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Cation-π interactions of curved polycyclic systems: M^+ (M=Li and Na) ion complexation with buckybowls☆

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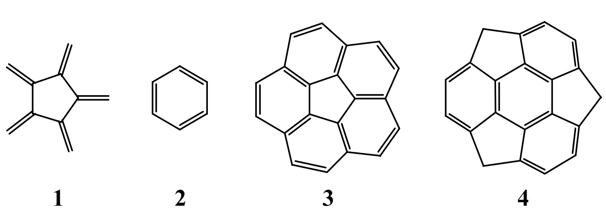
Abstract—B3LYP/6-311+G** calculations on alkali metal ion (Li^+ and Na^+) complexation with corannulene and sumanene indicate stronger binding compared to [5]-radialene or benzene. The dependence of binding to the convex and concave site is marginal, albeit the preference was consistent for convex binding in the range of 1–4 kcal/mol. The bowl-to-bowl inversion barriers are only marginally affected, below 2 kcal/mol, by metal ion complexation.

Non-covalent interactions such as dispersive forces, van der Waals interactions, hydrogen bonding, hydrophilic and hydrophobic forces are the dominant supramolecular and biological macromolecular interactions. Recently, cation-π interactions have also been identified as another intermolecular interaction and have been found to play an important role in drug-receptor interactions, substrate binding and other biological processes.[1–3] These interactions are also expected to play a key role in host–guest complexes involving crown ethers with some cationic hosts.[1–5] These findings resulted in a number of elegant computational and carefully designed experimental studies to understand the binding strengths and structural features of cation-π complexes.[6–10]

So far the studies have been limited to complexes where the metal ion complexation was subjected only to flat π-systems. Buckybowls, the fragments of fullerenes, have generated a lot of interest in the past decade and a number of buckybowls have been synthesized.[11] Corannulene, **3** and sumanene, **4** are two fundamentally important buckybowls, which can be viewed as C_{20} and C_{21} fragments of buckminsterfullerene (C_{60}) along the C_5 and C_3 axes respectively (Scheme 1). Corannulene was synthesized long before the discovery of C_{60} and a large number of experimental and theoretical studies are available.[12] In contrast, several attempts targeting sumanene have not been successful; however, a heteroanalog of sumanene has been synthesized together with many theoretical studies on this C_3-fragment and its heteroanalogs.[13–15] The main structural feature that makes buckybowls and planar polycyclic hydrocarbons different is that the former has two distinct π-faces due to the curvature prevalent in them, whereas in the latter, the two π-faces are identical by symmetry. The study of cation interactions with the twin faces of buckybowls, namely the convex and concave faces, is interesting in its own right. Many studies involving fullerenes where one or more metal atoms are trapped inside the cage are available and these compounds have been shown to have potential applications in superconductivity.[16] Similarly, exohedral transition metal complexes have also been synthesized[17] and Jemmis et al. have studied the binding of transition metal fragments to sumanene to model the transition metal binding in fullerenes.[18]



Scheme 1.

In the present study, for the first time, the binding of metal ions (Li^+ and Na^+) to the two distinct faces, namely the convex, **X** and concave, **V** surfaces (Scheme 2), of corannulene, **3** and sumanene, **4** are considered.

Keywords: cation-π interactions; buckybowls; corannulene; sumanene; theoretical studies.

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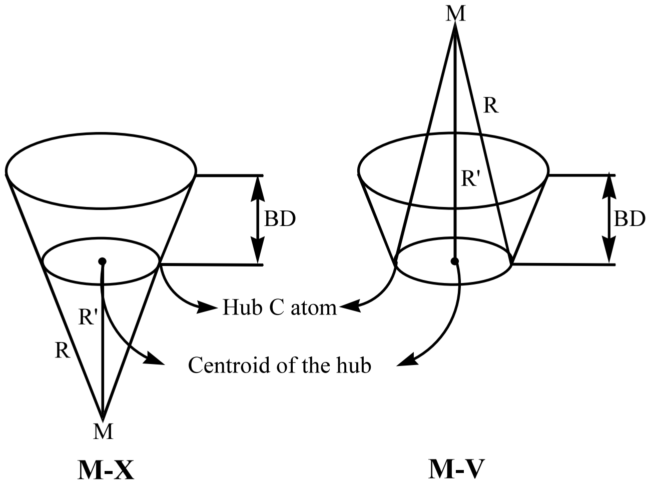


Scheme 2.

Previous experimental and theoretical studies have been focused on the reduction of fullerenes and corannulenes by metals, which involve the interaction between M^{+} and the anion.[19] The present computational study is aimed at the estimation of the relative binding of the metal ion to the two sides and the deviation of the binding energy from the planar model structures **1** and **2**. We have also examined the effect of metal ion complexation on the bowl depth, curvature and bowl-to-bowl inversion barrier of the buckybowls.

The structures given in Scheme 1, their metal ion complexes and the transition states corresponding to the bowl-to-bowl inversion barriers were optimized at the B3LYP level using the 6-31G* basis set. The frequency calculations characterize the bowl structures of **2**, **3**, **4** and their metal ion complexes as minima, indicating that both faces of the curved surfaces are open for metal ion complexation. However, the D_{5h} [5]-radialene and, its Li^{+} and Na^{+} complexes were second order saddle points, which were traced to the repulsion of the *peri* hydrogens.[13] For the effective estimation of the binding energy with the π-face, only the D_{5h} [5]-radialene and C_{5v} structures of its metal complexes were considered, although they are second order saddle points, as the real minima are nonplanar. The transition states (**3-TS**, **4-TS**, **3Li^{+}-TS**, **4Li^{+}-TS**, **3Na^{+}-TS** and **4Na^{+}-TS**) for the bowl-to-bowl inversion process were located and confirmed as saddle points by frequency calculations. Previous computational studies indicated that the use of triple-ζ basis set is essential in obtaining reliable binding energies and bowl-to-bowl inversion barriers.[6,10,14,20] Hence, we performed single point calculations at the B3LYP/6-311+G** level. All calculations were performed using the Gaussian 98 package.[21]

The principal geometric parameters (R and R′), and the POAV (π-orbital axis vector) angles[22] (only those at the hub positions are given for bowl structures) are given in Table 1 and the bowl depths (BD) are given in Figure 1. The POAV angle is the angle between the C–C bond and the vector perpendicular to the pyramidal base of the three idealized C–C bonds. Bowl depth (BD) is the interplanar distance between the two planes formed by the hub and rim atoms. The notations BD, R and R′, are illustrated in Scheme 2. Examination of the structural parameters reveals that the metal ion complexation has very little effect on the skeleton of the buckybowls. The curvature of **3** and **4**, as measured by bowl depth and the POAV angles at the hub position, slightly increase upon metal ion complexation from either face except in **4Li^{+}-X**. In this case, the bowl depth and POAV angle slightly decrease compared to the parent buckybowl, namely, sumanene **4** leading to a reduced bowl-to-bowl inversion barrier (vide infra). The

Table 1. The binding energies (BE in kcal/mol) of the complexes obtained at the B3LYP level using the 6-31G* and 6-311+G** basis sets. The point groups (PG) and the number of imaginary frequencies (NIMG), principal geometric parameters (R and R′ in Å), and POAV angles at the hub positions (°) obtained at the B3LYP/6-31G* level are also given

Structure[a]	PG (NIMG)	BE[b]	BE[c]	R	R′	POAV
1-Li^{+}	C_{5v} (2)	36.9	33.2	2.344	1.967	90.0
1-Na^{+}	C_{5v} (2)	27.1	23.7	2.711	2.393	90.0
2-Li^{+}	C_{6v} (0)	42.3	38.3	2.349	1.882	90.0
2-Na^{+}	C_{6v} (0)	28.5	23.8	2.761	2.377	90.0
3Li^{+}-X	C_{5v} (0)	48.2	44.5	2.281	1.934	98.1
3Li^{+}-V	C_{5v} (0)	46.5	40.3	2.252	1.899	98.3
3Li^{+}-TS	C_{5v} (1)	46.1	42.4	2.254	1.913	90.0
3Na^{+}-X	C_{5v} (0)	34.2	30.7	2.680	2.391	98.4
3Na^{+}-V	C_{5v} (0)	33.6	28.0	2.690	2.403	98.6
3Na^{+}-TS	C_{5v} (1)	31.6	28.3	2.672	2.392	90.0
4Li^{+}-X	C_{3v} (0)	45.6	41.9	2.343	1.866	98.5
4Li^{+}-V	C_{3v} (0)	47.4	40.9	2.288	1.796	99.0
4Li^{+}-TS	C_{3v} (1)	45.9	42.4	2.302	1.836	90.0
4Na^{+}-X	C_{3v} (0)	33.2	29.8	2.726	2.329	98.7
4Na^{+}-V	C_{3v} (0)	34.4	28.5	2.714	2.315	99.1
4Na^{+}-TS	C_{3v} (1)	31.9	28.5	2.709	2.327	90.0

[a] **TS** corresponds to the bowl-to-bowl transition states and **X** and **V** correspond to the convex and concave binding, respectively.

[b] Obtained at the B3LYP/6-31G* level of theory.

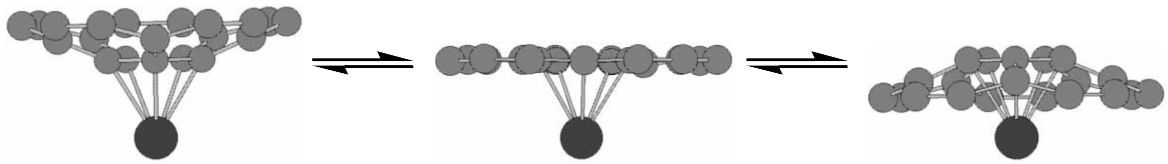
[c] Obtained at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory.

M–C distance (R) and M-centroid distance (R′) in the complexes involving buckybowls, **3** and **4** are shorter compared to the corresponding planar model structures (**1** and **2**, respectively). This stronger binding of metals to the buckybowls is also reflected in the magnitude of the binding energies (Table 1). The binding energies of the complexes involving corannulene are higher compared to [5]-radialene, **1**. The differences in the binding energies of complexes involving **1** and **3** are 7–11 kcal/mol when M = Li^+ and 4–5 kcal/mol when M = Na^+. Comparison of the binding energies of the complexes of **2** and **4** results in similar observations, albeit the magnitude of the differences are less when M = Li^+. The complexation energy seems to depend critically on the quality of the basis set employed. In corannulene, binding to the convex face is favored compared to the concave surface consistently at both levels of theories employed. In the case of sumanene, the concave binding is computed to be more favorable compared to that of the convex side when the 6-31G* basis set is used. However, when the 6-311+G** basis set was employed, the binding energy of the convex bound sumanene (**4M-X**) is more compared to that of the concave bound sumanene (**4M-V**). In general, the binding of metal ions to the convex face is marginally preferred over binding to the concave face.

The structures of the metal ion complexes of corannulene and sumanene, and the corresponding transition states for the bowl-to-bowl inversion are depicted in Figure 1. The relative energies of the minimum energy bowl structures and the bowl-to-bowl transition states of the parent and the metal ion complexed bowls are given in the same figure. The relative energies of the transition states correspond to the inversion barrier. In all the cases, complexes where the cation is bound to the convex face are more stable than the concave bound complexes at the B3LYP/6-311+G** level of theory. While, the relative energies obtained using the 6-31G* and 6-311+G** basis sets show different trends, the qualitative trend of the computed bowl-to-bowl inversion barriers are very similar. The inversion barrier of corannulene increases by about 2 kcal/mol upon Li^+ and Na^+ complexation. In contrast, the Li^+ bound sumanene exhibits a lower inversion barrier compared to sumanene itself; the curvature and bowl depth are also slightly less.

The present study, to our knowledge, is the first attempt to study cation-π interactions in curved polycyclic aromatic hydrocarbons, buckybowls. Local minima could be located for the metal ion complexation with both the concave and convex faces of corannulene, **3** and sumanene, **4**, and binding energy differences are minor. The binding energies of the complexes of **3** and **4** are comparatively higher than the planar model compounds, **1** and **2**. The binding to the convex face seems to be marginally favored over concave binding. Cation binding has a minor effect on the inversion barrier; the barrier is found to increase upon complexation in the majority of the cases.

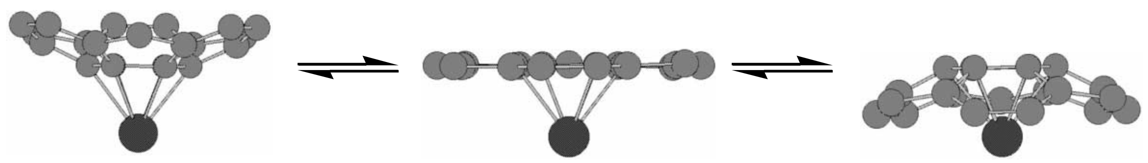
(a) Corannulene:



3M-X **3M-TS** **3M-V**

	3M-X		3M-TS		3M-V	
M	BD	ΔE	BD	ΔE	BD	ΔE
–	0.863	0.0 (0.0)	0.000	8.6 (10.7)	0.863	0.0 (0.0)
Li^+	0.876	0.0 (0.0)	0.030	10.7 (12.7)	0.883	1.7 (4.2)
Na^+	0.892	0.0 (0.0)	0.019	11.2 (13.1)	0.905	0.6 (2.7)

(b) Sumanene:



4M-X **4M-TS** **4M-V**

	4M-X		4M-TS		4M-V	
M	BD	ΔE	BD	ΔE	BD	ΔE
–	1.121	0.0 (0.0)	0.000	16.8 (18.9)	1.121	0.0 (0.0)
Li^+	1.109	0.0 (0.0)	0.000	16.5 (18.4)	1.161	–1.8 (1.0)
Na^+	1.126	0.0 (0.0)	0.014	18.2 (20.3)	1.190	–1.2 (1.3)

Figure 1. The three dimensional structures of the complexes of corannulene (a) and sumanene (b) and the bowl-to-bowl inversion transition states. The bowl depth (BD in Å) and relative energies (Δ*E* in kcal/mol) obtained at the B3LYP/6-31G* level are given below the corresponding structures. The relative energies obtained at the B3LYP/6-311+G** level are given in parentheses.

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