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Tetrahedron 60 (2004) 3037–3043
ELSEVIER
Tetrahedron

A computational study of cation–π interactions in polycyclic systems: exploring the dependence on the curvature and electronic factors[☆]

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Received 23 November 2003; revised 6 January 2004; accepted 29 January 2004

Abstract—Density functional theory (B3LYP) calculations with double and triple-ζ quality basis sets were performed on the Li^+ and Na^+ π-complexes of corannulene **2**, sumanene **3CH$_2$**, heterosumanenes **3X**, triphenylene **4** and heterotrindenes **5X**. The metal ions bind to both convex and concave faces of buckybowls, with a consistent preference to bind to the convex surface by about 1–4 kcal/mol. The metal ion complexation with the π-framework of the central six-membered ring span wider range compared to benzene, indicating the control of size, curvature and electronic perturbations over the strength of cation–π interactions. Computations show that the bowl-to-bowl inversion barriers are only slightly altered upon metal complexation, indicating the continuity of bowl-to-bowl inversion despite metal complexation. We have calculated the binding energies of model systems, triphenylene (**4**) and heterotrindenes (**5X**), which indicate that the interaction energies are controlled by electronic factors. While the inversion barrier is dependent mainly on the size of the heteroatom, the extent of binding is independent of the size of the atom or the bowl depth.

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1. Introduction

Non-covalent interactions such as van der Waals interactions, hydrogen bonding, dispersive forces, hydrophilic and hydrophobic interactions play a major role in dictating the structures and functions of biological macromolecules and supramolecular assemblies.[1,2] These interactions are responsible for molecular recognition like substrate–enzyme, antigen–antibody, neurotransmitter–neuroreceptor, protein–protein, protein–DNA interactions, etc. Dougherty and co-workers have identified the interaction between a cation and the π-face of an aromatic ring namely the cation–π interaction.[3] Cation–π interactions are ubiquitous in biological systems and arguably the strongest among the non-covalent interactions.[3–5] The interaction of metal ions with the π-system of various aromatic hydrocarbons and aminoacids containing aromatic rings have generated interest recently.[6,7] A recent study of the dependence of the strength of cation–π interaction on the curvature of polycyclic system showed a marginal preference for binding to the convex face.[8] Thus, the curvature was expected to show only a slight facial selectivity in cation–π interaction. To our knowledge, the influence of electronic factors and the aromaticity of the π-system on the cation binding ability have not been explored.

A theoretical study on a designed series of model systems where the curvature and electronic factors can be systematically modulated should help in discerning the causative factors of the binding energies. The C_{20} and C_{21} fragments of C_{60} along its C_5 and C_3 axes have been subjects of a number of experimental and theoretical studies.[9,10] There has been a lot of interest in this class of compounds, which resulted in a flurry of research activity concentrating on this C_3-fragment of fullerene.[9–13] Theoretical study on trisubstituted trindenes and sumanenes indicated that the type of substituent imparts a marked effect on the central six-membered ring of both the systems.[13] Thus, these systems provide benzene rings modified by varied extents and we felt a systematic study of M^+ (Li^+, Na^+) ion binding to the central six-membered ring (Scheme 1) would be worthwhile. Many experimental studies on the endohedral and exohedral complexes of fullerene with various metal ions, which have potential applications in superconductivity, are available.[14,15] Similarly, a buckybowl bound to a transition metal fragment has been synthesized and theoretical studies on a similar class of compounds have been reported.[16,17] In the present paper, we report a density functional theory study of the cation–π interactions of a series of polycyclic aromatic compounds (**2**, **3X**, **4** and **5X**) (Scheme 1). Unlike planar aromatics, the cation has the possibility to bind to the

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[☆] IICT Communication No. 031113.

Keywords: Cation–π interaction; Polycylic aromatic hydrocarbons; Buckybowls; Heterobuckybowls; Computational.

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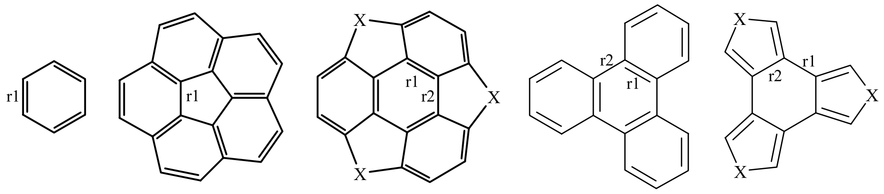
0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.01.086

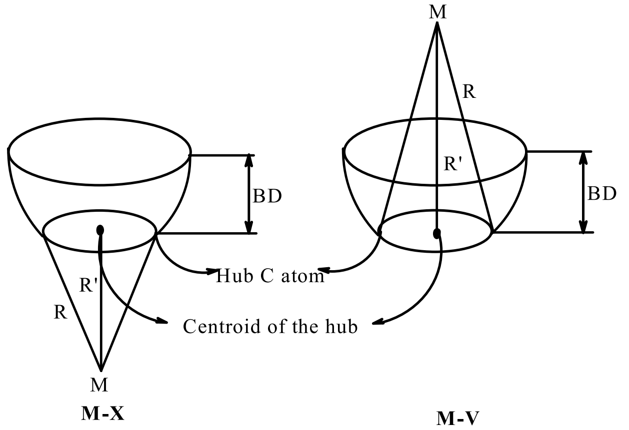


1 **2** **3X** **4** **5X**

X = O, NH, CH_2, BH, S, PH, PH_3, Si, SiH_2, AlH

Scheme 1.

two distinct faces, namely convex, **X** and concave, **V** (Scheme 2) of these bowl structures. The relative binding of the metal ions namely, Li^+ and Na^+, to either face of the buckybowls are analyzed. The buckybowls considered in the present study exhibit bowl depth (BD) ranging from 0.0 to 1.5 Å and possess substituents with varying electronegativities.[13] Hence, it would be interesting to see how these factors dictate the binding energies and other physicochemical properties such as curvature, BD, in this class of compounds. Cation–π interactions of model systems, **4** and **5X**, are studied to understand the electronic factor dependence on the binding energies. The heterotrindenes (**5X**) which are devoid of curvature (except **5PH**) are expected to single out the effect of electronic perturbations on the binding energies. We have also examined the effect of cation binding on the bowl-to-bowl inversion barriers of the bowl structures. Hybrid density functional theory (B3LYP) calculations were performed to address the above points.



Scheme 2.

2. Methodology

All the structures considered in the study were optimized within the given symmetry constraints using the hybrid density functional theory B3LYP level using the 6-31G* basis set. The nature of the stationary points thus obtained was assessed based on frequency calculations. The planar forms of corannulene (**2**) and sumanenes, **3X**, (X=O, NH, CH_2, BH and S) were computed to be transition states corresponding to the bowl-to-bowl inversion. The planar forms of **3X** (X=PH_3, Si, SiH_2 and AlH) were characterized as minima on the potential energy surface, thus, precluding the possibility for a bowl structure. The planar form of **3PH** is a third order saddle point; the normal modes of the imaginary frequencies correspond to the out-of-plane bending of the hydrogen atoms connected to phosphorus. The minimum energy structures corresponding to the bowl forms of **3X** (X=O, NH, CH_2, BH and S) have been located and the frequency calculations characterize them as minima. The Li^+ and Na^+ complexes of all the minimum energy structures were optimized and characterized as minima except **3O-Na$^+$-V**, which is a second order saddle point. The transition states corresponding to the bowl-to-bowl inversion barriers of the metal ion complexed buckybowls were also obtained and their nature was confirmed by frequency calculations. **4**, **5X** and their Li^+ and Na^+ complexes were optimized at the B3LYP/6-31G* level. Planar structures were considered for all except **5PH**, where the three hydrogen atoms connected to P lie out-of-plane. **5Si** and **5AlH** were third order saddle points, which was traced to the *peri*-hydrogen interactions.[13] The complexes of these two trindenes and **5BH** are also higher order saddle points (Table 1). Previous computational studies on buckybowls and cation–π interactions reveal that employing the triple-ζ basis set is crucial in obtaining reliable inversion barriers of buckybowls and cation–π binding energies.[18–21] Therefore, single point calculations were employed at the B3LYP level using the 6-311+G** basis set for all the systems considered in the present study. The discussion on the energetics will be based on those obtained at the B3LYP/6-311+G** basis set unless otherwise specified. All computations were performed using Gaussian 98 suite of programs.[22] The curvature of the buckybowls and their complexes were assessed based on the π-orbital axis vector (POAV) angles.[23,24]

3. Results and discussion

The equilibrium geometries and effect of metal ion binding on the geometric parameters of all the compounds and curvature of buckybowls are discussed first. This is followed by a discussion on the variation of the interaction energies arising from binding to the convex and the concave faces of the buckybowls and the role of varying heteroatoms in the strength of binding. Finally, the deviation of the bowl-to-bowl inversion barriers of the parent buckybowl molecules upon cation binding is presented.

3.1. Equilibrium geometries

The principal equilibrium geometries of **1**, **2**, **3X**, **4**, **5X**, and their metal ion complexes are given in Table 1 The notations used in Table 1 are to be deciphered from Schemes 1 and 2. POAV angle is the angle between the vector normal to the

Table 1. The principal geometric parameters (r, $r2$, R and R'), bowl depth (BD) and POAV angles at the hub position of **1**, **2**, **3X**, **4** and **5X**, their metal ion (Li$^+$ and Na$^+$) complexes and bowl-to-bowl inversion transition states. The notations used in this table are illustrated in Schemes 1 and 2. All bond lengths are given in Å and angles in degrees. The number of imaginary frequencies are also given

Structure	$r1$	$r2$	R	R'	BD	POAV (hub)	N_{Img}	Structure	$r1$	$r2$	R	R'	N_{Img}
1	1.397	—	—	—	—	—	0	**2-TS**	1.398	—	—	—	1
1-Li$^+$	1.406	—	2.349	1.882	—	—	0	**2-Li$^+$-TS**	1.401	—	2.254	1.913	1
1-Na$^+$	1.404	—	2.761	2.377	—	—	0	**2-Na$^+$-TS**	1.401	—	2.672	2.392	1
2	1.385	—	—	—	0.862	98.1	0	**3O-TS**	1.348	1.369	—	—	1
2-Li$^+$-X	1.393	—	2.281	1.934	0.876	98.1	0	**3O-Li$^+$-TS**	1.354	1.375	2.345	1.907	1
2-Li$^+$-V	1.393	—	2.252	1.899	0.883	98.3	0	**3O-Na$^+$-TS**	1.353	1.374	2.766	2.406	1
2-Na$^+$-X	1.391	—	2.680	2.391	0.892	98.4	0	**3NH-TS**	1.354	1.375	—	—	1
2-Na$^+$-V	1.391	—	2.690	2.403	0.905	98.4	0	**3NH-Li$^+$-TS**	1.362	1.381	2.294	1.839	1
3O	1.399	1.428	—	—	1.486	101.9	0	**3NH-Na$^+$-TS**	1.361	1.380	2.700	2.326	1
3O-Li$^+$-X	1.406	1.436	2.398	1.931	1.484	101.9	0	**3CH$_2$-TS**	1.366	1.400	—	—	1
3O-Li$^+$-V	1.405	1.435	2.373	1.901	1.504	103.3	0	**3CH$_2$-Li$^+$-TS**	1.372	1.406	2.302	1.836	1
3O-Na$^+$-X	1.405	1.435	2.771	2.379	1.491	102.0	0	**3CH$_2$-Na$^+$-TS**	1.371	1.405	2.709	2.327	1
3O-Na$^+$-V	1.403	1.432	2.861	2.485	1.513	102.0	2	**3BH-TS**	1.367	1.420	—	—	1
3NH	1.399	1.422	—	—	1.325	100.6	0	**3BH-Li$^+$-TS**	1.373	1.425	2.310	1.839	1
3NH-Li$^+$-X	1.407	1.428	2.341	1.863	1.303	100.6	0	**3BH-Na$^+$-TS**	1.371	1.425	2.727	2.341	1
3NH-Li$^+$-V	1.408	1.428	2.380	1.785	1.308	100.8	0	**3S-TS**	1.382	1.403	—	—	1
3NH-Na$^+$-X	1.407	1.428	2.709	2.308	1.315	100.6	0	**3S-Li$^+$-TS**	1.390	1.409	2.342	1.878	1
3NH-Na$^+$-V	1.405	1.426	2.721	2.324	1.315	98.7	0	**3S-Na$^+$-TS**	1.388	1.408	2.754	2.373	1
3CH$_2$	1.387	1.433	—	—	1.121	98.5	0	**4**	1.421	1.467	—	—	0
3CH$_2$-Li$^+$-X	1.392	1.440	2.343	1.866	1.109	99.0	0	**4-Li$^+$**	1.431	1.475	2.342	1.837	0
3CH$_2$-Li$^+$-V	1.393	1.442	2.288	1.796	1.161	98.7	0	**4-Na$^+$**	1.428	1.475	2.734	2.316	0
3CH$_2$-Na$^+$-X	1.392	1.440	2.726	2.329	1.126	99.1	0	**5O**	1.452	1.453	—	—	0
3CH$_2$-Na$^+$-V	1.391	1.440	2.714	2.315	1.190	96.5	0	**5O-Li$^+$**	1.459	1.464	2.357	1.850	0
3BH	1.377	1.439	—	—	0.890	96.5	0	**5O-Na$^+$**	1.458	1.462	2.741	2.320	0
3BH-Li$^+$-X	1.383	1.443	2.345	1.871	0.891	96.7	0	**5NH**	1.451	1.445	—	—	0
3BH-Li$^+$-V	1.383	1.445	2.387	1.798	0.902	96.9	0	**5NH-Li$^+$**	1.458	1.456	2.291	1.764	0
3BH-Na$^+$-X	1.382	1.445	2.743	2.351	0.915	96.9	0	**5NH-Na$^+$**	1.458	1.453	2.663	2.230	0
3BH-Na$^+$-V	1.381	1.444	2.719	2.323	0.934	94.0	0	**5CH$_2$**	1.460	1.489	—	—	0
3S	1.391	1.414	—	—	0.642	95.1	0	**5CH$_2$-Li$^+$**	1.467	1.500	2.348	1.819	0
3S-Li$^+$-X	1.398	1.420	2.367	1.902	0.643	95.1	0	**5CH$_2$-Na$^+$**	1.466	1.467	2.709	2.267	0
3S-Li$^+$-V	1.400	1.421	2.319	1.841	0.677	95.4	0	**5BH**	1.390	1.483	—	—	0
3S-Na$^+$-X	1.398	1.421	2.761	2.374	0.679	95.4	0	**5BH-Li$^+$**	1.393	1.493	2.458	1.988	2
3S-Na$^+$-V	1.398	1.421	2.748	2.360	0.703	95.6	0	**5BH-Na$^+$**	1.397	1.492	2.825	2.428	2
3PH	1.388	1.423	—	—	0.107	90.0	0	**5S**	1.462	1.449	—	—	0
3PH-Li$^+$-X	1.396	1.430	2.324	1.854	0.094	90.0	0	**5S-Li$^+$**	1.469	1.457	2.352	1.841	0
3PH-Li$^+$-V	1.396	1.430	2.329	1.851	0.102	90.0	0	**5S-Na$^+$**	1.468	1.455	2.732	2.308	0
3PH-Na$^+$-X	1.395	1.431	2.735	2.342	0.273	91.8	0	**5PH**	1.468	1.480	—	—	0
3PH-Na$^+$-V	1.394	1.429	2.745	2.355	0.028	90.0	0	**5PH-Li$^+$**	1.474	1.487	2.368	1.849	0
3PH$_3$	1.390	1.432	—	—	0.027	90.0	0	**5PH-Na$^+$**	1.474	1.485	2.732	2.297	0
3PH$_3$-Li$^+$	1.400	1.442	2.308	1.820	0.018	90.0	0	**5PH$_3$**	1.469	1.500	—	—	0
3PH$_3$-Na$^+$	1.396	1.441	2.711	2.314	0.102	91.1	0	**5PH$_3$-Li$^+$**	1.479	1.512	2.365	1.833	0
3Si	1.386	1.435	—	—	0.000	90.0	0	**5PH$_3$-Na$^+$**	1.479	1.509	2.756	2.289	0
3Si-Li$^+$	1.394	1.442	2.313	1.827	0.094	90.0	0	**5Si**	1.464	1.527	—	—	3
3Si-Na$^+$	1.392	1.442	2.728	2.331	0.177	91.1	0	**5Si-Li$^+$**	1.471	1.533	2.415	1.891	2
3SiH$_2$	1.401	1.446	—	—	0.000	90.0	0	**5Si-Na$^+$**	1.470	1.530	2.775	2.334	2
3SiH$_2$-Li$^+$	1.402	1.453	2.322	1.831	0.003	90.0	0	**5SiH$_2$**	1.478	1.512	—	—	0
3SiH$_2$-Na$^+$	1.401	1.452	2.730	2.328	0.034	90.0	0	**5SiH$_2$-Li$^+$**	1.478	1.522	2.388	1.855	0
3Al	1.404	1.468	—	—	0.000	90.0	0	**5SiH$_2$-Na$^+$**	1.484	1.519	2.756	2.311	0
3Al-Li$^+$	1.412	1.474	2.298	1.788	0.008	90.0	0	**5AlH**	1.487	1.537	—	—	3
3Al-Na$^+$	1.410	1.474	2.699	2.282	0.023	90.0	0	**5AlH-Li$^+$**	1.497	1.547	2.359	1.803	3
								5AlH-Na$^+$	1.495	1.544	2.722	2.259	3

triangle formed by the three idealized C–C bonds[23,24] and BD is the distance between the two planes formed by the hub and the rim atoms. The parameter R is the distance between the hub carbon atom and the metal ion, and R' is the distance from the centroid of the hub to the metal ion. All the bond lengths of the central six-membered ring are uniformly elongated in all cases upon complexation with either Li$^+$ or Na$^+$. However, the variation of the other bond lengths upon cation binding is marginal in most of the cases. Among **3X**, R is longer in case of **3O** and among **5X**, M–C bond length is longer in case of **5BH** indicating the weak interaction in these two compounds. The weak binding is also reflected in the low binding energies compared to that of the other systems (vide infra). BD and POAV angles have been extensively used to evaluate the curvature of buckybowls. The BD of the heterosumanenes decreases upon increasing the size of the heteroatom. The planar structures are the minima, when X=PH$_3$, Si, SiH$_2$ and AlH; hence, these do not have two distinct faces (convex and concave). In general, Na$^+$ imparts more curvature on the buckybowl skeleton compared to Li$^+$. When Li$^+$ binds to the convex face of the bowls, the BD slightly decreases or remains almost the same compared to that of the parent buckybowl. On the other hand, those complexes where Li$^+$ is bound to the concave face or Na$^+$ is bound to either of the faces, exhibit a comparatively deeper bowl skeleton. In the case of

3NH, all the complexes exhibit lower BDs compared to the parent buckybowl. A similar trend is observed when POAV angle is used as a measure of curvature (Table 1).

3.2. Binding energies

The interaction energies of the compounds under study when binding with Li^+ and Na^+ obtained at the B3LYP level using the 6-31G* and 6-311+G** basis sets are given in Table 2. The binding energies are uniformly overestimated when 6-31G* basis set was used except for **5NH**. Importantly, the trend of the binding energies between the convex and concave faces obtained using the 6-31G* basis set is different compared to those obtained using 6-311+G** basis set in many cases, emphasizing the importance of employing triple-ζ quality basis set. Thus, the complexation energy mainly depends on the quality of the basis set and this is in agreement with our recent study on metal ion complexation with corannulene and suamanene.[8] A comparison of the binding energies of the convex and concave bound complexes reveals that the selectivity between the two is marginal. However, binding to the convex face is consistently preferred over the concave face in all cases. The preference is about 3–4 kcal/mol when X=O, NH and BH, whereas in case of X=CH_2, S and PH, the selectivity for binding between the two faces is marginal. The binding energies of the cation complexes exhibit wide ranges with both Li^+ (25–59 kcal/mol) and Na^+ (15–43 kcal/mol) with varying substituents. The correlation of the interaction energies of all the compounds considered in the study with Li^+ and Na^+ is depicted in Figure 1. As the difference between the binding energies of the convex and concave bound complexes are marginal, those of only the convex complexes are depicted in the figure for clarity. Consistent with the previous studies, Li^+ binds strongly to the π-systems compared to Na^+ in all the cases. The trend of the binding energies of the Li^+ and Na^+ complexes remains the same with respect to the varying substituents. Any straight correlation of the BD, curvature or electronegativity of the heteroatom with the complexation energy could not be obtained, indicating the intricate factors involved in deciding the affinity. The two factors affecting the binding energies are the curvature and the electronic perturbation caused by the substitutents. A comparison of the binding energies of the bowl molecules (**2**, **3X**) and the corresponding planar molecules (**2-TS** and **3X-TS**) reveals that they are comparable; the qualitative trend of the variation of binding energies with varying

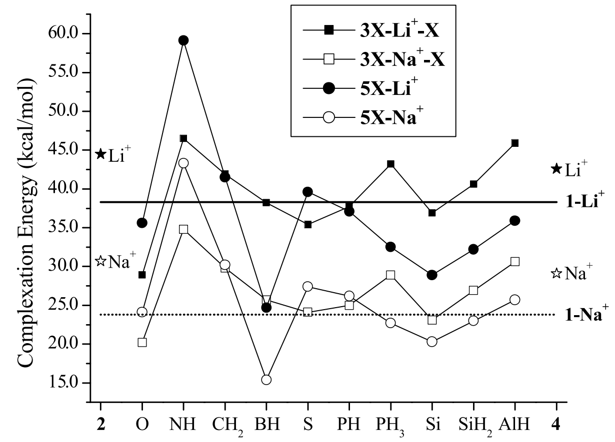


Figure 1. The correlation of the interaction energies of benzene (**1**), corannulene (**2**), heterosumanenes (**3X**), triphenylene (**4**) and heterotrindenes (**5X**) with Li^+ and Na^+ obtained at the B3LYP/6-311+G** level.

Table 2. The interaction energies (in kcal/mol) of the compounds considered in the present study with Li^+ and Na^+ ions obtained at the B3LYP level using the 6-31G* (in parentheses) and 6-311+G** basis sets

Structure	Li^+-X	Li^+-V	Na^+-X	Na^+-V
1	38.3 (42.3)	—	23.8 (28.5)	—
2	44.5 (48.2)	40.3 (46.5)	30.7 (34.2)	28.0 (33.6)
2-TS	42.4 (46.1)	—	28.3 (31.6)	—
3O	28.9 (33.5)	25.5 (33.9)	20.2 (24.3)	17.4 (25.2)
3O-TS	28.1 (32.3)	—	17.2 (21.1)	—
3NH	46.5 (51.4)	42.9 (51.0)	34.8 (39.2)	30.5 (38.1)
3NH-TS	46.3 (50.8)	—	31.9 (36.4)	—
$3CH_2$	41.9 (45.6)	40.9 (47.4)	29.8 (33.2)	28.5 (34.4)
$3CH_2$-TS	42.5 (45.9)	—	28.7 (31.9)	—
3BH	38.2 (41.5)	34.7 (40.2)	25.7 (28.9)	21.9 (26.9)
3BH-TS	37.4 (40.8)	—	23.6 (27.0)	—
3S	35.4 (37.6)	33.8 (37.9)	24.1 (26.1)	22.5 (25.9)
3S-TS	35.0 (37.4)	—	22.8 (25.3)	—
3PH	37.7 (40.2)	37.2 (40.2)	25.0 (27.1)	24.4 (27.4)
$3PH_3$	43.2 (45.9)	—	28.9 (31.6)	—
3Si	36.9 (39.6)	—	23.1 (25.6)	—
$3SiH_2$	40.6 (43.3)	—	26.9 (29.6)	—
3AlH	45.9 (48.8)	—	30.6 (33.5)	—
4	42.6 (46.4)	—	29.1 (33.1)	—
5O	35.6 (40.3)	—	24.1 (28.5)	—
5NH	59.1 (54.7)	—	43.3 (38.6)	—
$5CH_2$	41.5 (44.9)	—	30.2 (33.5)	—
5BH	24.7 (27.5)	—	15.4 (18.2)	—
5S	39.6 (42.2)	—	27.4 (30.1)	—
5PH	37.1 (39.6)	—	26.2 (28.6)	—
$5PH_3$	32.5 (35.2)	—	22.7 (25.3)	—
5Si	28.9 (30.2)	—	20.3 (21.4)	—
$5SiH_2$	32.2 (34.7)	—	23.0 (25.3)	—
5AlH	35.9 (38.3)	—	25.7 (27.9)	—

Table 3. NICS values calculated at 1 Å above the centroid of the six-membered ring, total charge and the perimeter at the central six-membered ring obtained at the B3LYP level using 6-31G* basis set

Structure	NICS	Charges	Perimeter
1	−11.2	−0.771	8.380
2[a]	$\underline{2.6}$, *−2.3*, **5.3**	−0.257	7.085
3O[a]	$\underline{1.7}$, *−9.5*, −**6.3**	−0.110	8.481
3NH[a]	$\underline{1.4}$, *−9.1*, −**6.5**	−0.155	8.463
$3CH_2$[a]	$\underline{-1.6}$, *−10.6*, −**6.7**	0.074	8.460
3BH[a]	$\underline{-2.7}$, *−8.0*, −**6.5**	0.004	8.448
3S[a]	$\underline{-2.4}$, *−7.6*, −**5.4**	0.462	8.415
3PH	−6.3	0.465	8.433
$3PH_3$	−6.3	0.535	8.466
3Si	−7.4	0.470	8.463
$3SiH_2$	−6.4	0.254	8.526
3AlH	−6.7	0.253	8.616
4	−6.1	0.422	8.541
5O	−12.0	0.362	8.715
5NH	−3.2	0.280	8.688
$5CH_2$	−1.0	0.711	8.847
5BH	22.8	0.344	8.619
5S	0.8	0.821	8.733
5PH	0.7	0.710	8.844
$5PH_3$	0.9	0.881	8.907
5Si	0.8	0.787	8.973
$5SiH_2$	0.6	0.555	8.970
5AlH	0.6	0.554	9.072

[a] The three values correspond to the NICS values calculated for the bowl structure from the convex (underlined) and concave (italicized) face and calculated for the planar form (bold).

Table 4. The bowl-to-bowl inversion barriers (in kcal/mol) of the buckybowls (**2** and **3X**) and their metal ion complexes obtained at the B3LYP level using 6-31G* (in parentheses) and 6-311+G** basis set

Structure	Convex (**X**)	Transition state (**TS**)	Concave (**V**)
2	0.0 (0.0)	10.7 (8.6)	0.0 (0.0)
2-Li$^+$	0.0 (0.0)	8.5 (9.0)	4.2 (1.6)
2-Na$^+$	0.0 (0.0)	10.4 (10.6)	2.7 (−0.6)
3O	0.0 (0.0)	70.4 (68.3)	0.0 (0.0)
3O-Li$^+$	0.0 (0.0)	67.8 (69.9)	3.4 (−0.4)
3O-Na$^+$	0.0 (0.0)	70.6 (72.4)	2.8 (1.0)
3NH	0.0 (0.0)	44.6 (42.1)	0.0 (0.0)
3NH-Li$^+$	0.0 (0.0)	41.1 (42.4)	3.6 (0.4)
3NH-Na$^+$	0.0 (0.0)	43.2 (43.9)	4.3 (−1.2)
3CH$_2$	0.0 (0.0)	19.1 (16.8)	0.0 (0.0)
3CH$_2$-Li$^+$	0.0 (0.0)	17.5 (18.3)	1.0 (−1.8)
3CH$_2$-Na$^+$	0.0 (0.0)	18.9 (19.3)	1.3 (1.2)
3BH	0.0 (0.0)	7.4 (5.9)	0.0 (0.0)
3BH-Li$^+$	0.0 (0.0)	4.7 (5.3)	3.5 (1.3)
3BH-Na$^+$	0.0 (0.0)	5.7 (5.9)	3.8 (−2.0)
3S	0.0 (0.0)	2.9 (1.8)	0.0 (0.0)
3S-Li$^+$	0.0 (0.0)	1.8 (2.3)	1.6 (−0.3)
3S-Na$^+$	0.0 (0.0)	2.6 (2.5)	1.6 (−0.2)

substituents remain unaltered. This indicates that the BD has very little effect on the binding energies of the buckybowls. Hence, the complexation energies are mainly controlled by electronic factors. The qualitative trend of the binding energies of **3X** and **5X** for the various substituents are comparable except when X=S and PH$_3$. While the lowest binding energy is observed for **3X** when X=O; the complexation energy is lowest for **5X** when X=BH, when binding to either Li$^+$ or Na$^+$. The weak binding in these compounds is also witnessed in the long M–C bond lengths (Table 1). The π-complexes exhibit higher binding energies when X=NH, in both **3X** and **5X**, which is about 21 kcal/mol higher than that of benzene in **5NH-Li$^+$**. We have studied the effect of aromaticity of the central six-membered ring on the binding energies using the nucleus independent chemical shift (NICS) criterion.[25] The NICS (1) values are calculated both in the convex and concave surfaces for the bowl shaped molecules and are given in Table 3. The six-membered ring in **5X** exhibits non-aromatic character in all the cases except when X=O and BH. While **5O** is designated as highly aromatic, **5BH** is found to have antiaromatic character according to NICS. This is in line with our observation that the bond length alternation in **3O** is close to zero and that of **3BH** is around 0.09 Å.[13,26] We also have examined the total charge and the perimeter of the hub six-membered ring (Table 3). No straightforward correlation between any of these parameters and the binding energy could be drawn. Thus we feel that the electronic effects of the substituent atoms are not of columbic origin and operate in a more intricate way.

3.3. Bowl-to-bowl inversion barriers

The bowl-to-bowl inversion barriers of the parent buckybowls (**2** and **3X**; X=O, NH, CH$_2$, BH and S) and their corresponding Li$^+$ and Na$^+$ complexed bowl structures are given in Table 4. In the case of parent buckybowls, the inversion process normally leads to identical bowl structures. In contrast, the metal ion bound buckybowls generate two distinct species upon inversion (Fig. 2). Among the heterosumanenes (**3X**), the bowl-to-bowl inversion barriers decrease with the increase in the size of the heteroatom; calculations predict that the bowl-to-bowl inversion process does not happen when X=PH$_3$, Si, SiH$_2$ and AlH. Metal ion (both Li$^+$ and Na$^+$) complexation to the bowl molecules results in a slight lowering of the inversion barrier for the bowl-to-bowl. The maximum difference between the inversion barriers of the parent buckybowl and its corresponding metal ion complex is 3.5 kcal/mol in the case of **3NH-Li$^+$**. Therefore, the inversion barrier corresponding to the bowl-to-bowl inversion process is controlled mainly by the size of the substituent and not due to the electronic perturbations.

4. Conclusions

B3LYP/6-311+G** calculations were performed to assess the effect of curvature and remote electronic perturbations on the cation–π interactions of a large series of aromatic hydrocarbons and their hetero analogs. In all cases, except corannulene, the π-system is a structurally and electronically modified aromatic six-membered ring. The metal ions (Li$^+$ and Na$^+$) bind to both the faces of the buckybowls arising to two possibilities for π-complexes; convex face binding is preferred over concave binding in all the cases by about 1–4 kcal/mol. Both the bowl and planar forms yield similar binding energies, indicating that the curvature of the buckybowls has very little effect on the complexation energies. The strength of cation binding to the six-membered ring is mainly controlled by electronic factors, while the curvature plays only a marginal role. Heterosumanene or heterotrindene has a very high complexation energy compared to other compounds when X=NH. The present study indicates that there is no straightforward correlation between either the charge on

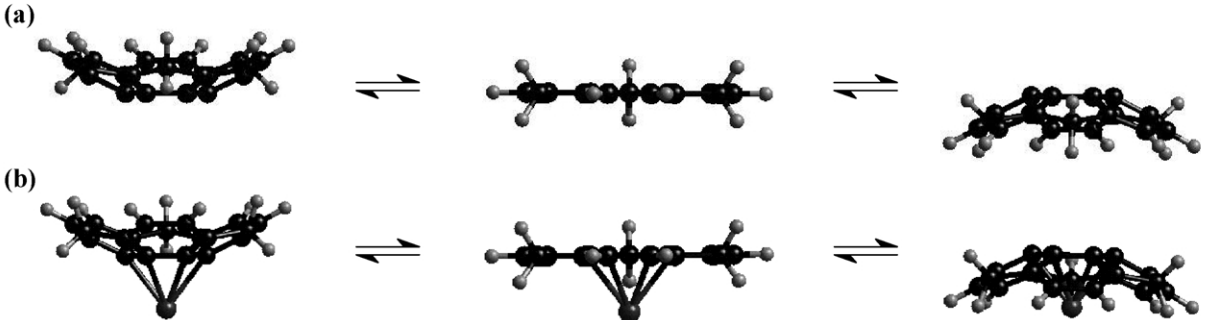


Figure 2. The bowl-to-bowl inversion processes of parent buckybowls (a) and their metal ion complexes (b).

the hub or the size of the system with the binding energies. The interaction energies observed in this class of compounds exhibit a wide range from 25–59 and 15–43 kcal for Li^+ and Na^+ ions, respectively. Importantly, the present study reveals that the curvature and flexibility of the curved surfaces are virtually undisturbed upon metal ion complexation and the solvation might have an important role in cation–π interactions but it is not considered in the present study due to the computational demand at this level of theory. A careful tuning of the electronic factors can make the strength of cation–π interactions comparable to that of covalent interactions! While the strength of binding is controlled by electronic factors, the bowl-to-bowl inversion barrier is exclusively controlled by the size of the heteroatom.

Acknowledgements

U.D.P thanks UGC, New Delhi for a research fellowship. We thank Dr. J. S. Yadav, Director, IICT, for his support and encouragement.

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