

# AB INITIO AND DFT STUDY OF INTERACTION BETWEEN CORANNULENE AND ALKALI CATIONS

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## 1. Abstract

Corannulene is an unsaturated hydrocarbon composed of fused rings, one central five-membered ring and five peripheral six-membered rings. Its structure can be considered as a portion of C<sub>60</sub>. Corannulene is a curved  $\pi$  surface, but unlike C<sub>60</sub>, it has two completely different faces: one concave (inside) and one convex (outside). In this work, computational modeling of the binding between alkali metals cations and corannulene has been performed at the DFT and MP2 levels. Different isomers of the corannulene-M<sup>+</sup> binding have been studied and the transition states interconnecting local minima were located. The alkali cations can be bound to five or six membered rings in both faces. In DFT calculations, the binding to the convex face (outside) is favored relative to the concave face for the three alkali cations as it already has been published. For Li<sup>+</sup> and Na<sup>+</sup>, MP2 calculations are very similar and show the same trend, but for K<sup>+</sup> the results are quite different and the trend is reversed. According to our results, migration of cations can take place over the convex or the concave  $\pi$ -face. There are two ways to transform a concave complex in a convex complex: migration across the edge of corannulene and bowl-to-bowl inversion.

## 2. Introduction

In biological and molecular chemistry non-covalent interactions (hydrogen bonding, hydrophobic interactions, van der Waals interactions,...) are very important, as they give structure and function of biological macromolecules. One of these non-covalent interactions is the cation- $\pi$  interaction, to which studies<sup>1-3</sup> give a great importance in biological processes; molecular recognition (substrate-enzyme, antigen-antibody, protein-protein,...), cellular catalysis, neurological signalling and functioning of ion channels are some of these processes. This makes theoretical and experimental studies of interactions between cations and  $\pi$  surfaces a topic of great interest<sup>4-11</sup>.

The study of interactions with flat surfaces from benzene to graphite is a topic that has been very studied. In last years curved  $\pi$  surfaces, as fullerenes, have gained interest, and there have appeared some studies of compounds with curved surfaces. The smallest example of curved  $\pi$  surface is corannulene<sup>12-15</sup>,  $C_{20}H_{10}$ , which is the simplest buckybowl. It is the smallest fragment of buckminsterfullerene,  $C_{60}$ , and it is composed for one central five-membered ring and five peripheral six-memberer rings. It is an special aromatic polycyclic hydrocarbon because it has a curved  $\pi$  surface, and unlike typical aromatic flat hydrocarbon corannulene has two different faces: one concave face and other convex face. Moreover, unlike  $C_{60}$  the two faces are available to interact with different compounds. These facts make interesting the study of the properties of the interaction with this compound.

To date, several studies have been realized about interaction of corannulene with different compounds of transition metals. However, about the interaction of corannulene with cations (not cations of transition metals) few works exist, only a little number of theoretical studies with alkaline cations. Frash et al.<sup>16</sup> made a study of corannulene as a Lewis base, making a computational modelling of protonation and  $Li^+$  cation binding. Dunbar<sup>17</sup> performed a work about structure and energy of different corannulene- $M^+$  isomers for  $Na^+$ ,  $K^+$  and some cations of transition metals. Priyakumar et al.<sup>18,19</sup> in their work made a comparison of

interaction energies between convex and concave face of corannulene, sumanene and other similar compounds. They also studied energy of bowl-to-bowl inversion for these compounds. Finally, Carrazana-García et al.<sup>20</sup> made a complete study of interaction of alkaline cations with corannulene and other molecular bowls. All these studies have been performed at the DFT level with hybrid functionals. In general, all these works concluded the following: alkaline cations bind to corannulene on sites centered over rings and never over C-C bond, interaction energy is bigger than for flat similar compounds, the interaction with the convex face always is more favourable than the interaction with the concave face, and energy barriers for bowl-to-bowl inversion are around 10 Kcal/mol.

In this work, a study of the interaction between corannulene and alkali cations Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> was carried out. Different sites of interaction, relative energy between isomers, *endo-exo* preference, transition states interconnecting isomers and concave-convex transformation have been studied, and different trends analyzed. The calculations have been performed at DFT level as works cited above. As is well known DFT theory fails predicting interaction energy when there is a large contribution of dispersion energy; for this, although in cation- $\pi$  complex dispersion usually not is very important, it would be interesting to perform MP2 calculations. Therefore, all calculations are performed also at MP2 level, and a comparison between both methods realized.

### **3. Computational details.**

This work is divided in two parts. In the first part the geometry and interaction energy of minima<sup>16,17</sup> on the potential energy surface (PES) of the complexes formed by corannulene and the alkali cations Li<sup>+</sup>, Na<sup>+</sup> y K<sup>+</sup> is studied. For this the hybrid functional B3LYP<sup>21-23</sup> and MP2 method have been used. Results of each method were analyzed and a comparison between them was performed. For B3LYP functional geometries were optimized with the cc-pVDZ basis set<sup>24-27</sup>, and single points energy calculations were realized with the cc-pVTZ basis set<sup>24-27</sup>. In the protocol used for MP2 calculations geometrical optimizations are performed with the cc-pVDZ basis set, and MP2 energies are obtained as a combination of

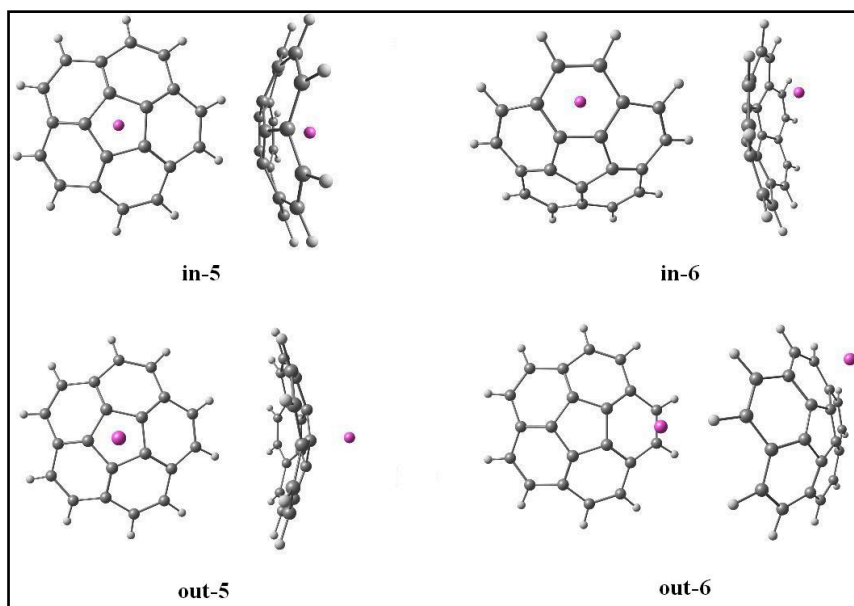
HF/cc-pVTZ energy with the MP2 correlation energy extrapolated to complete basis set [ $E_{\text{corr}}(\text{MP2})/\text{CBS}$ ] from cc-pVDZ and cc-pVTZ basis sets. For  $\text{K}^+$  atoms QZVPP<sup>28</sup> basis set were used because Dunning basis set does not exist for them. The size of QZVPP basis set make us consider that can give results as good as CBS extrapolation of Dunning basis sets. The interaction energy calculations are performed with the supermolecule method, correcting the basis set superposition error (BSSE) with counterpoise correction<sup>29</sup> for each dimer. In this part all the calculations are performed with Turbomole<sup>30</sup> program. To optimize the computation time the RI approximation was employed as implemented in this program for DFT calculations<sup>31,32</sup> and MP2 calculations<sup>33-35</sup>.

In a second part of this work geometries and energetic barriers of transition states which interconnect minima of the PES of the complexes have been studied<sup>16</sup>. In this section the geometrical optimizations are performed in Gaussian09<sup>36</sup> program with B3LYP functional and 6-31G\* basis set, level of calculation that previous works have indicated as good to obtain good geometries and good vibrational frequencies<sup>37-39</sup>. The single point energy calculations were performed for DFT and MP2 as described for the first part, using the Turbomole program also. In this case all the energies obtained are corrected with the corresponding ZPE obtained with B3LYP/6-31G\* level.

## 4. Results and Discussion

**4.1. Study minima on PES.** Different modes of coordination for alkali cations to corannulene were explored<sup>16,17</sup>. Four structures as minima of PES were found. Figure 1 shows the four complexes for  $\text{C}_{20}\text{H}_{10}\text{-Li}^+$ . In two geometries the coordination occurs for the convex face: one with  $\eta^5$  coordination between cation and the five-membered central ring (out-5), and the other with  $\eta^6$  coordination between cation and one of the six-membered peripheral rings (out-5). Similarly, the same results for concave face were found (in-5 and in-6), except minimum in-6, which only exist for  $\text{Li}^+$  cation. For  $\text{Na}^+$  and  $\text{K}^+$  compounds the cation is located at a greater distance from the ring so that in-5 and in-6 have geometries very close, and all attempts to optimize the in-6 minimum converged at in-5 minimum. The

geometries with  $\eta^5$  coordination have  $C_{5v}$  symmetry and the geometries with  $\eta^6$  coordination have  $C_s$  symmetry. Table 1 show bowl depth (BD) and the distance from cation to center of the ring to which coordinates (R) for each dimer. It can be seen how geometric parameters are very similar for DFT and MP2, with BD and R values slightly higher for MP2 (except R for the complexes of  $K^+$ , where the use of the QZVPP basis set makes them smaller in MP2 than DFT). In general the values of BD are very similar to the isolated corannulene (0.91 Å to MP2 and 0.88 Å for DFT), except for the isomers in-5 where the depth of the bowl increases slightly.



**Figure 1.** Different structures for coordination to  $C_{20}H_{10}-M^+$ .

The values obtained for interaction energies (Table 2) at DFT level are very similar to those published previously by Dunbar<sup>17</sup>. In molecular electrostatic potential maps of corannulene published by Carrazana-Garcia et al.<sup>20</sup> and Green et al.<sup>40</sup> the corannulene has a permanent dipole moment, with an electrostatic potential more negative in convex face than concave face. Therefore the system corannulene-cation can be treated as a charge-dipole system. Thus, as when increasing the size of the cation increases the distance between corannulene and cation, the interaction energy decreases approximately in proportion to  $1/r^2$ . Due to orientation of the dipole, binding to the convex face (outside) is favored relative to the concave face (inside) for the three alkali cations. Comparing values for isomers with coordination  $\eta^5$  we can see the difference in-5/out-5 decreases from

4.30 kcal/mol for Li<sup>+</sup> to 3.02 kcal/mol for Na<sup>+</sup> and to 1.05 kcal/mol for K<sup>+</sup>. This trend can be explained by the fact that increasing the distance between cation and corannulene the effects that favour binding for convex face decreases, and opposite effects to binding for concave face also decrease. Thus, treating the system as a classical charge-dipole is possible to explain all the observed trends. For Li<sup>+</sup> coordination by the concave face of corannulene can be observed a clear preference for  $\eta^6$  coordination. For the convex face the trend observed indicates that increasing the size of cation favors  $\eta^5$  coordination against  $\eta^6$  coordination, for Li<sup>+</sup> out-6 is the most stable, the same energy for the two isomers of Na<sup>+</sup> and a greater interaction energy for isomer out-5 of K<sup>+</sup>.

**Table 1.** Distance from the metal ion to ring which coordinate (R) and bowl-depth (BD) for all isomers of compounds (Å).

	MP2		DFT	
	R	BD	R	BD
			<b>In-5</b>	
Li <sup>+</sup>	1.94	0.93	1.91	0.90
Na <sup>+</sup>	2.46	0.95	2.44	0.91
K <sup>+</sup>	2.69	0.98	2.82	0.90
			<b>In-6</b>	
Li <sup>+</sup>	1.86	0.91	1.82	0.87
Na <sup>+</sup>	-	-	-	-
K <sup>+</sup>	-	-	-	-
			<b>Out-5</b>	
Li <sup>+</sup>	1.97	0.91	1.95	0.90
Na <sup>+</sup>	2.43	0.93	2.42	0.91
K <sup>+</sup>	2.72	0.91	2.84	0.90
			<b>Out-6</b>	
Li <sup>+</sup>	1.92	0.91	1.88	0.89
Na <sup>+</sup>	2.43	0.92	2.39	0.90
K <sup>+</sup>	2.74	0.90	2.84	0.88

For Li<sup>+</sup> and Na<sup>+</sup> MP2 values of interaction energy are very similar to DFT ones, and only the interaction energy for in-5 isomers is slightly different, with an increase around 2 kcal/mol over DFT values. Other small difference is the preference for  $\eta^5$  coordination about  $\eta^6$  for convex face in both compounds. The big difference between MP2 and DFT is in isomers of K<sup>+</sup>, with interaction energy values considerably higher than in DFT. The biggest difference compared to DFT is in isomer in-5, so that for K<sup>+</sup> in MP2 interaction by concave face is favoured over

convex face. Looking at energy differences in-5/out-5 (2.33 kcal/mol for Li<sup>+</sup>, 0.88 kcal/mol for Na<sup>+</sup> and -3.30 kcal/mol for K<sup>+</sup>) the same trend observed in DFT (a bigger cation size less in/out difference) can be seen but shifted to lower values, so that even the preference in/out is reversed for K<sup>+</sup>.

**Table 2.** Interaction energies (kcal/mol) of different isomers of corannulene-M<sup>+</sup> compounds.

	<b>In-5</b>	<b>In-6</b>	<b>Out-5</b>	<b>Out6</b>
			<b>DFT<sup>a</sup></b>	
<b>Li<sup>+</sup></b>	-40.72	-42.79	-45.02	-45.46
<b>Na<sup>+</sup></b>	-27.24	-	-30.26	-30.17
<b>K<sup>+</sup></b>	-21.09	-	-22.14	-21.62
			<b>MP2<sup>b</sup></b>	
<b>Li<sup>+</sup></b>	-42.45	-42.77	-44.78	-43.99
<b>Na<sup>+</sup></b>	-29.39	-	-30.19	-29.52
<b>K<sup>+</sup></b>	-29.63	-	-26.33	-25.26

a. Computacional level B3LYP/cc-pVDZ//B3LYP/cc-pVTZ.

b. Computacional level MP2/cc-pVDZ//MP2//CBS.

In deeper analysis of MP2 results we can observe that the HF values of interaction energy are similar to those obtained with DFT. The introduction of electronic correlation energy at the MP2/CBS level for Li<sup>+</sup> and Na<sup>+</sup> complexes gives similar values to DFT for out-5 and out-6 isomers. For in-5 isomers MP2/CBS correlation energy increases DFT values around 2 kcal/mol. For K<sup>+</sup> isomers the introduction of MP2/CBS electronic correlation energy modifies significantly the total interaction energy, with an increase of 50% over HF energy in the isomer in-5. A possible explanation for these results for K<sup>+</sup> may be their size. K<sup>+</sup> is a large cation and it can interact with a greater area of  $\pi$  surface and interact with neighboring rings. In the concave face the neighboring rings are oriented towards the cation, and therefore the greatest increase in interaction energy is produced in the isomer in-5. This interaction with neighboring rings could also explain the increase of 2 kcal/mol in interaction energy for in-5 isomers of Li<sup>+</sup> and Na<sup>+</sup> and the slightly increase of bowl depth in three isomers in-5. If this effect only is observed in MP2 calculations and not in DFT may be due to dispersion energy. As is well known B3LYP neglects dispersion energy, while MP2 can overestimate it, and for the explained above the dispersion energy can play an important role in isomers

with concave interaction, and become more important with the increase of ion size.

**4.2. Study of the interconversion between minima.** The energy barriers that are necessary to overcome and transform one isomer into another have been studied. The different bridge structures that interconnect the different minima and its energy, corrected with ZPE ( $E_0$ ), has been calculated. The first step for this study was to obtain the structure and zero-point energy of different isomers at selected calculation level. Geometrical optimizations of minima do not show significant differences compared with those obtained previously for DFT. The relative energy of each minimum for DFT and MP2 are shown in Table 3. The relative energies of minima do not vary significantly with respect to those calculated in section 3.1, and all the trends are preserved in both levels, DFT and MP2.

**Table 3.** Relative energies<sup>a</sup> (kcal/mol) of different isomers of corannulene- $M^+$  compounds.

	<b>In-5</b>	<b>In-6</b>		<b>Out-5</b>	<b>Out6</b>
			<b>DFT<sup>b</sup></b>		
<b>Li<sup>+</sup></b>	5.17	3.07		0.50	0.0
<b>Na<sup>+</sup></b>	3.10	-		0.0	0.0
<b>K<sup>+</sup></b>	1.06	-		0.0	0.39
			<b>MP2<sup>c</sup></b>		
<b>Li<sup>+</sup></b>	2.97	3.06		0.0	1.44
<b>Na<sup>+</sup></b>	0.84	-		0.0	1.07
<b>K<sup>+</sup></b>	0.0	-		3.63	4.79

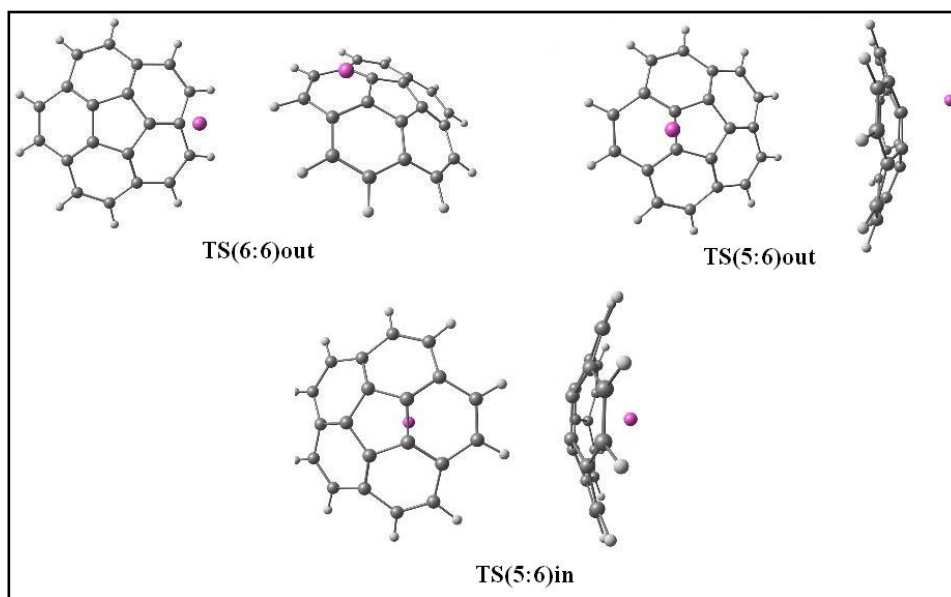
a. Energies corrected with ZPE.

b. Computacional level B3LYP/6-31G\*\*//B3LYP/cc-pVTZ.

c. Computacional level B3LYP/6-31G\*\*//MP2//CBS.

For the interconversion between different isomers of corannulene- $M^+$  seven structures that interconnect the different minima of the PES were obtained. For each structure a vibrational frequency study have been realised to prove they are first order saddle-points and the imaginary frequency corresponds to the transition state interconnecting two corresponding minima.





**Figure 2.** Transition states for migration of cation over corannulene surface.

Three of these transition states correspond to the movement of cations on the surface of corannulene (Figure 2). Two transition states, TS(6:5)out and TS(6:6)out are related to movements by the convex surface. The first one interconnects structures out-5 and out-6 and the second transition state interconnects two equivalent out-6 structures. These two transition states exist for three compounds. TS(6:5)in corresponds to a transition state which interconnects in-5 and in-6 structures. This transition state only exists for  $C_{20}H_{10}Li^+$  complex because as explained in section 3.1 the in-6 isomers do not exist for complexes of  $Na^+$  and  $K^+$ . In this transition state the cation is located over the bond that connects the rings between the cation moving. Transition states connecting two minima in-6 was not possible to optimize, and previous works also failed to get this transition state, so it is likely there does not exist a transition state which connects these two minima. Thus, migration from in-6 isomer to other equivalent structure must be through an in-5 minimum. Energy barriers (Table 4) are not very high and decrease much when cation size increases. For transition states of  $K^+$  the highest barriers are 1.72 and 2.40 kcal/mol in DFT and MP2 respectively, two very small values. MP2 energy barriers are higher than DFT barriers, except for TS(5:6)in. In  $Li^+$  and  $Na^+$  complexes the barrier for migration between two out-6 isomers are higher than the barrier for migration between out-5 and out-6 isomers. For  $K^+$  is the opposite. Energy barriers for the movement of  $Li^+$  for the concave face of

corannulene are very small, only  $\Delta E_2$  (in-6 to in-5) with DFT has a value greater than 1 kcal/mol. Therefore, the movement of cations on the external side of corannulene is quite available especially for the cations  $\text{Na}^+$  and  $\text{K}^+$ . For concave face of corannulene MP2 predicts a constant movement of  $\text{Li}^+$ , DFT predicts a energy barrier much higher to migrate from in-6 to in-5 than the barrier to migrate from in-5 to in-6, therefore the isomer most likely is in-6.

**Table 4.** Energy barriers (kcal/mol) for migration of cations over the surface of corannulene, and imaginary vibrational frequencies of corresponding transition states.

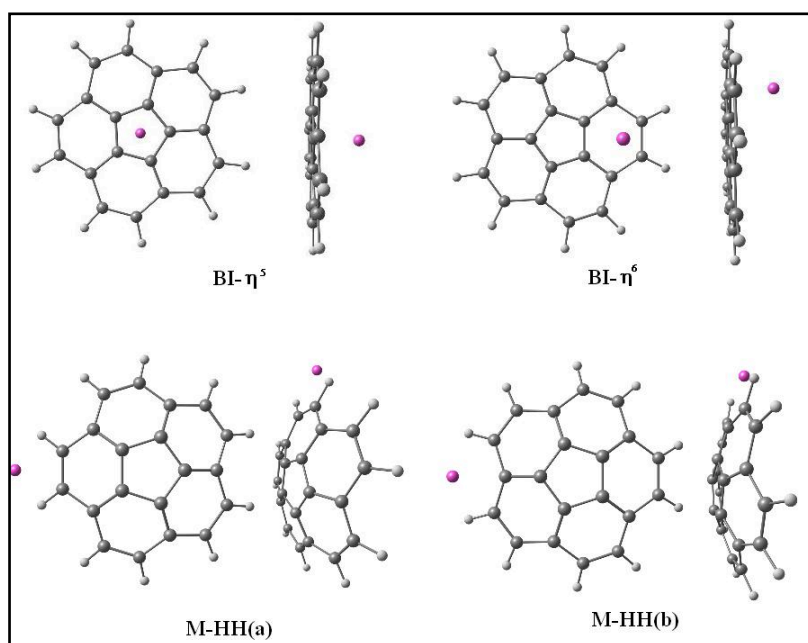
	DFT		MP2		$\nu_{\text{imag}}$
	$\Delta E_1$	$\Delta E_2$	$\Delta E_1$	$\Delta E_2$	
	<b>TS(5:6)out<sup>a</sup></b>				
$\text{Li}^+$	5.09	5.59	6.75	5.31	-113.25
$\text{Na}^+$	2.02	2.02	3.60	2.53	-53.34
$\text{K}^+$	1.54	1.15	2.40	1.24	-39.46
	<b>TS(6:6)out<sup>b</sup></b>				
$\text{Li}^+$	6.52	6.52	6.81	6.81	-122.56
$\text{Na}^+$	2.63	2.63	3.72	3.72	-56.14
$\text{K}^+$	1.72	1.72	2.08	2.08	-36.03
	<b>TS(5:6)in<sup>a</sup></b>				
$\text{Li}^+$	0.34	2.44	0.85	0.76	-138.77
$\text{Na}^+$	-	-	-	-	-
$\text{K}^+$	-	-	-	-	-

a.  $\Delta E_1$  is a barrier to pass of  $\eta^5$  structure to  $\eta^6$  structure.  $\Delta E_2$  is a barrier to pass of  $\eta^6$  structure to  $\eta^5$  structure.

b.  $\Delta E_1$  and  $\Delta E_2$  are equivalents and have the same value.

To transform a concave structure in a convex structure (or backwards) two alternative ways were found: bowl-to-bowl inversion<sup>16,18,19</sup> and migration of the cation across the edge of corannulene. In Figure 3 are represented the transition states structures. For bowl-to-bowl inversion there are two transition states. In both transition states the corannulene structure is flat. In one the cation is pentacoordinated to central ring, BI- $\eta^5$ , and in other the cation is hexacoordinated to one peripheral six-membered ring, BI- $\eta^6$ . The first connects structures in-5 and out-5, and second connects structures in-5 and out-6 for  $\text{Na}^+$  and  $\text{K}^+$ , and structures in-6 and out-6 for  $\text{Li}^+$ . For migration over the edge of corannulene two transition

states have also been found. In one the cation is located between the two hydrogen of a six-membered ring, M-HH(a), and in the other the cation is placed between two hydrogens of different (and neighboring) six-membered rings, M-HH(b). These transition states connect isomers in-6 and out-6 for  $\text{Li}^+$  and isomers in-5 and out-6 for  $\text{Na}^+$  and  $\text{K}^+$ . The values of energy barriers are shown in Table 4. For bowl-to-bowl inversion and only considering  $\Delta E_2$ , barriers to convex-concave transformation, it can be observed that all barriers have similar values, with values between 10 and 12.4 kcal/mol. In all the cases, the energy barrier for pentacoordinate transition states is slightly higher than for hexacoordination transition states. The size of cation does not have influence in energy barrier to bowl-to-bowl inversion, and MP2 and DFT values are very similar in all the cases. Differences in  $\Delta E_1$  values are determined by the relative differences in/out for each compound. For interpreting the migration over the edge of corannulene, only  $\Delta E_2$  energy barrier considered, the necessary energy for this migration is quit higher than the barrier to bowl-to-bowl inversion (more than double in some cases). This energy is very similar for the two transition states. In both transition states energy barriers decreases with the increase of cation size. MP2 values are around 3-4 kcal/mol higher than DFT values.



**Figure 3.** Transition states for bowl-inversion and migration of cation over the edge of corannulene.

**Table 5.** Energy barriers (kcal/mol) of transition states for bowl-inversion and migration over the edge of corannulene, and imaginary vibrational frequency of each transition state.

	DFT		MP2		$\nu_{\text{imag}}$
	$\Delta E_1^a$	$\Delta E_2^b$	$\Delta E_1^a$	$\Delta E_2^b$	
	<b>BI-<math>\eta^5</math></b>				
<b>Li<sup>+</sup></b>	7.64	12.32	9.43	12.40	-110.39
<b>Na<sup>+</sup></b>	9.25	12.34	11.52	12.36	-109.95
<b>K<sup>+</sup></b>	10.31	11.37	14.04	10.41	-103.39
	<b>BI-<math>\eta^6</math></b>				
<b>Li<sup>+</sup></b>	7.52	10.59	9.11	10.73	-106.77
<b>Na<sup>+</sup></b>	8.13	11.23	11.81	11.57	-103.07
<b>K<sup>+</sup></b>	10.08	10.76	14.83	10.04	-100.44
	<b>M<sup>+</sup>-HH(a)</b>				
<b>Li<sup>+</sup></b>	21.10	24.17	25.18	26.44	-216.83
<b>Na<sup>+</sup></b>	16.49	19.59	23.08	22.84	-131.00
<b>K<sup>+</sup></b>	15.18	15.86	24.35	19.56	-62.66
	<b>M<sup>+</sup>-HH(b)</b>				
<b>Li<sup>+</sup></b>	20.10	23.17	24.78	26.84	-242.10
<b>Na<sup>+</sup></b>	16.35	19.45	22.98	22.74	-130.04
<b>K<sup>+</sup></b>	15.66	16.34	26.10	21.31	-57.32

a. Energy barrier to concave-convex transformation.

b. Energy barrier to convex-concave transformation.

## 5. Conclusions

DFT and MP2 studies of the PES of complexes formed between corannulene and the alkali cations Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> has been performed. Minima on PES have been found and its interaction energy were calculated. Transition states for interconversion between minima and their energy barriers have been obtained. Four structures exists that are minima in the PES of corannulene...alkali cations complexes, two with interaction with the convex face, and two with interaction with the concave face (for Na<sup>+</sup> and K<sup>+</sup> only one for concave face). Interaction energy of this minima decrease as the cation size is increased and is bigger when the interaction is by the convex face of corannulene (except for K<sup>+</sup> in MP2 calculations). In MP2 calculations, compared with DFT, an increase of interaction energy has been observed for concave isomers, probably due to dispersion energy.

Energy barriers for migration of cations over the convex face of corannulene are small. These barriers decrease with increasing the cation size. The energy barrier for migration of Li<sup>+</sup> in the concave face of corannulene is very small. Only a transition state for the interconversion in-5/in-6 exists, whereas conversion between in-6 equivalent minima is done through a in-5 minimum. For interconversion between concave and convex structures two possibilities exists: bowl-to-bowl inversion and migration over the edge of corannulene. Its much more energetically favourable the bowl-to-bowl inversion than migration of cation over the edge of corannulene.

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