

# Cation – $\pi$ complexes between alkaline cations and molecular bowls related with fullerene: a DFT study.

*Jorge A. Carrazana-García<sup>(a,\*)</sup>, Enrique M. Cabaleiro-Lago<sup>(a)</sup> and Jesús Rodríguez-Otero<sup>(b)</sup>*

*(a) Departamento de Química Física, Facultade de Ciencias, Universidade de Santiago de Compostela. Campus de Lugo. Avda. Alfonso X El Sabio s/n 27002 Lugo (Spain).*

*(b) Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela. Avda. das Ciencias s/n, 15782 Santiago de Compostela (Spain).*

**\*e-mail: jorge-carrazana@usc.es**

## 1. Abstract.

The formation of complexes between alkaline cations and molecular bowls (MBs), curved conjugated systems related with fullerene ( $C_{60}$ ), is studied using DFT calculations. The series of MBs is constructed starting with benzene and additional hexagonal or pentagonal rings are added symmetrically to complete the  $C_{60}$  structure. All the MBs studied form stable cation– $\pi$  complexes by both of its sides: concave and convex. In all cases complexes with the cation in the convex side are more stable than their corresponding partner inside the bowl. The stability of the complexes is determined by the polarizing power of the cation and by the molecular electrostatic potential and the polarizability of the bowl. Additionally, size effects are observed when bulky cations are placed in the concave side of the largest bowls.

## 2. Introduction.

Noncovalent interactions play a variety of roles in many areas of chemistry and biochemistry because it is believed that all take part in determining the structures and controlling the functions of biological macromolecules. Among the noncovalent binding forces are included salt bridges, hydrophobic interactions, hydrogen bonds,  $\pi$ -stacking interactions and ion- $\pi$  interactions. In the case of cation- $\pi$  interactions, many studies suggest its involvement in molecular recognition processes<sup>1</sup> and ion channels.<sup>2</sup> For that reason, the interaction of  $Na^+$  and  $K^+$  with a variety of  $\pi$  systems have been widely studied because they are the most biologically important alkali metal cations.<sup>3</sup> Cation- $\pi$  interactions also influence the stability of proteins and protein-DNA complexes.<sup>4</sup> Finally, it is believed that through the appropriate addition of substituents to the aromatic ring, the strength of cation- $\pi$  interactions between a metal cation and  $\pi$ -binding ligands can be tailored so as to devise new chemical separation strategies for the removal of unnecessary and toxic species from environmental sources such as water streams.<sup>5</sup>

Studies of alkali metal cations binding to model aromatic systems and characterization of these metal-ligand interactions in the gas phase are an important part of the process for understanding the nature and strength of cation- $\pi$  interactions. To obtain a complete picture of cation- $\pi$  interactions, the contributions that the fundamental intermolecular forces make to these interactions need to be elucidated. The prevailing opinion is that electrostatic interactions play the main role in cation- $\pi$  interactions.<sup>6</sup> Other theoretical studies have shown that polarization is also an important factor in determining the strength of cation- $\pi$  interactions because the cation produces a strong electric field.<sup>7</sup> In systems with extended conjugation the inductive effect acquires more importance and its relative contribution to the total interaction can be bigger than the contribution made by the electrostatic interaction. Furthermore, the geometry of the  $\pi$  system is another variable to take in account. In the absence of desymmetrizing substituents, the two faces of planar  $\pi$  systems must have equivalent electrostatic potentials. However, in non-planar  $\pi$  systems that symmetry is broken, and the electrostatic potentials of the two faces no longer remain the same because one surface is more electron rich than the other. That is the situation in sumanene, semibuckminsterfullerene, circumtrindene and other curved conjugated systems related with buckminsterfullerene (see Fig. 1). The molecules that consist of fragments of  $C_{60}$  are also known as buckybowls, open geodesic polyarenes,  $\pi$  bowls or simply as molecular bowls (MBs). From a coordination chemistry viewpoint, MBs are unique because they can provide not only convex surfaces but also open concave surfaces for metal binding. The preparation and characterization of MBs complexes of various metals that are in a variety of coordination modes, have been reported for over a decade.<sup>8</sup> The face preference of the metal in the MBs/cation complexes and the nature of the contributions to their interaction are matter of theoretical study, sometimes with controversial results.

In this work the formation of complexes between alkaline cations and MBs is systematically studied using DFT calculations. All the MBs structures of the series considered here have a hexagonal ring in its center (bottom). Both extreme structures: benzene (a planar system) and  $C_{60}$  (the complete, closed ball) are included in the study too (see Fig. 1) and binding of ions to both, concave and convex faces of the curved surfaces, are considered.

### 3. Computational Details.

All the calculations were carried out with Gaussian03 suite of programs,<sup>9</sup> with the B3LYP method.<sup>10</sup> The 6-31+G\* basis set was used for all MBs and for  $Li^+$ ,  $Na^+$  and  $K^+$  cations. For  $Rb^+$  and  $Cs^+$ , the effective core potential basis set LANL2DZ (Los Alamos National Laboratory 2 double  $\zeta$ ) was employed.<sup>11</sup> This combination of hybrid DFT method with a split valence plus polarization basis set quality has proven<sup>12</sup> to be a good choice for obtaining reliable results with low-to-moderate computational cost in similar systems.

The studied complexes were fully optimized without symmetry restrictions starting from structures with the cation originally located centered on the benzene ring, the bottom of the MBs and one hexagonal face of fullerene. The curved  $\pi$  systems (MBs and  $C_{60}$ ) were explored by their both sides, concave (inner) and convex (outer). All the complexation energies were corrected for the basis set superposition error using the Boys and Bernardi method.<sup>13</sup>

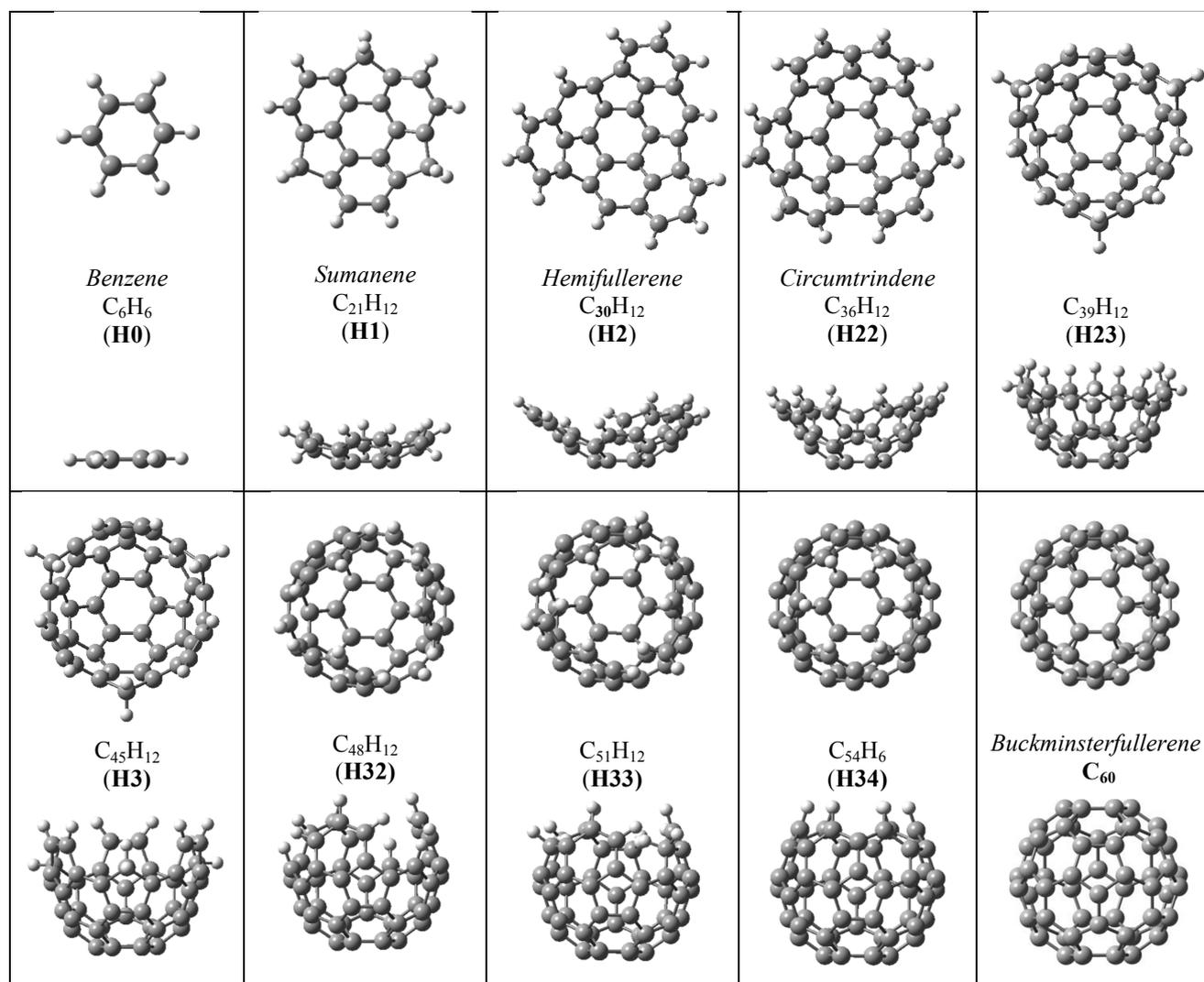
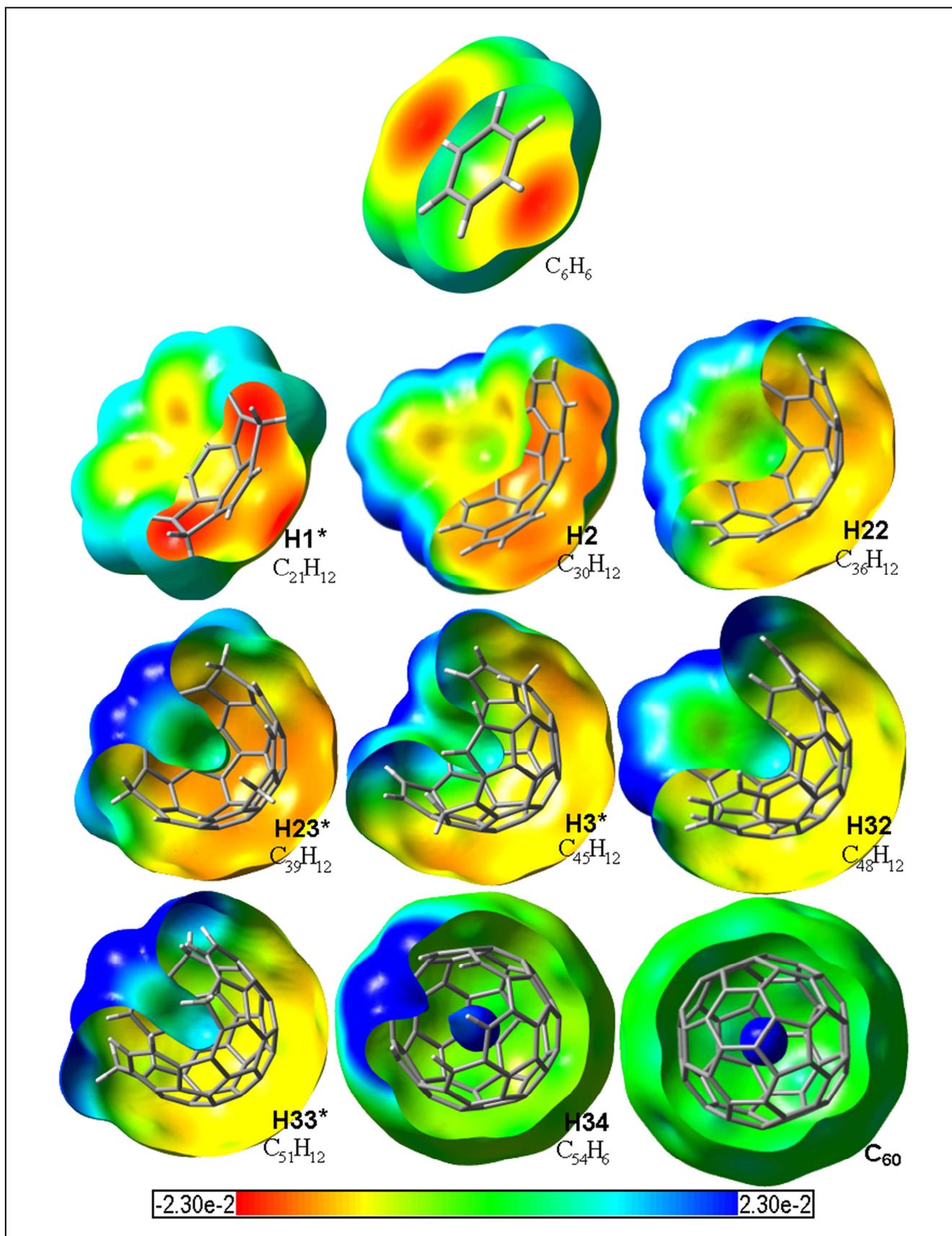


Fig. 1. Top and side views of benzene, fullerene and the Molecular Bowls studied.

## 4. Results and Discussion.

**Molecular Bowls.** Structures of benzene, the MBs and fullerene are shown in Fig. 1. Starting with benzene, the proper addition of further hexagonal and pentagonal rings causes the curvature of the conjugated system. The progressive growing from  $C_{21}$  to  $C_{60}$  is achieved conserving the 3-fold symmetry of the structures. The saturation of the rim with hydrogen atoms forces the introduction of  $sp^3$  carbon atoms in some of these structures (H1, H23, H3 and H33). In the other MBs the carbon atoms are all  $sp^2$ . This causes irregularities in the conjugation pattern that reflects in the progression of the properties of these MBs along the series.



**Fig. 2.** Molecular electrostatic potential maps generated at B3LYP/6-31+G\* level for benzene, the molecular bowl series and fullerene. Electrostatic potentials are mapped on the surface of the electron density of 0.0002 au. The red zones corresponds to a negative regions of the electrostatic potential ( $-0.023$  au), whereas the blue color corresponds to regions where the potential is positive ( $+0.023$  au).

The molecular electrostatic potential (MEP) of the MBs studied is shown in Fig. 2. Benzene MEP's concentrates zones of a high negative charge in the regions around the C6 axis and distributes symmetrically on both sides of the plane of the molecule. In all the curved structures the convex (outer) sides present MEP values more negative than the corresponding concave (inner) positions. The concave side changes from slightly negative to markedly positive MEP values in the H1-to-C<sub>60</sub> sequence. In H23, H3, H32 and H33 the concave side presents a tube-like appearance with the deepest region of the cavity more positive than zones of the tube wall located at different depths. This is decisive for understanding the equilibrium position adopted by the least polarizing cations (K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>) in their inner complexes with the MBs from H23 to H33. The closed cavities with high positive MEP values observed in H34 and C<sub>60</sub> are repulsive sites for cations. Nevertheless, as we will see later, the total interaction energy reaches significant negative values in the inner complexes between these two MBs and the smallest alkaline cations, indicating that the electrostatic contribution is not always the more important one in these systems. In fact, the polarizabilities of this series increase significantly with the sizes until it stabilizes at values close to those of fullerene (9.8, 35.2, 55.2, 61.0, 62.2, 71.7, 79.4, 79.2, 78.6 and 81.0 in Å<sup>3</sup>, from H0 to C<sub>60</sub>, at the level of calculation used here) suggesting a major role of inductive effects as the MB grows.

**Table 1.** Distances (in Ångstrom) from the cations to the benzene plane, to the bottom plane of the MBs and to the plane of the nearest hexagonal face of fullerene. In the inner complexes of C<sub>60</sub> with K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> the cation is placed in the center of the fullerene structure. The MBs with unsaturated carbon atoms are marked with an \*.

MBs	Li <sup>+</sup> in	Na <sup>+</sup> in	K <sup>+</sup> in	Rb <sup>+</sup> in	Cs <sup>+</sup> in	Li <sup>+</sup> out	Na <sup>+</sup> out	K <sup>+</sup> out	Rb <sup>+</sup> out	Cs <sup>+</sup> out
H0 = C <sub>6</sub> H <sub>6</sub>	1.886	2.391	2.909	3.252	3.535	1.886	2.391	2.909	3.252	3.535
*H1 = C <sub>21</sub> H <sub>12</sub>	1.791	2.325	2.829	3.161	3.436	1.874	2.352	2.859	3.175	3.452
H2 = C <sub>30</sub> H <sub>12</sub>	1.801	2.410	2.889	3.272	3.615	1.904	2.393	2.886	3.196	3.482
H22 = C <sub>36</sub> H <sub>12</sub>	1.795	2.432	2.887	3.513	3.882	1.904	2.354	2.898	3.186	3.539
*H23 = C <sub>39</sub> H <sub>12</sub>	1.795	2.433	2.840	3.470	4.240	1.872	2.365	2.872	3.213	3.476
*H3 = C <sub>45</sub> H <sub>12</sub>	1.805	2.503	3.356	4.639	4.638	1.895	2.354	2.890	3.195	3.435
H32 = C <sub>48</sub> H <sub>12</sub>	1.773	2.729	3.448	4.513	5.077	1.876	2.396	2.893	3.204	3.514
*H33 = C <sub>51</sub> H <sub>12</sub>	1.758	2.884	2.890	3.845	4.206	1.857	2.378	2.903	3.164	3.443
H34 = C <sub>54</sub> H <sub>6</sub>	1.748	2.607	3.192	3.437	3.355	1.875	2.365	2.870	3.237	3.455
H face of C <sub>60</sub>	1.737	2.408	3.258	3.258	3.258	1.916	2.376	2.909	3.196	3.534

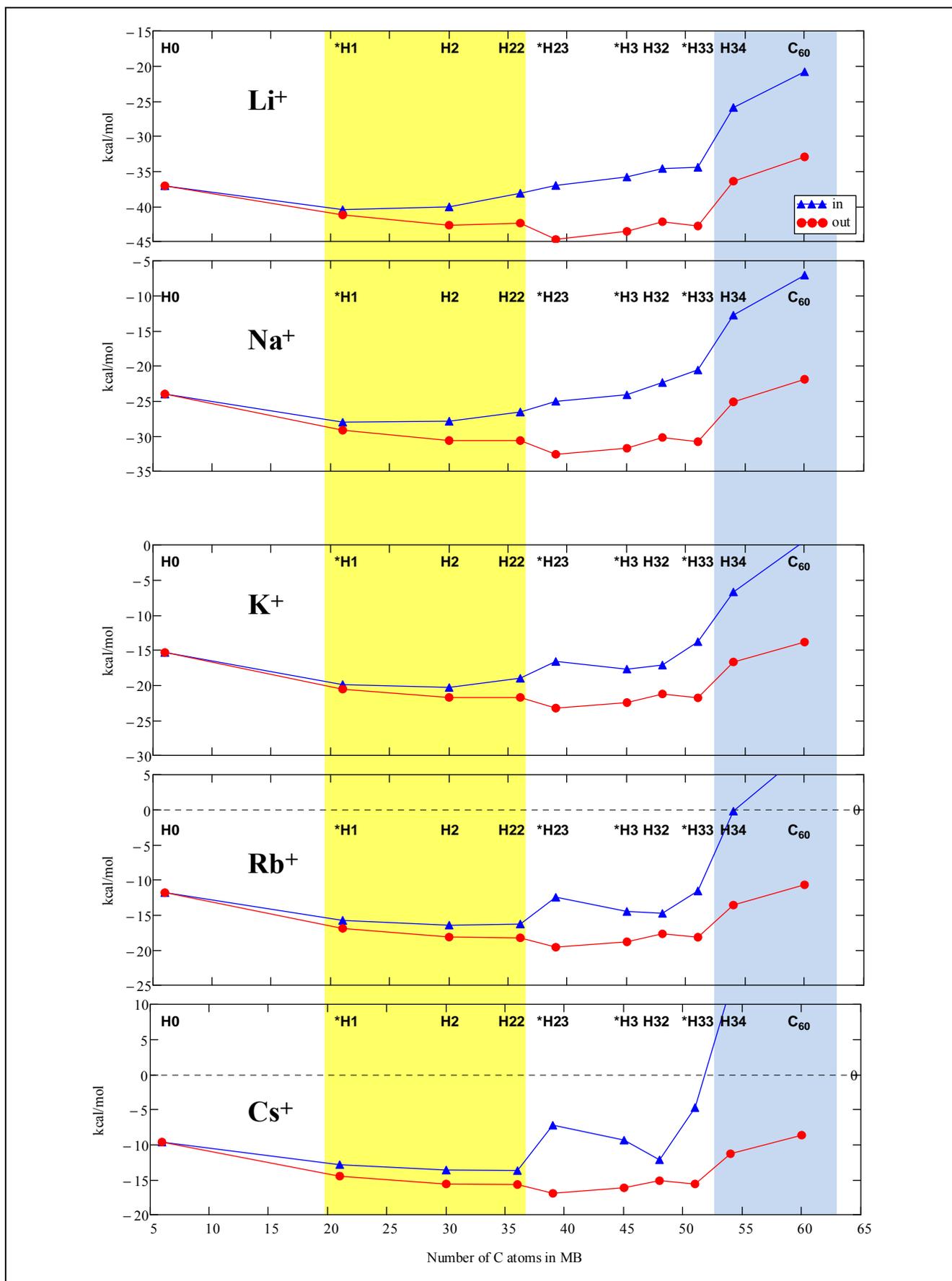
**Complexes (MB/cation).** At the level of calculation used in this work the alkaline cations form stable complexes with all the studied bowls on both sides, convex and concave. Table 1 shows the distances between the cation and the center of the bottom face for complexes with the ion inside and outside of the MBs. In complexes by the convex side of all bowls and C<sub>60</sub> the distances face-cation are similar to the separation observed in other complexes between π systems (for example benzene) and the same alkaline cation. On the other hand, in the concave side only Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>

show a similar behavior and only in the first half of the series (from H0 to H23). Into the bigger MBs (from H3 to C<sub>60</sub>), all the alkaline cations locate at different distances. For bigger cations (Rb<sup>+</sup> and Cs<sup>+</sup>) inside the MBs a pulling out of the cation is observed after just the first bowl whereas for the smaller cations the furthering becomes later (Na<sup>+</sup> and K<sup>+</sup> in H3, and Li<sup>+</sup> in H33). In H34 the walls of the bowl start closing over the cations and repulsion forces move them to positions nearer the bottom. In the inner complexes of C<sub>60</sub> with K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> the cations are placed in the center of the fullerene cage, its interaction energy is positive (see below) and increases with the cation size. So, there are two different behaviors: that of the closed structures of H34 and C<sub>60</sub> and that of the open structures of H1-to-H22 ; with H3-to-H33 with an almost tubular cavity showing an intermediate and more complicated behavior.

**Table 2.** Counterpoise corrected complexation energies (in kcal/mol) for complex formation between alkaline cations and benzene, the bottom face of the molecular bowls and the hexagonal face of fullerene, calculated with the B3LYP method and 6-31+G\* (for C, H, Li, Na and K) or LANL2DZ (for Rb and Cs) basis set. The structures with unsaturated carbon atoms are marked with \*.

MBs	Li <sup>+</sup> in	Li <sup>+</sup> out	Na <sup>+</sup> in	Na <sup>+</sup> out	K <sup>+</sup> in	K <sup>+</sup> out	Rb <sup>+</sup> in	Rb <sup>+</sup> out	Cs <sup>+</sup> in	Cs <sup>+</sup> out
H0 = C <sub>6</sub> H <sub>6</sub>	-37.06		-24.01		-15.33		-11.82		-9.64	
*H1 = C <sub>21</sub> H <sub>12</sub>	-40.47	-41.21	-28.03	-29.16	-19.90	-20.56	-15.77	-16.94	-12.85	-14.49
H2 = C <sub>30</sub> H <sub>12</sub>	-40.06	-42.68	-27.87	-30.64	-23.31	-21.74	-16.45	-18.15	-13.61	-15.60
H22 = C <sub>36</sub> H <sub>12</sub>	-38.12	-42.37	-26.58	-30.64	-19.00	-21.74	-16.31	-18.25	-13.71	-15.68
*H23 = C <sub>39</sub> H <sub>12</sub>	-37.01	-44.71	-25.05	-32.60	-16.61	-23.27	-12.48	-19.61	-7.24	-16.94
*H3 = C <sub>45</sub> H <sub>12</sub>	-35.80	-43.56	-24.13	-31.74	-17.70	-22.48	-14.51	-18.83	-9.36	-16.16
H32 = C <sub>48</sub> H <sub>12</sub>	-34.61	-42.20	-22.36	-30.21	-17.12	-21.24	-14.77	-17.68	-12.16	-15.14
*H33 = C <sub>51</sub> H <sub>12</sub>	-34.43	-42.80	-20.57	-30.80	-13.81	-21.78	-11.59	-18.17	-4.72	-15.62
H34 = C <sub>54</sub> H <sub>6</sub>	-25.92	-36.41	-12.77	-25.12	-6.71	-16.69	-0.20	-13.61	+12.38	-11.29
H face of C <sub>60</sub>	-20.81	-32.95	-7.07	-21.90	+0.58	-13.86	+8.27	-10.71	+21.98	-8.65

Table 2 presents the complexation energies for the complexes between the alkaline cations and benzene, C<sub>60</sub> and the MBs studied. With all curved structures the outer complexes are always more stable than their inner partners. These results are in agreement with previous calculations of complexes between cations and curved  $\pi$  systems<sup>14</sup> as well as with some experimental results.<sup>15</sup> The reverse situation, i.e. the preferential binding of cations to the concave side of MBs or some of these kind of molecules with more negative MEP inside has been reported also,<sup>16</sup> nevertheless, the level of calculation used in these works (AM1 in ref. 16 a, AM1; HF/6-31G\* and pBP/DN\*\* in ref. 16 b and B3LYP/3-21G in ref. 16 c) seems to be not enough for describing well the electronic properties of MBs and their interactions with cations.



**Fig. 3.** Interaction energies for the complexes of benzene, the molecular bowls and fullerene with alkaline cations. The MBs that contain saturated carbon atoms are highlighted with\*. Colored bands group the open bowls (from H1 to H22, in the yellow strip) and the closed ones (H34 and C<sub>60</sub> in the blue strip) with the transition structures (from H23 to H33) with tubular cavity, in the middle (see Fig. 1).

The complexation energies are represented in Fig. 3 that shows graphically the mentioned stability differences caused by the in/out asymmetry of the MBs as well as the influence of the MBs size. In comparison with benzene, all the alkaline cations form complexes more stable with the first members of the MBs series by both of their sides. This stabilization occurs despite of the augment of the MEP values on both sides of the bottom hexagone, which are less negative as the MBs grow, and must be caused by the conjugation enhancement. The general pattern exhibited by the interaction energies can be rationalized as the result of two main contributions: the electrostatic interaction, which reduces with the size of the MBs, and the inductive interaction, that increases with the extension of the conjugation. For the convex side of the MBs the best combination of these two contributions is found in H23 that forms the most stable outer complexes with all the alkaline cations. MEP behave more complicatedly by the concave side and the best electrostatic + polarization combination is presented in different bowls, depending on the polarizing power of the cation; the most stable inner complexer are formed by H1 with  $\text{Li}^+$  and  $\text{Na}^+$ , by H2 with  $\text{K}^+$  and  $\text{Rb}^+$ , and by H22 with  $\text{Cs}^+$ . For the largest ions ( $\text{K}^+$ ,  $\text{Rb}^+$  and especially  $\text{Cs}^+$ ) inside the closed MBs (H34 and  $\text{C}_{60}$ ) size effect adds to the previous contributions distorting the trends, the interaction being weaker than expected, even repulsive for  $\text{Cs}^+$  inside H34 and for  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  inside  $\text{C}_{60}$ .

It is interesting to observe the different influence of the saturated carbon atoms in the stability of the complexes depending on the side where the cation is placed. The unique difference among the members of the couples H22 - H23 and H32 - H33 are three  $\text{sp}^3$  carbon atoms. In both cases, the complexes between the five alkaline cations with the bigger bowl (the one with the  $\text{sp}^3$  atoms) of each couple are more stable if the cation is outside but less stable if the cation is in the inner side. This last behavior can be the result of the cation repulsion by the hydrogen atoms bonded to the  $\text{sp}^3$  carbon atoms and directed into the bowl. The additional stabilization of the outer complexes of these MBs pairs need to be studied in more detail and could be produced by subtle effects in the electrostatic and/or the inductive contributions.

## 5. Conclusions.

In this work we have studied the interaction of alkaline cations and molecular bowls (MBs), curved  $\pi$  systems derived from  $\text{C}_{60}$ , using B3LYP method with 6-31+G\* (for C, H, Li, Na and K) and LANL2DZ (for Rb and Cs) basis sets. At this level of calculation, all the alkaline cations form stable complexes with the cation centered on the hexagonal ring at the bottom of the MBs by both of their sides: concave and convex. The curvature of these  $\pi$  systems generates an in/out asymmetry in the electrostatic potential of the bowls that shows more negative MEP always in its convex (outer) side. In consequence, for every MB/cation combination, the more stable complexes are always formed with the cation in the outer side. A combination of electrostatic and inductive forces governs

the interaction energy. The MEP distributions obtained show that the first of these contributions reduces with the size of the MBs while the second increases, as indicated the calculated polarizabilities. The most favourable electrostatic + inductive combination determines which MB forms the most stable complex with each cation. Additionally, when the MB has a closed structure and the cation is in the concave (inner) side, the repulsive interactions play an important role in the complexation with larger cations ( $K^+$ ,  $Rb^+$  and  $Cs^+$ ). When is analyzed the influence of the MBs size on the stability of the complexes formed, the presence of unsaturated carbon atoms in some of the structures studied causes irregularities in the patterns followed.

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