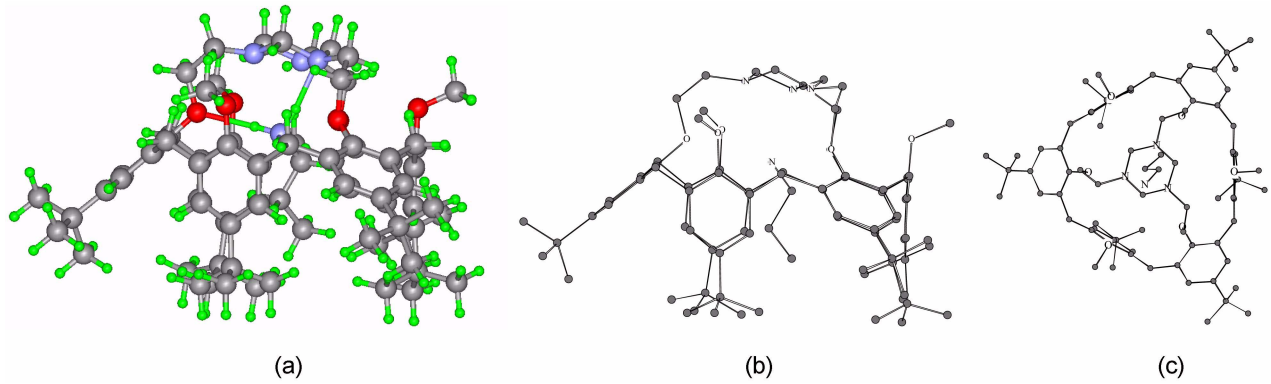


Figure 6. Calculated structure of the *n*-propylammonium complex (**1**+$CH_3CH_2CH_2NH_3^+$).

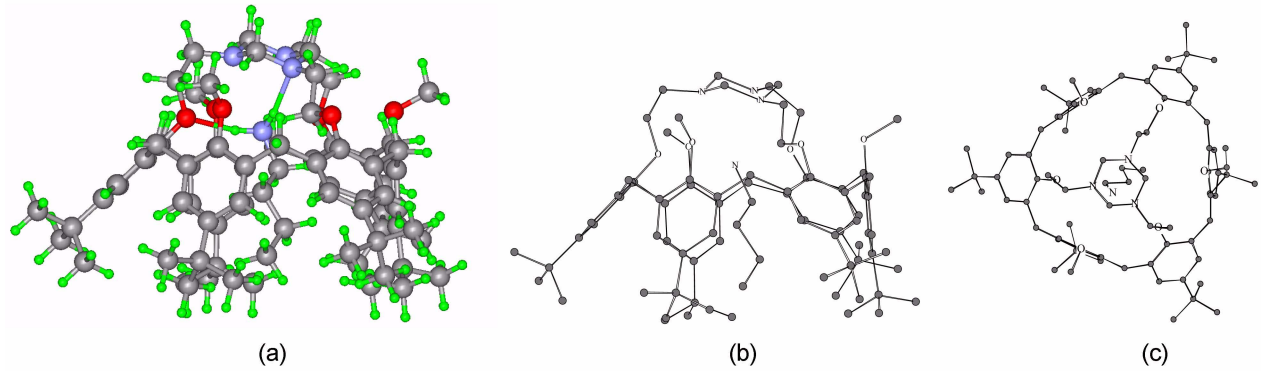


Figure 7. Calculated structure of the *n*-butylammonium complex (**1**+$CH_3CH_2CH_2CH_2NH_3^+$).

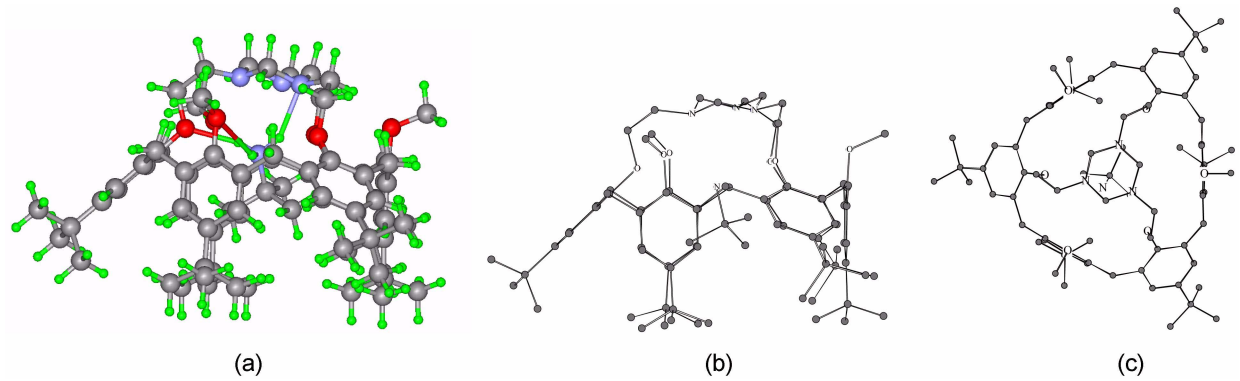


Figure 8. Calculated structure of the *t*-butylammonium complex (**1**+$C(CH_3)_3NH_3^+$).

chemically induced shift (CIS) values.[11] This suggests that they sit in the center of the π-basic cavity of the aromatic walls. Bridging oxygen atoms between the TAC and the calix core group are projected toward the inside of the cavity of host molecule to form hydrogen bondings with the nitrogen atom of ammonium cation. The hydrogen bondings as well as the cation-π and CH-π interactions resulted in the high stability of the **1**+RNH_3^+ complex.

Table 2 shows some of the distances from the nitrogen atom in the ammonium cation to the hydrogen-bonded nitrogen atom of the TAC cap [*d*(N···N) = ~ 2.95 Å] and to the oxygen atom belonging to the calixarene unit [*d*(N···O) = ~3.15 Å] and reports the angles of hydrogen bonding (N-H···N or N-H···O). These hydrogen-bonded distances are slightly longer than those of the experimental X-ray structure of the complex of calix[6]TAC with the propyl ammonium cation.[11,20]

The ^{1}H NMR measurement also shows that the CH_2N and CH_2O resonances belonging to the arms between the TAC and the calix core group are strongly downfield shifted whereas one of the two signals corresponding to the NCH_2N protons is shifted upfield.[11] This finding indicates a dramatic change in the conformation of the cap upon complexation, the two methylene groups of the arms being projected toward the outside of the cavity. These structural characteristics are also represented in Figures 3-8, which present the *ab initio* calculations of the alkylammonium complexes.

The top views in Figures 4-8 show that the three *p-tert*-butylanisole rings in the **1**+RNH_3^+ complex become more vertical to the horizontal plane of the core calix due to the

Table 2. HF/6-31G Optimized Hydrogen-Bonded Distances (Å) and Angles (°) of the Alkylammonium Complexes of Calix[6]TAC

Hydrogen bonding		NH_4^+	Me	Et	*n*-Pr	*n*-Bu	*iso*-Bu	*sec*-Bu	*tert*-Bu
N-H···N	NN Distance	2.942	2.927	2.967	2.927	2.956	2.934	3.175	3.196
	Angle	154.1	147.3	155.3	171.9	160.2	174.1	159.0	148.8
N-H···O	NO Distance	3.137	3.230	3.215	3.116	3.090	3.107	3.172	3.096
	Angle	168.0	164.3	167.6	167.2	157.9	164.3	161.5	152.3

Table 3. B3LYP/6-31G(d) Energies (A.U.)[a] of the Complexes of Calix[6](aza)cryptand with Alkylammonium Cations

B3LYP/6-31G(d) energies Using Gaussian 98		Alkylammonium guest					
		NH_4^+	Me	Et	*n*-Pr	*n*-Bu	*tert*-Bu
		–56.89389	–96.21487	–135.53740	–174.85321	–214.16808	–214.17887
Host		Complexes with host					
–3651.06742		–3708.10506	–3747.41859	–3786.73328	–3826.01856	–3865.33892	–3865.34907
Host **1**+Guest complexation	ΔE (kcal/mol)	–90.20	–85.53	–80.61	–61.45	–64.90	–64.49
	ΔΔE (kcal/mol)	0.00	4.67	9.59	28.75	25.31	25.71

[a]Refer the footnotes of Table 1.

steric effect of the alkyl group of the guest cation. The *p-tert*-butyl groups tilted inward in Figures 2 and 3 are now pushed back outward by the alkyl group.

Table 3 summarizes the B3LYP/6-31G(d) single point energies of the final structures considering the effect of an electron correlation and the basis set with a polarization function. The trend of the complexation energies for host **1** by using the DFT method is represented in the order of NH_4^+ > $MeNH_3^+$ > $EtNH_3^+$ > *n*-$BuNH_3^+$ ~ *tert*-$BuNH_3^+$ > *n*-$PrNH_3^+$, which is slightly different from that of the HF/6-31G(d) calculation. As well, the B3LYP/6-31G(d) complexation efficiency of **1** with the bulkier *tert*-butylammonium is almost the same as that with *n*-butylammonium, and higher than that with *n*-propylammonium. This differences may suggest that, with the influences of the CH-π interactions between the alkylammonium and the aromatic walls of the host, the B3LYP/6-31G(d) calculation method rather than the HF/6-31G method favors the bulky alkyl group. Another comment for the discrepancy is that the B3LYP/6-31G(d) result is obtained not from an optimization of the complex but from the single point calculation which could have more uncertainty on the relative binding energy. Overall trend of binding efficiencies of **1** for alkylammoniums by using the B3LYP/6-31G(d) single point calculation might be reasonable, but one or two values could be less convincing than the HF/6-31G optimization method.

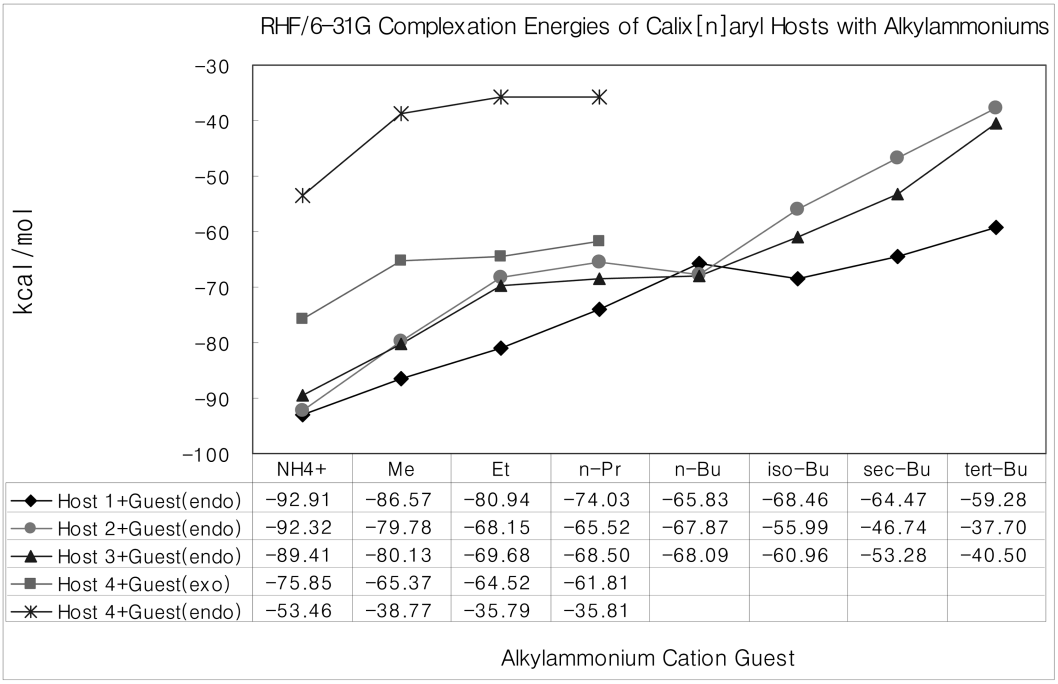
Table 4 and Figure 9 list the *ab initio* HF/6-31G complexation energies (kcal/mol) of four different calix[n]aryl hosts with alkylammonium cations. The complexation efficiency of calix[6](aza)cryptand (**1**) for NH_4^+ is slightly better than that of the calix[5]aryl host (**2**). However, in complexation for methyl, ethyl, and propyl ammonium ions, host **1** is much better (~8 kcal/mol) than the calix[5]arene derivatives (**2** and **3**), and much more (~15 kcal/mol) efficient than that of the calix[4]crown-6-ether (**4**). When one compares the binding energy of individual host toward ethyl, *n*-propyl, or *n*-butyl ammonium ions, host **2** or **3** displays comparable efficiencies. However, host **1** shows gradual decrease in the complexation stability as the length of the alkyl chain of guest increases. A plausible explanation is that the more steric hindrance is created between the methyl group of the longer alkylammonium and the bulky *p-tert*-butyl groups since the ammonium end of the longer guest blocked by the TAC group of host **1** is pushing the other end closer to the *p-tert*-butyl groups. (See the Figures 5-7(a))

Calix[6]TAC also displays much better complexation ability than that of the calix[5]aryl hosts (**2** and **3**) for branched butylammonium cations. Overall, these complex-

Table 4. *Ab initio* RHF/6-31G Complexation Energies (kcal/mol) of Calix[n]aryl Hosts[a] with Alkylammonium Cations

ΔE[b]	Reference[c]	Alkylammonium guest							
		NH_4^+	Me	Et	*n*-Pr	*n*-Bu	*iso*-Bu	*sec*-Bu	*tert*-Bu
Host **1** + Guest (endo)	This study	–92.91	–86.57	–80.94	–74.03	–65.83	–68.46	–64.47	–59.28
Host **2** + Guest (endo)	12	–92.32	–79.78	–68.15	–65.52	–67.87	–55.99	–46.74	–37.70
Host **3** + Guest (endo)	13	–89.41	–80.13	–69.68	–68.50	–68.09	–60.96	–53.28	–40.50
Host **4** + Guest (exo)[d]	14	–75.85	–65.37	–64.52	–61.81				
Host **4** + Guest (endo)	14	–53.46	–38.77	–35.79	–35.81				

[a]Refer Figure 1 for the structures of hosts **1**-**4**. [b]Complexation energy (ΔE) = $E_{Complex} - E_{Host} - E_{Guest}$. [c]Refer the each reference for the 3-D optimized structures. [d]The "exo" means the complexation into the center of the crown-ether ring in calix[4]crown-6-ether.



	NH4+	Me	Et	n-Pr	n-Bu	iso-Bu	sec-Bu	tert-Bu
Host 1+Guest(endo)	-92.91	-86.57	-80.94	-74.03	-65.83	-68.46	-64.47	-59.28
Host 2+Guest(endo)	-92.32	-79.78	-68.15	-65.52	-67.87	-55.99	-46.74	-37.70
Host 3+Guest(endo)	-89.41	-80.13	-69.68	-68.50	-68.09	-60.96	-53.28	-40.50
Host 4+Guest(exo)	-75.85	-65.37	-64.52	-61.81				
Host 4+Guest(endo)	-53.46	-38.77	-35.79	-35.81				

Figure 9. Plot of the RHF/6-31G complexation energies (kcal/mol) of four different calix[n]aryl hosts with alkylammonium cations.

ation energies suggest that *p-tert*-butylcalix[6](aza)cryptand is probably the best alkylammonium-complex ever obtained with a calixaryl host. These calculated results show a good agreement with those obtained from previous experimental data,[11,21,22] in which host **1** was found to have the highest "percent extraction" values and the free energy of binding with alkylammonium picrates.

Conclusion

By using the *ab initio* RHF/6-31G and B3LYP/6-31G(d) methods, we have calculated the absolute and complexation energies of the *p-tert*-butylcalix[6](aza)cryptand **1** with various alkylammonium ions. Based on the RHF/6-31G method, the ammonium cation containing a small alkyl group has much better complexation ability than those of other alkylammonium guests in the order of NH_4^+ > $MeNH_3^+$ > $EtNH_3^+$ > *n*-$PrNH_3^+$ > *n*-$BuNH_3^+$ ~ *iso*-$BuNH_3^+$ ~ *sec*-$BuNH_3^+$ > *tert*-$BuNH_3^+$. The structure of the host became more C_{3v}-symmetric upon complexation with alkylammonium ion, due to (i) hydrogen bondings to both the aza cap and the phenolic units of the calixarene and to (ii) cationic and CH-π interactions between the ammonium and the aromatic walls of the host. The calculated complexation efficiencies of **1** for alkylammonium cations are much better than those of the previously reported calix[5]aryl hosts (**2** and **3**) and calix[4]crown-6-ether (**4**).

Acknowledgement. This research was supported by a Chung-Ang University research grant in 2004. Most of the computations were carried out by using the computer facilities at the Research Center for Computational Science of the Okazaki National Research Institutes.

References

1. (a) Gutsche, C. D. *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge, 1998. (b) *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer: Dordrecht, 2001. (c) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer: Dordrecht, 1991.
2. (a) *Cation Binding by Macrocycles*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker; New York, 1990. (b) Balzani, V.; De Cola, L. *Supramolecular Chemistry*; Kluwer: Dordrecht, 1992.
3. *Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Elsevier: Oxford, 1996; Vol. 1, Molecular Recognition: Receptors for Cationic Guests.
4. (a) Chang, S.-K.; Hwang, H.-S.; Son, H.; Youk, J.; Kang, Y. S. *J. Chem. Soc., Chem. Commun*. **1991**, 217. (b) Chang, S.-K.; Jang, M.; Han, S. Y.; Lee, J. H.; Kang, M. H.; No, K. T. *Chem. Lett*. **1992**, 1937. (c) Han, S. Y.; Kang, M.-H.; Jung, Y. E.; Chang, S.-K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 835.
5. *Computational Approaches in Supramolecular Chemistry*; Wipff, G., Ed.; Kluwar: Dordrecht, 1994.
6. (a) Choe, J.-I.; Chang, S.-K.; Nanbu, S. *Bull. Korean Chem. Soc*. **2002**, *23*, 891. (b) Choe, J.-I.; Kim, K.; Chang, S.-K. *Bull. Korean Chem. Soc*. **2000**, *21*, 200.
7. Pappalardo, S.; Parisi, M. F. *J. Org. Chem*. **1996**, *61*, 8724.
8. Arnaud-Neu, F.; Fuangswasdi, S.; Notti, A.; Pappalardo, S.; Parisi, M. *Angew. Chem. Int. Ed*. **1998**, *37*, 112.
9. Salvo, G. D.; Gattuso, G.; Notti, A.; Parisi, M.; Pappalardo, S. *J. Org. Chem*. **2002**, *67*, 684.
10. Jabin, I.; Reinaud, O. *J. Org. Chem.* **2003**, *68*, 3416.
11. Darbost, U.; Giorgi, M.; Reinaud, O.; Jabin, I. *J. Org. Chem.* **2004**, *69*, 4879.
12. Choe, J.-I.; Lee, S. H.; Oh, D.-K.; Chang, S.-K.; Nanbu, S. *Bull. Korean Chem. Soc*. **2004**, *25*, 190.
13. Choe, J.-I.; Chang, S.-K.; Satoshi, M.; Nanbu, S. *Bull. Korean Chem. Soc*. **2003**, *24*, 75.
14. Choe, J.-I.; Chang, S.-K.; Ham, S. W.; Nanbu, S.; Aoyagi, M. *Bull. Korean Chem. Soc*. **2001**, *22*, 1248.
15. *HyperChem Release 6.3*; Hypercube, Inc.: Waterloo, Ontario, 2001.

16. Choe, J.-I.; Kim, K.; Chang, S.-K. *Bull. Korean Chem. Soc.* **2000**, *21*, 465.
17. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002.
18. Lee, S. J.; Kim, K. S. *POSMOL* Molecular Viewer; Pohang University of Science and Technology: Korea, 1999.
19. *Chem3D Molecular Modeling and Analysis, Version 7.0*; Cambridge Soft: Cambridge, MA, U.S.A., 2001.
20. Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.
21. (a) Han, S. Y.; Kang, M.-H.; Jung, Y. E.; Chang, S.-K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 835. (b) Jung, Y. E.; Song, B. M.; Chang, S.-K. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2031. (c) Lee, J. H.; Kim, T. H.; Chang, S.-K.; Choe, J.-I. *Supramolecular Chemistry* **1995**, *4*, 315.
22. (a) Li, J.; Chen, Y.; Lu, X. *Tetrahedron* **1999**, 10365. (b) Chen, Y.; Yang, F.; Lu, X. *Tetrahedron* **2000**, 1571. (c) Chen, Y.; Yang, F. *Chem. Lett.* **2000**, 484. (d) Li, J.-S.; Chen, Y.-Y.; Lu, X.-R. *Eur. J. Org. Chem.* **2000**, 485.