1848 *J. Org. Chem.* **2002,** *67,* 1848−1851

A New Type of Ionophore Family Utilizing the Cation-Olefinic π Interaction: Theoretical Study of [*n*]Beltenes

Hyuk Soon Choi, Dongwook Kim, P. Tarakeshwar, Seung Bum Suh, and Kwang S. Kim*

National Creative Research Initiative Center for Superfunctional Materials, Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, Hyojadong, Namgu, Pohang 790-784, Korea

kim@postech.ac.kr

Received January 17, 2002

The possible utilization of [*n*]beltenes as a new family of ionophores, which exhibit a cation-olefinic π type of interaction in contrast to the cation-aromatic π type of interaction exhibited by [*n*]collarenes, has been investigated using both ab initio calculations and molecular dynamic simulations. Like [*n*]collarenes, *n* ethene groups are linked by $-CH_2-$ linkages in the [*n*]beltenes. Our calculations indicate that these [*n*]beltenes exhibit strong binding affinities and high selectivity for alkali metal cations ([5]beltene to Li^+, [6]beltene to Na^+, [7]beltene to Na^+ and K^+, [8]beltene to K^+ and Rb^+, and [9]beltene to Cs^+ and Rb^+). Compared to [*n*]collarenes, [*n*]beltenes are expected to have a finer ion selectivity because their cavity sizes can be varied with integral number *n*, while that of the former can be varied with an even number *n*. Suitable substituents could be employed to enhance both the binding and specificity of various sizes of [*n*]beltenes to different cations, as well as to increase the solubility.

Introduction

The importance of cation-π interactions in wide areas of biology and chemistry is amply illustrated in recent reports.[1,2] Our efforts in understanding the cation-π interaction[3] have led to the design and development of a number of novel ionophores based on this interaction.[4] Interestingly, all the non oxygen- or nitrogen-containing ionophores designed to date are based only on the aromatic-π interaction. However, recent results from our laboratory[5] indicated that interactions involving the olefinic-π interaction could be effectively harnessed to design an entirely new series of ionophores. The search for suitable molecular frameworks, exhibiting the olefinic-π interaction, was facilitated by our earlier findings that suitable changes in the nature of the intervening C−C bonds in carbon nanotubelike frameworks yielded materials with unusual electronic and magnetic properties.[4b]

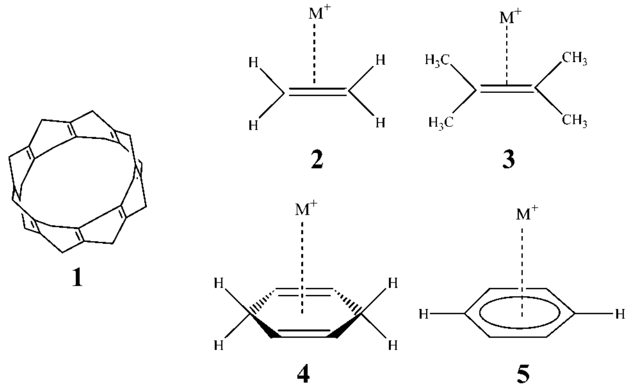

Figure 1. Schematic view of [*n*]beltene (**1**). A comparison of the olefinic and aromatic cation-π interaction in ethene (**2**), 2,3-dimethyl-2-butene (**3**), 1,4-cyclohexadiene (**4**), and benzene (**5**).

While several efforts are underway to design and synthesize novel host molecules,[6] the [*n*]beltenes (**1** in Figure 1), wherein *n* ethane groups are linked by $-CH_2-$ linkages, conceived by Alder, Sessions, McMurry, et al. seem to be promising candidates as novel ionophores.[7] Interestingly, several authors have conjectured that various sizes of [*n*]beltenes (where *n* represents the number of rings constituting the cylinder) could be employed to encapsulate small ions or molecules.[8] Despite

---

(1) (a) Dougherty, D. A.; Stauffer, D. A. *Science* **1990**, *250*, 1558. (b) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708. (c) Dougherty, D. A. *Science* **1996**, *271*, 163. (d) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.

(2) (a) Carbacos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1998**, *108*, 5151. (b) Carbacos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110*, 8429. (c) De Wall, S. L.; Barbour, L. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 8405. (d) De Wall, S. L.; Meadows, E. S.; Barbour, L. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 5613. (e) De Wall, S. L.; Meadows E. S.; Barbour, L. J.; Gokel, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 6271. (f) Hong, B. H.; Lee, J. Y.; Lee, C.-W.; Kim, J. C.; Bae. S. C.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 10748. (g) Hong, B. H.; Bae. S. C.; Lee, C.-W.; Jeong, S.; Kim, K. S. *Science* **2001**, *294*, 348. (h) Kim, K. S. *Curr. Appl. Phys.* **2002**, in press.

(3) (a) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D.-H. *J. Am. Chem. Soc.* **1994**, *116*, 7399. (b) Lee, J. Y.; Lee, S. J.; Choi, H. S.; Cho, S. J.; Kim, K. S.; Ha, T.-K. *Chem. Phys. Lett.* **1995**, *232*, 67. (c) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145.

(4) (a) Choi, H. S.; Suh, S. B.; Cho, S. J.; Kim, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 12094. (b) Choi, H. S.; Kim, K. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 2256. (c) Oh, D.-W.; Park, J. M.; Kim, K. S. *Phys. Rev. B* **2000**, *62*, 1600. (d) Oh, K. S.; Lee, C.-W.; Choi, H. S.; Lee, S. J.; Kim, K. S. *Org. Lett.* **2000,** *2*, 2679.

(5) (a) Tarakeshwar, P.; Choi, H. S.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 3323. (b) Tarakeshwar, P.; Choi, H. S.; Lee, S. J.; Lee, J. Y.; Kim, K. S.; Ha, T. K.; Jang, J. H.; Lee, J. G.; Lee, H. *J. Chem. Phys.* **1999**, *111*, 5838. (c) Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **2000**, *112*, 1769.

(6) (a) Elben, U.; Vögtle, F. *J. Chem. Res.* **1978**, 316. (b) Muller, W. M.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 623. (c) Lehn, J.-M.; Lilienbaum, D.; de Mendoza, J.; Mesa, E.; Rodriguez-Ubis, J.-C.; Vazquez, P.; Windscheif, P.-M.; Ziessel, R.; Rissanen, K.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1331. (d) Seel, Ch.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 528. (e) Vögtle, F.; Gross, J.; Seel, Ch.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1069.

10.1021/jo016335w CCC: $22.00

the difficulties in synthesizing ionophores, which are based on the cation-olefinic π interaction, considerable synthetic efforts have been made in this direction.[9] Spurred by some recent reports of the synthesis of [4]-beltenes,[10] we report in this study the efficacy of varying sizes of [*n*]beltenes and substituted [*n*]beltenes as novel ionophores incorporating the olefinic-π interaction.

To compare the relative binding efficacies of [*n*]collarenes and [*n*]beltenes, we initially investigated the cation binding efficacies of various model systems. These include ethene (**2**), 2,3-dimethyl-2-butene (**3**), 1,4-cyclohexadiene (**4**), and benzene (**5**). Although 1,4-cyclohexadiene (**4**) and benzene (**5**) are not adequate models to represent the interaction of [*n*]collarenes and [*n*]beltenes, we believe that the qualitative and quantitative information provided by these calculations would be useful in understanding the mechanism and efficacy of the interaction of cations with [*n*]beltenes and [*n*]collarenes. Furthermore, their small size as compared to beltenes and collarenes makes them amenable to high-level theoretical calculations.

Computational Methods

Full geometry optimizations were carried out on all the complexes investigated in this study using the Gaussian suite of programs.[11] Density functional theory (DFT) calculations were carried out using the Becke's three-parameter hybrid functional using the Lee, Yang, and Parr functional (B3LYP) method. Calculations on the smaller systems were also carried out using the second-order Møller−Plesset perturbation (MP2) method. Basis set superposition error (BSSE) corrections were carried out using the counterpoise method. While both the 6-31+G* and 6-311++G** basis sets were employed in calculations involving the smaller systems, the 3-21G basis set was used for the larger [*n*]beltene calculations. The binding energy ratios are given by the expression, {binding energy ratio = ΔE([*n*]beltene-cation)/ΔE(ethene-cation)}, i.e., the ratio of the binding energy of [*n*]beltene with the cation to that of the building unit, ethene, with the cation.

The binding energies were decomposed using the symmetry-adapted perturbation theory (SAPT) method.[12] In SAPT, the total binding energy (E_{int}) of the complex is obtained as a sum of the electrostatic (E_{es}), exchange (E_{exch}), induction (E_{ind}), and dispersion (E_{disp}) energies. More details on the method and its application for the decomposition of the binding energies of these π-system-containing complexes can be obtained from a recent review.[3c]

The MD simulations reported in this study were carried out using the AMBER 5 program.[13] For treatment of the polarizable potential, we used the approach of Kollman and coworkers.[14] The polarizable potential is obtained from the restrained electrostatic potential (RESP) charges,[15] the van der Waals parameters,[16] and the atomic polarizabilities,[17] excepting for the benzene sp^2 carbon (0.36 Å^3) and the POL3 water potential.[18] The Gibbs free-energy perturbation MD simulations were carried out as an NPT ensemble (298 K, 1 atm). The cutoff distance was 8 Å. The number of simulation windows is 20. Each simulation consisted of 10 ps equilibration and 10 ps sampling. A 2 fs time step was used with all OH bonds and HOH bond angles of water molecules constrained by the SHAKE algorithm.[18] For more details on the use of free-energy perturbation methods in obtaining the binding affinities of other π-system-containing ionophores, see our earlier work on collarenes.[4a]

Results and Discussion

Compared to [*n*]collarenes,[4a] [*n*]beltenes are expected to have a finer ion selectivity because their cavity sizes can be varied with integral numbers *n*, while that of the former can be varied with an even number *n*. Before we discuss the binding characteristics of these [*n*]beltenes, we think it would be useful to examine the efficacy of various methods in describing the cation-π interaction in these olefinic π systems. It can be seen from Table 1, wherein the MP2- and B3LYP-predicted binding energies of Li^+ and Na^+ complexed with ethane (**2**) and 2,3-dimethyl-2-butene (**3**) are listed, that DFT methods yield geometries and binding energies that are nearly equal to those obtained using the MP2 method. Given the accuracy of the DFT-calculated results and the computational effort in carrying out the MP2 calculations on the larger systems, we thought it would be appropriate to carry out the calculations on the [*n*]beltene systems using DFT-based methods.

In an effort to understand the origin of the binding energies in these systems, we have decomposed the binding energies of the ethene and 2,3-dimethyl-2-butene cation complexes (MP2/6-31+G*-optimized geometries) into the individual interaction energy components. It can be seen from Table 1, that the induction energies (E_{ind}) are the dominant contributors to the total binding energy of these complexes. This can be readily understood from the fact that complex formation, and in particular the close approach of the cation to the π system, leads to a pronounced polarization of the electron density of the π system. The resulting induced dipoles lead to strong

---

(7) (a) Alder, R. W.; Sessions, R. B. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1849. (b) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Mitchell, J. *J. Am. Chem. Soc.* **1986**, *108*, 515. (c) McMurry, J. E.; Swenson, R. *Tetrahedron Lett.* **1987**, *28*, 3209. (d) Falcetta, M. F.; Jordan, K. D.; McMurry, J. E.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1990**, *112*, 579.

(8) Schröder. A.; Mekelburger, H.-B.; Vögtle. F. *Top. Curr. Chem.* **1994**, *172*, 179.

(9) (a) Angus, R. O., Jr.; Johnson, R. P. *J. Org. Chem.* **1988**, *53*, 314. (b) Ashton, P. R.; Isaacs, N. S.; Kohnke, F. H.; Slawin, A. M. Z.; Spencer, C. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 966. (c) Godt, A.; Enkelmann, V.; Schülter, A. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1680.

(10) (a) Galsso, V.; Grimme, W.; Lex, J.; Jones, D.; Modelli, A. *Chem. Phys.* **1999**, *242*, 203. (b) Grimme, W.; Geich, H.; Lex, J.; Heinze, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1955.

(11) 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.; 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.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Jeziorski, B.; Moszy′nski, R.; Ratkiewicz, A.; Rybak, S.; Szalewicz, K.; Williams, H. In *Methods and Techniques in Computational Chemistry: METECC-94*; Clementi, E., Ed.; STEF: Cagliari, 1993; Vol. B, pp 79−129.

(13) Case, D. A.; Pearlman, D. A.; Caldwell, J. W.; Cheatham, T. E.; Ross, W. S.; Simmerling, C. L.; Dearden, T. A.; Merz, K. M.; Stanton, R. V.; Cheng, A. L.; Vincent, J. J.; Crowley, M.; Ferguson, D. M.; Radmer, R. J. Seibel, G. L.; Singh, U. C.; Weiner, P. K.; Kollman, P. A. *AMBER 5*; University of California, San Francisco: San Francisco, 1997.

(14) Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 4177.

(15) Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Profeta, S.; Weiner, P. *J. Am. Chem. Soc.* **1984**, *106*. 765

(16) Aqvist, J. *J. Phys. Chem.* **1990**, *94*, 8021.

(17) Applequist, J.; Carl, J. R.; Fung, K. K. *J. Am. Chem. Soc.* **1972**, *94*, 2952.

(18) Duan, Y.; Kumar, S.; Rosenberg, J. M.; Kollman, P. A. *J. Comput. Chem.* **1995**, *16*, 1352.

Table 1. Comparison of the MP2- and B3LYP-Predicted Binding Energies of the Li^+ and Na^+ Complexes of Ethane (2) and 2,3-Dimethyl-2-butene (3) along with a Decomposition of the Binding Energies[a]

	2		3	
	Li^+	Na^+	Li^+	Na^+
	B3LYP/6-31+G*			
ΔE	−21.71	−14.88	−30.30	−20.03
ΔE^B	−21.43	−14.58	−29.88	−19.23
$r_{M-\Phi}$	2.30	2.66	2.16	2.61
	MP2/6-31+G*			
ΔE	−21.63	−14.53	−31.91	−21.72
ΔE^B	−19.63	−12.85	−26.59	−16.72
$r_{M-\Phi}$	2.31	2.68	2.15	2.60
	SAPT Energy Decomposition (MP2/6-31G* Equivalent)			
E_{int}	−20.49	−13.50	−28.79	−17.81
E_{es}	−15.52	−12.79	−15.68	−16.40
E_{exch}	15.30	19.45	25.49	36.23
E_{ind}	−20.11	−19.92	−38.09	−37.11
E_{disp}	−0.16	−0.24	−0.51	−0.54

[a] All energies are in kcal/mol and distances are in Å. ΔE and ΔE^B are the binding energies without and with basis set superposition error (BSSE) correction, respectively. $r_{M-\Phi}$ denotes the distance between the metal cation and the ethene/2-butene π plane. The SAPT interaction energy (E_{int}), which is nearly equivalent to the BSSE-corrected binding energy (ΔE^B), is obtained as $E_{int} = E_{es} + E_{exch} + E_{ind} + E_{disp}$, where E_{es} is the electrostatic energy, E_{exch} is the total exchange-repulsion energy, E_{ind} is the induction energy, and E_{disp} is the dispersion energy.

Table 2. MP2/(6-31+G* and 6-311++G)-Predicted Binding Energies and Structures of Model Systems**[a]

	4			5		
	Li^+	Na^+	K^+	Li^+	Na^+	K^+
	MP2/6-31+G*					
ΔE^B	−35.1	−24.0	−15.8	−37.1	−24.5	−16.6
$r_{M-\Phi}$	1.928	2.355	2.869	1.909	2.391	2.895
	MP2/6-311++G**					
ΔE^B	−34.6	−22.3		−37.6	−23.7	
$r_{M-\Phi}$	1.892	2.389		1.847	2.401	

[a] All energies are in kcal/mol and distances are in Å. ΔE^B values are the BSSE-corrected interacted energies. $r_{M-\Phi}$ denotes the distance between the metal cation and the plane composed of carbon atoms.

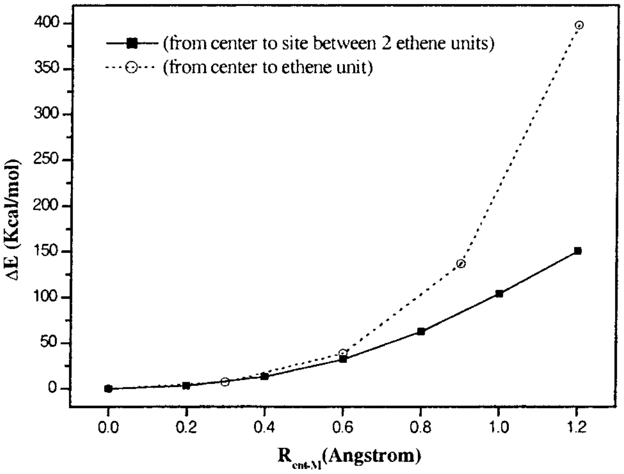

Figure 2. Plot depicting the increase in the potential energy as Li^+ moves from the center of [5]beltene to its walls.

attractive induction forces. The smaller size of the Li^+ as compared to that of Na^+ leads to its closer approach to the π system because of decreased exchange-repulsion. However, this close approach also leads to the higher electrostatic energies in the Li^+ complexes. The contribution of dispersion forces to the total interaction energy is negligible, and hence DFT methods provide a reasonably accurate description of the binding of these complexes.

The data pertaining to the decomposition of the binding energies of the substituted butene complexes in Table 1 yield interesting insights into the effects of methyl substitution on the cation affinity of these olefinic π systems. Since methyl substituents enhance the π electron density, the electrostatic and inductive energies are much higher, with the enhancement in the latter being more pronounced (inductive contributions are nearly doubled). However, the presence of four methyl substituents also leads to a pronounced increase in the exchange-repulsion. As would be seen later, this increase in the exchange-repulsion plays a vital role in localizing the cation to the center of the beltene.

Armed with this information, we found it is useful to examine the binding energies of systems possessing more than one olefinic double bond. Since these results have a more direct bearing on the binding affinities of the [*n*]beltenes discussed in this study, we can note from the MP2 results listed in Table 2 that the number of π-electrons contributing (four for **4** and six for **5**) to the interaction has little effect on the observed binding energies. Thus, the binding energy differences between **4** and **5** are quite small, 2.0, 0.5, and 0.8 kcal/mol for Li^+, Na^+, and K^+, respectively, at the MP2/6-31+G* level. Except for Li^+-containing complexes, $r_{M-\Phi}$ values in **4** are smaller than those in **5**. The relatively flexible $-CH_2-$ linkages in **4** can also maximize the olefinic π-cation interaction between the metal cation and two C−C double bonds. The flexibility of $-CH_2-$ linkage groups is clearly shown in the change of angles and dihedral angles (given as Supporting Information) when 1,4-cyclohexadiene forms complexes. As discussed earlier, the substitution of the $-CH_2-$ hydrogens with methyl groups results in an enhanced interaction of the cation with 1,4-cyclohexadiene.

Though B3LYP calculations were not carried out on the above systems, one can readily note from Table 2 that the use of larger basis sets does not alter the observed trends. What is more important is that the above results provide justification to our investigations of the use of [*n*]beltenes as novel ionophores. We initially optimized the cationic complexes of [*n*]beltenes ($n = 4-9$) at both the B3LYP/3-21G and 6-31G* levels of theory with the ions being placed at the center of the [*n*]beltene. Since the 6-31G* basis sets contain polarization functions, the results obtained at the B3LYP/6-31G* level should be considered to be more reliable. However, the unavailability of the 6-31G* basis set for the Rb^+ and Cs^+ cations forces us to use the B3LYP/3-21G results in evaluating the trends in the binding energy. It can be seen from the B3LYP results in Figure 3 that in the case of [6], [7], and [8]beltenes, Li^+ and Na^+, Na^+ and K^+, and K^+ and Rb^+, respectively, are competitive. It can be seen that [*n*]beltenes, which possess D_{nh} point group symmetry, have well-defined spherical cavities. Since their radii are dependent on the value of *n*, ion-specific [*n*]beltenes can be designed on the basis of the host−guest size relationship. These radii and, hence, their binding with different ions can be tweaked by substituting the methylene hydrogens with different substituents.

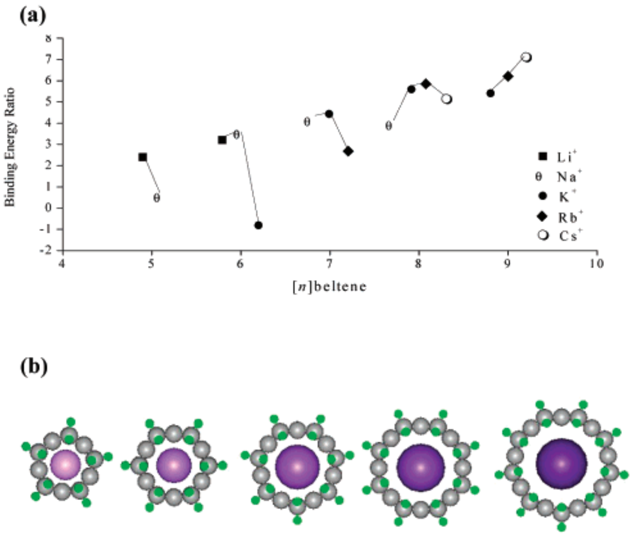

Figure 3. (a) Binding energy ratios of various [*n*]beltene–cation complexes. (b) Various cations captured by [*n*]beltenes (Li^+, Na^+, K^+, Rb^+, and Cs^+ are captured by [5], [6], [7], [8], and [9]beltene, respectively).

Before we proceed further, it is useful to examine the effect of moving the ion from the center of the [*n*]beltene to its walls. In Figure 2, we depict the potential energy plot obtained at the B3LYP/6-31G* level for various positions of Li^+ in [5]beltene. One can readily note that small shifts in the position of Li^+ toward the walls lead to a dramatic decrease in the binding energies. As was observed earlier in the course of our discussion on the energy decomposition of the ethene- and methyl-substituted 2-butene complexes, a small increase in the binding energy is always accompanied by a much larger increase in the exchange-repulsion. Though the attractive electrostatic and inductive energies would be enhanced when the Li^+ cation moves toward the walls of the [5]beltene, the much larger increase in the exchange-repulsion would lead to a lower binding energy.

In our previous studies of ionophores,[4a] we had suggested that the binding energy ratio can be a good index for determining the selectivity of host molecules in the solution phase. In Figure 3a, the calculated binding energy ratios of various [*n*]beltene-cation complexes were plotted. It can be seen that [5]beltene is specific for Li^+, [6]beltene for Na^+, [7]beltene for K^+, [8]beltene for Rb^+, and [9]beltene for Cs^+. The size relationships between [*n*]beltenes and metal cations can be seen in Figure 3b.

To investigate the ion selectivity of [*n*]beltenes in the aqueous phase, we carried out molecular dynamics simulations in conjunction with statistical perturbation theory. The relative stabilities of [*n*]beltene···cation complexes in aqueous solution are listed in Table 3.

Table 3. MD Simulation Predicted Relative Stabilities of [*n*]Beltene···Cation Complexes in Aqueous Solutions[a]

	[5]beltene		[6]beltene	
host reaction[b]	$Na^+ \rightarrow Li^+$		$Na^+ \rightarrow Li^+$	$Na^+ \rightarrow K^+$
$\Delta\Delta G_{aq}$[c]	−40.9		5.1	1.7
	[7]beltene		[8]beltene	
host reaction[b]	$K^+ \rightarrow Na^+$	$K^+ \rightarrow Rb^+$	$Rb^+ \rightarrow K^+$	$Rb^+ \rightarrow Cs^+$
$\Delta\Delta G_{aq}$[c]	−0.3	5.1	−0.3	3.4
	[9]beltene			
host reaction[b]	$Rb^+ \rightarrow Cs^+$			
$\Delta\Delta G_{aq}$[c]	−0.4			

[a] Energies in kcal/mol. [b] $M_1 \rightarrow M_2$ denotes the substitution reaction in aqueous solution: [*n*]beltene···$M_1^+ + M_2^+ \rightarrow$ [*n*]beltene···$M_2^+ + M_1^+$. [c] For the notation of $\Delta\Delta G_{aq}$, see ref 4a. The positive sign of $\Delta\Delta G_{aq}$ indicates that the [*n*]beltene···M_1^+ complex is more stable.

It emerges from Table 3 that in solution, Li^+ is preferred over Na^+ by 40.9 kcal/mol in [5]beltene, and Na^+ is preferred over Li^+ and K^+ by 5.1 and 1.7 kcal/mol, respectively, in [6]beltene. Therefore, [5] and [6]-beltene would exhibit a significant selectivity for Li^+ and Na^+ in aqueous phases. In [7]beltene, K^+ competes with Na^+ within a free energy difference of 0.3 kcal/mol, while K^+ is more favored than Rb^+ by nearly 5.1 kcal/mol. The $\Delta\Delta G_{aq}$ for those two cations is so small that the two cations can be competitively captured by [7]beltene. Similarly, in [8]beltene, Rb^+ is slightly less favorable than but competes with K^+, while Rb^+ is preferred over Cs^+. In [9]beltene, Cs^+ is slightly more favorable than Rb^+ by 0.4 kcal/mol. In brief, Na^+ and K^+ can be captured selectively by [7]beltene, K^+ and Rb^+ by [8]beltene, and Rb^+ and Cs^+ by [9]beltene. As expected in the gas-phase studies, the trend of ion selectivity in the aqueous phase is mainly determined by size effects.

Continuing our quest to examine the effect of substitution of the methylene hydrogens by different groups, we carried out calculations of the interaction of the methyl-substituted [5]beltene with various cations. We find that the interaction of Li^+ with methylated [5]beltene is enhanced by nearly 5 kcal/mol as compared to the unsubstituted [5]beltene. This indicates that suitable subsituents could be employed to enhance both the binding and specificity of various sizes of [*n*]beltenes to different cations as well as to increase the solubility.

Conclusion

In conclusion, the present investigation details the structure and possible utilization of [*n*]beltenes as possible ionophores using cation-olefinic π interaction. Like [*n*]collarenes composed of benzene moieties, [*n*]beltenes are expected to have sufficient binding affinities to metal cations and selectivities of [5]beltene to Li^+, [6]beltene to Na^+, [7]beltene to Na^+ and K^+, [8]beltene to K^+ and Rb^+, and [9]beltene to Cs^+ and Rb^+. In addition, [*n*]beltenes have the excellent advantage that they show delicate ion selectivity because their cavity sizes can be varied with integral numbers *n* and also by the presence of suitable substitutents.

Acknowledgment. This work was supported by Creative Research Initiatives of the Korean Ministry of Science and Technology.

Supporting Information Available: The MP2/(6-31G* and 6-311++G**)-predicted structures of model complexes for cation-olefinic π interaction and cation-aromatic π interaction. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016335W