

DFT and MP2 study of the interaction between corannulene and alkali cations

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Abstract Corannulene is an unsaturated hydrocarbon composed of fused rings, with one central five-membered ring and five peripheral six-membered rings. Its structure can be considered as a portion of C_{60} . Corannulene is a curved π surface, but unlike C_{60} , it has two accessible different faces: one concave (inside) and one convex (outside). In this work, computational modeling of the binding between alkali metal cations (Li^+ , Na^+ , and K^+) and corannulene has been performed at the DFT and MP2 levels. Different corannulene $\cdots M^+$ complexes have been studied and the transition states interconnecting local minima were located. The alkali cations can be bound to a five or six membered ring in both faces. At the DFT level, binding to the convex face (outside) is favored relative to the concave face for the three alkali cations studied, as it was previously published. This *out* preference was found to decrease as cation size increases. At the MP2 level, although a similar trend is found, some different conclusions related to the *in/out* preference were obtained. According to our results, migration of cations can take place on the convex or on the concave face. Also, there are two ways to transform a concave complex in a convex complex: migration across the edge of corannulene and bowl-to-bowl inversion.

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Introduction

Cation- π interactions have received great attention in recent years, in part as a result of the role they are believed to play in protein folding, neurological signaling, control of certain ion channels, and other diverse biological phenomena [1–3]. From these studies, it seems clear that the degree to which cations are attracted to the electron-rich π clouds correlates with the electrostatic potential of the π systems [4–9].

When the π system is curved, other aspects arise in the description of the interaction, as a consequence of the asymmetry in the electrostatic potential of these species. These compounds have two different faces (concave and convex sides), and there is a remarkable presence of significant inductive effects. One of the most important compounds that possess a curved surface is corannulene, $C_{20}H_{10}$. It is the simplest structure of so-called buckybowls, fragments of fullerene or open geodesic polyaromatic hydrocarbons.

The interaction between corannulene and metal cations has been fairly studied in recent years by DFT calculations. So Frasch et al. studied the interaction of corannulene with Li^+ at the B3LYP/6-311G(d,p) level [10]. Priyakumar et al. have also evaluated the interaction with Li^+ and Na^+ at the B3LYP level [11, 12]. Dunbar carried out a more exhaustive DFT study with alkali cations (Li^+ , Na^+ , and K^+) and transition-metal ions (Ti^+ , Cr^+ , Ni^+ , and Cu^+), interacting with corannulene and coronene [13]. More recently Vijay et al. have just published a study at the M05-2X/cc-pVDZ level that explores the binding possibilities of cations (Li^+ , Na^+ , K^+ , and Cu^+) to the concave and convex sides of rings of corannulene and the other prototypical buckybowl, sumanene ($C_{21}H_{12}$) [14]. The interaction of cations with increasing buckybowls (going from

corannulene to buckminsterfullerene, C₆₀) has also been analyzed recently at the DFT level [15, 16]. According to previous calculations, the complex where the metal cation binds to the convex side (outside of the bowl, exo) is the most stable one. This trend decreases as cation size increases, but small differences between B3LYP and M05-2X functionals are observed. Thus, B3LYP results stress the exo preference, so that even for K⁺, the external complexation is favored. However, M05-2X results soften the exo preference, so that for K⁺, the internal complexation is slightly favored.

In order to expand and study in depth the corannulene⋯alkali cation interaction, a comprehensive study has been performed in the present paper. It comprises two main aspects. The first one is the evaluation of all possible complexes between corannulene and alkali cations (Li⁺, Na⁺, and K⁺) at the DFT and MP2 levels. Several DFT calculations have already been performed previously [10–14]; however, to our knowledge, no MP2 study has been performed before. The second aspect of the present work is the DFT and MP2 study of the potential energy surface, PES, for the corannulene⋯alkali cation complex, looking for the transition states between the minima. So far, this study was only performed at the DFT level and only for the Li⁺ cation [10]. Now we expand the study including Na⁺ and K⁺ and, moreover, we also carried out all the energetic calculations at the MP2/CBS level.

Computational details

All the minima for the corannulene⋯alkali cation complex were optimized at the B3LYP/cc-pVDZ and MP2/cc-pVDZ levels. DFT interaction energies were computed at the B3LYP/cc-pVTZ level, by the supermolecule method, avoiding the basis set superposition error, BSSE, with counterpoise correction [17]. From single point energy calculations (MP2/cc-pVDZ and MP2/cc-pVTZ), the MP2 interaction energies was extrapolated to complete basis set, CBS, according to the following procedure [18]. The MP2 correlation energy at CBS was obtained as:

$$\Delta E_{corr,MP2}^{CBS} = \frac{X^3}{X^3 - (X-1)^3} \Delta E_{corr,MP2}^{cc-pVXZ} - \frac{(X-1)^3}{X^3 - (X-1)^3} \Delta E_{corr,MP2}^{cc-pV(X-1)Z}$$

In our case $X=3$ since cc-pVTZ and cc-pVDZ basis sets were used for extrapolating. Then the MP2 interaction energy at the basis set limit is obtained as:

$$\Delta E_{MP2}^{CBS} = \Delta E_{HF}^{cc-pVTZ} + \Delta E_{corr,MP2}^{CBS}$$

where $\Delta E_{HF}^{cc-pVTZ}$ is the interaction energy at the HF/cc-pVTZ level. In these expressions, BSSE corrected HF and

MP2 interaction energies are obtained by performing single point calculations using MP2/cc-pVDZ optimized geometries. In all cases, the QZVPP Ahlrichs basis set was used for the potassium atom since there is not Dunning basis set for this atom.

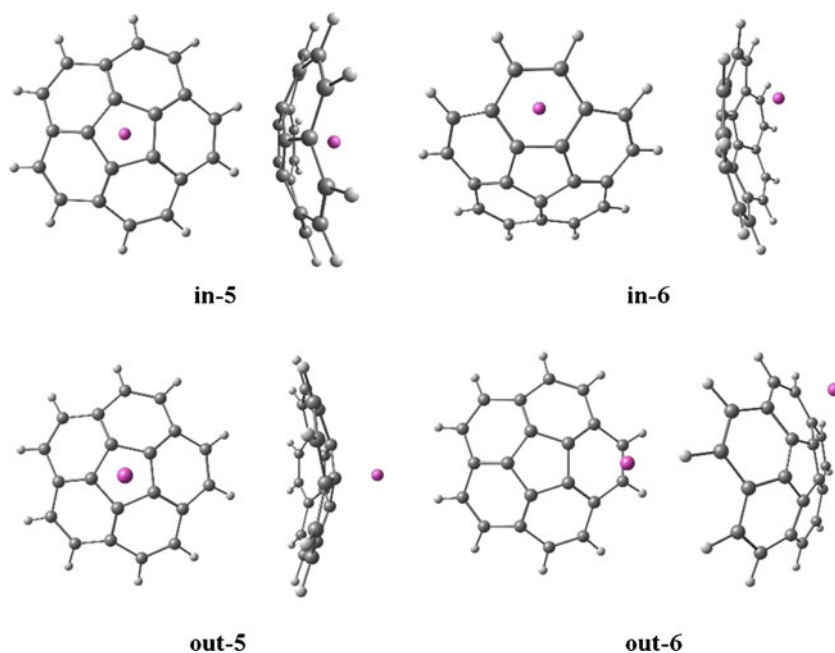
The above DFT and MP2 calculations were performed with the Turbomole program [19]. In order to optimize the computation time, the resolution of the identity approximation, RI, was used with the RI-DFT [20, 21] and RI-CC2 implementations [22–24].

In order to study the interconversion between minima of the PES, geometrical optimizations were performed with the Gaussian09 [25] package at the B3LYP/6-31G(d) level. This level seems to work well to obtain good geometries and vibrational frequencies [26, 27]. All stationary points were characterized as minima or transition structures by calculating the harmonic vibrational frequencies, using analytical second derivatives. All the transition states were checked by animation of the imaginary frequency and, in cases where there was any doubt, intrinsic reaction coordinate calculations (IRC) were performed to ensure that the minima are connected by the found transition state (see [Supplementary material](#)). With the optimized geometries, single point energy calculations were performed at the DFT and MP2 levels, using Turbomole program and the above commented procedure (with extrapolation of MP2 results to complete basis set). All the energies were corrected with the corresponding zero point vibrational energy, ZPVE, obtained at the B3LYP/6-31G(d) level.

Results and discussion

Minima on the potential energy surface, PES

Four types of coordination were found on PES. Figure 1 shows these four structures for C₂₀H₁₀⋯Li⁺ complex. In two cases interaction takes place on the concave face of corannulene: one with η^5 coordination between the cation and the central five-membered ring (in-5), and one with η^6 coordination between the cation and one of the six-membered rings (in-6). Analogously, structures out-5 and out-6 were found for the interaction between the cation and the convex face of corannulene. Minimum in-6 only is located for Li⁺ cation, both at the DFT and MP2 levels. For Na⁺ and K⁺ all optimizations starting from an in-6 structure led to an in-5 minimum. Probably the large size of these two cations was the cause of this fact, since the inside of the bowl is not large enough to ‘hold’ two minima so close. η^5 structures have C_{5v} symmetry while η^6 structures have C_s symmetry. Table 1 shows some geometric parameters of the minima: BD is the bowl depth and R is the distance between the cation and the center of the ring to which is coordinated. It is noteworthy

Fig. 1 Structures for the corannulene...alkali cation complex

that DFT and MP2 geometric parameters are very similar, being the MP2 values slightly larger than the DFT ones for complexes with Li^+ and Na^+ . This trend is reversed for K^+ , probably due to the use of QZVPP basis set for the cation. In general, BD values are very

Table 1 Distance (Å) from the cation to the center of the ring to which is coordinated (R), and bowl-depth (BD) of corannulene for all the complexes

	DFT		MP2	
	R	BD	R	BD
	in-5			
Li^+	1.91	0.90	1.94	0.93
Na^+	2.44	0.91	2.46	0.95
K^+	2.82	0.90	2.69	0.98
	in-6			
Li^+	1.82	0.87	1.86	0.91
Na^+	–	–	–	–
K^+	–	–	–	–
	out-5			
Li^+	1.95	0.90	1.97	0.91
Na^+	2.42	0.91	2.43	0.93
K^+	2.84	0.90	2.72	0.91
	out-6			
Li^+	1.88	0.89	1.92	0.91
Na^+	2.39	0.90	2.43	0.92
K^+	2.84	0.88	2.74	0.90

^a B3LYP/cc-pVDZ^b MP2/cc-pVDZ

similar to that of the isolated corannulene (0.91 and 0.88 Å at MP2 and DFT levels, respectively), which show the almost insignificant deformation of corannulene bowl upon complexation.

The values obtained for interaction energies at the DFT level (Table 2) are very similar to those previously published [13, 24]. Molecular electrostatic potential, MEP, maps showed a slightly more negative potential on the convex face of corannulene which generates a permanent dipole moment pointing from inside to outside the bowl [15, 16, 28]. Therefore the system corannulene...cation can be treated as a dipole-charge system. The larger the cation, the larger the distance of the corannulene...cation, and consequently the smaller the interaction energy, as it is proportional to r^{-2} . According to Table 2 this trend is always true, so the largest interaction energy corresponds to Li^+ complexes, as expected.¹ Moreover, due to the dipole orientation, binding to the convex face (outside) is favored relative to the concave face (inside) for the three alkali cations. However, this trend becomes less pronounced as the size of the cation increases. For example, the difference in-5/out-5 decreases from 4.30 kcal mol⁻¹ for Li^+ to 3.02 for Na^+ and to 1.05 for K^+ . This trend can be

¹ With a calculated dipole moment of 2.23 D for corannulene, and taking into account that interaction between a charge a and a dipole b is given by $-q_a\mu_b/r^2$ if the dipole is aligned with the charge ($\alpha=0$), the following energies were obtained: -26, -19, and -15 kcal mol⁻¹ for the interaction between Li^+ , Na^+ , and K^+ , respectively, with the convex side of corannulene. These values show a similar trend to those of Table 2, though as we have shown recently, the interaction is mainly of inductive character rather than electrostatic [15].

Table 2 Interaction energy (kcal mol⁻¹) of corannulene⋯alkali cation complexes

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

^a B3LYP/cc-pVTZ^b MP2/ CBS

explained from the larger distance corannulene⋯cation, which decreases the difference between the convex and the concave face: if the cation is placed very far from corannulene, the interaction will be equal for both faces, as happens with standard planar polycyclic aromatic hydrocarbons, PAHs. For the *out* interaction it is noteworthy that there are not very significant differences between η^5 and η^6 coordination (*out*-5 vs. *out*-6). The larger cation, the more favored η^5 coordination; however the difference is very small. This difference is slightly greater (about 2 kcal mol⁻¹) in the case of *in* interaction (only for Li⁺, which is the only *in*-6 occurrence).

Table 2 also includes the MP2/CBS interaction energies. For Li⁺ and Na⁺ the values are reasonably similar to those of DFT calculations, especially those relating to *out* interaction. In the case of *in*-5 the differences are somewhat larger, the MP2 values being about 2 kcal mol⁻¹ more negative than the DFT ones. The same happens, even more accentuated, for all the complexes with K⁺, with important increases (4–8 kcal mol⁻¹) of the interaction energy. A more detailed analysis of MP2 results in Table 2 shows that significant increases in the binding energy are focused in complexes with interaction with the concave face of corannulene (*in* structures), especially in the case of K⁺ cation. As a result, the *out* preference of DFT method is considerably weakened by MP2; so that even the reverse preference (*in*) is reached in the case of K⁺. So, DFT calculations give rise to *in-out* interaction energy differences of 2.67, 3.02, and 1.05 kcal mol⁻¹, for Li⁺, Na⁺, and K⁺, respectively; while MP2 calculations led to 2.01, 0.80, and -3.30 kcal mol⁻¹. Therefore, moving from DFT to MP2 the difference decreases 0.66, 2.22, and 4.35 kcal mol⁻¹ for Li⁺, Na⁺, and K⁺, respectively. This represents a clear trend, which is directly related to the

size of the cation. The geometric results of Table 1 can supply a valuable clue to explain the underestimation of binding energy of DFT calculations for *in* structures. This table shows that only in two cases the corannulene bowl undergoes a not negligible deformation: this happens with *in*-5 complexes of Na⁺ and, especially, K⁺. In these cases the bowl depth is 0.95 and 0.98 Å, which represents an important increase relative to that of free corannulene (0.91 Å); the bowl becomes deeper, and therefore narrower, the outer atoms (the rim) get closer and they get closer to the cation. As stated above, this happens with Na⁺, and especially, with K⁺. This effect must be clearly linked to the increase of the dispersive contribution of the interaction when the size of the cation increases; this is accompanied by a clear reduction of the electrostatic contribution of the interaction (rigorously, when we talk about electrostatic contribution, we really mean the actual electrostatic contribution plus the induction contribution). So, for Li⁺ complexes the interaction is essentially electrostatic and for that reason interaction with the convex face (*out*) is favored since this face shows a slightly more negative electrostatic potential. As the cation size becomes larger the electrostatic component of the interaction, while being preponderant, becomes smaller so that the dispersion component, even though small, is beginning to have some effect. For that reason MP2 results led to similar *in-out* interaction energies for Na⁺ and, finally the concave face (*in*) is favored for K⁺. The same trend takes place for the DFT results; however it is not so pronounced, and therefore the convex face is the most favored for the three cations (although the difference *in-out* for K⁺ is very small). Probably the slight deficiency of DFT results is motivated by the known inability of standard functionals to reproduce rigorously dispersive effects. In this case the dispersive contribution must be small (because we are studying the interaction between a charge and a dipole), but important enough to modulate the overall effects.

Interconversion between minima

The energetic cost necessary to overcome a barrier and transform a minimum of the corannulene⋯cation PES into another has been calculated. All stationary points were characterized as minima or transition structures by calculating the harmonic vibrational frequencies, using analytical second derivatives. This also allowed us to include zero point vibrational energy, ZPVE, in the energetic values. All the minima were optimized at the B3LYP/6-31G* level and no significant geometric differences with respect to the DFT calculations discussed previously were found. Using these geometries, the energy of all minima (including ZPVE) was computed (Table 3). The

Table 3 Relative energies (kcal mol⁻¹) of different isomers of corannulene-M⁺ compounds. ZPVE is included

	In-5	In-6	Out-5	Out6
DFT ^a				
Li ⁺	5.17	3.07	0.50	0.00
Na ⁺	3.10	–	0.00	0.00
K ⁺	1.06	–	0.00	0.39
MP2 ^b				
Li ⁺	2.97	3.06	0.00	1.44
Na ⁺	0.84	–	0.00	1.07
K ⁺	0.00	–	3.63	4.79

^a B3LYP/cc-pVTZ//B3LYP/6-31G*^c MP2/CBS//B3LYP/6-31G*

relative energies of the minima are directly related to the interaction energies of Table 2, and there is not any significant discrepancy, as expected. So, the trends found for coordination *in/out* and the relation between the DFT and MP2 results are the same as those discussed above in terms of interaction energies.

Seven structures were found for the interconversion between minima of the corannulene⋯cation PES. Three of them corresponded to the movement of the cation on the corannulene surface (Fig. 2): TS(6:6)out and TS(6:5)out on the convex face, and TS(5:6)in on the concave face. Obviously TS(5:6)in exists only for the case of Li⁺. In this case (Li⁺ inside the bowl) it was not possible to locate the transition state connecting two equivalent in-6 structures, TS(6:6)in, probably due to the occurrence of a very flat PES. Thus, migration from one to another in-6 structure could take place through in-5 minimum. Table 4 shows that interconversion

barriers for the convex face (outside) are rather small, and they decrease quickly as the cation size increases, so for K⁺ they are very small (in consequence very small imaginary frequencies are also obtained). Therefore, migration of Na⁺ and K⁺ on the convex face of corannulene is a relatively free movement with a not very high energetic cost. Migration of Li⁺ is considerably more hindered and the cation remains more confined in its two kind of minima (out-5 and out-6), which have a quite similar stability.

It is noteworthy that, in general, MP2 barriers for the migration of the cation outside of the bowl are slightly higher than DFT ones, except in the case of interconversion between out-6 and out-5 (reverse TS(5:6)out) for Li⁺, where MP2 value is 0.28 kcal mol⁻¹ smaller than DFT value. This exception is motivated by the fact that only for Li⁺, MP2 calculations give out-5 as the most stable minimum, while DFT calculations give out-6 as the most stable one.

The smallest barrier (less than 1 kcal mol⁻¹) corresponds to migration of Li⁺ from in-5 to in-6, both for DFT and MP2 results. For MP2, this fact together with the energetic equality between the two minima (in-5 and in-6), means that movement of Li⁺ on the concave face (inside) is virtually free.

To transform a structure with concave interaction in a structure with convex interaction (or backward) two alternative ways can be found: bowl-to-bowl inversion or migration of the cation across the edge of corannulene (Fig. 3). For bowl-to-bowl inversion there are two possible transition states (both show a flat corannulene): with the cation penta-coordinated to the central ring, BI-η⁵, and with the cation hexacoordinated to the six-membered ring, BI-η⁶. The first one connects structures in-5 and out-5, and the second one connects structures in-6 and out-6 for Li⁺, and in-5 and out-

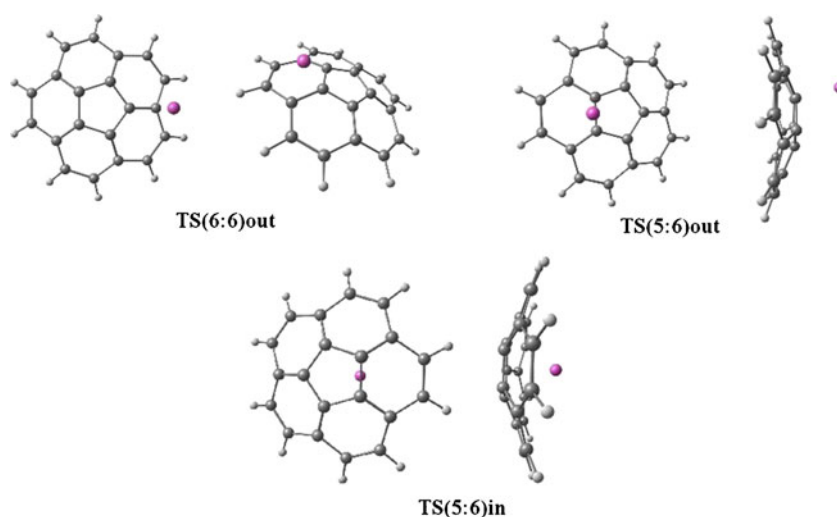
Fig. 2 Transition structures for migration of the cation on the corannulene surface

Table 4 Energy barriers (kcal mol⁻¹) for migration of cations over the surface of corannulene, and imaginary vibrational frequencies of transition states (cm⁻¹). ZPVE is included

	DFT	MP2	ν_{imag}
	TS(5:6)out ^a		
Li ⁺	5.09 (5.59)	6.75 (5.31)	-113.25
Na ⁺	2.02 (2.02)	3.60 (2.53)	-53.34
K ⁺	1.54 (1.15)	2.40 (1.24)	-39.46
	TS(6:6)out		
Li ⁺	6.52	6.81	-122.56
Na ⁺	2.63	3.72	-56.14
K ⁺	1.72	2.08	-36.03
	TS(5:6)in ^a		
Li ⁺	0.34 (2.44)	0.85 (0.76)	-138.77

^a Energy barrier from η^5 structure to η^6 structure, and (in parentheses) from η^6 to η^5

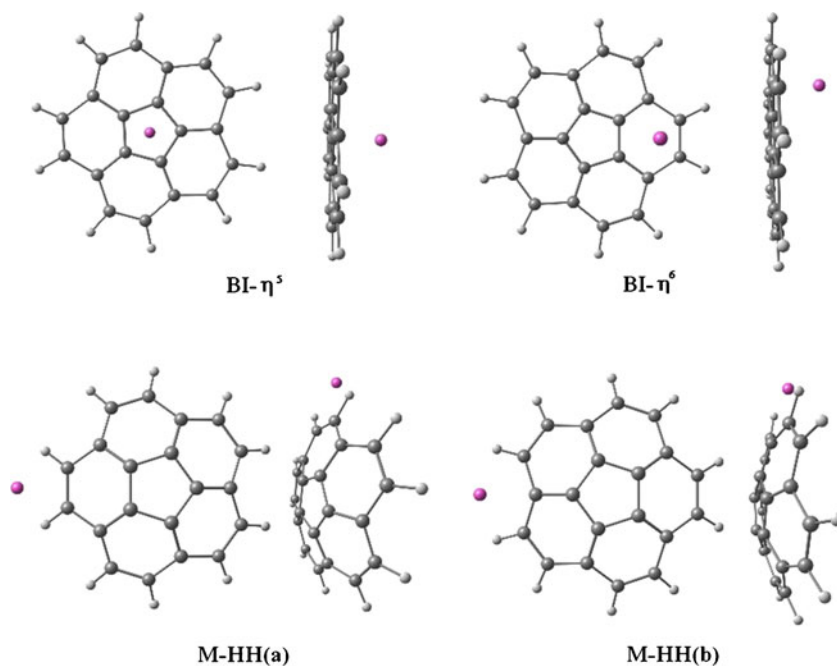
6 for Na⁺ and K⁺. For migration over the edge of corannulene two transition states were also found: with the cation placed between the two H atoms of a six-membered ring, M-HH(a), and with the cation placed between two H atoms of a different (and neighboring) six-membered ring, M-HH(b). These transition states connect isomers in-6 and out-6 for Li⁺ and isomers in-5 and out-6 for Na⁺ and K⁺. Table 5 shows all the barriers for these processes. According to this table, inversion through pentacoordinated or hexacoordinated structures does not lead to significant differences, both at DFT and MP2 levels. In general, they are moderately high barriers (8–15 kcal mol⁻¹) and they increase smoothly as the cation size increases. However, migration across the edge of

Table 5 Energy barriers (kcal mol⁻¹) for bowl-to-bowl inversion and migration over the edge of corannulene, and imaginary vibrational frequencies of transition states (cm⁻¹). ZPVE is included

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

^a Energy barrier for concave-convex transformation, and (in parentheses) for convex-concave transformation

corannulene is considerably more costly (15–27 kcal mol⁻¹), as expected since this process corresponds to the pass of a cation by a region with significant positive MEP. There are not significant energetic differences between M-HH(a) and M-HH(b) transition states, and, as for the TSs of Table 3, MP2 barriers in general are slightly higher than DFT.

Fig. 3 Transition structures for bowl-to-bowl inversion and for migration of the cation across the edge of corannulene

Conclusions

Alkali cations (Li^+ , Na^+ , and K^+) can form very stable complexes with corannulene. Coordination of the cation takes place with the center five-membered ring or with the six-membered ring. Moreover there are two different faces: convex (outside) and concave (inside), so four kinds of minima can be found. Corannulene shows a MEP slightly more negative on the convex face. For that reason, interaction with this face is favored for a cation. As the cation size increases this preference weakens, and this effect is manifested in a stronger way by the MP2/CBS calculations; so at this level the *out* preference is almost overcome for interaction with Na^+ , and already reversed for interaction with K^+ . This *in* preference that takes place for the interaction with K^+ can be explained by the increasing dispersive effects, which could beat the slight electrostatic preference. DFT results adequately reproduce this trend as the cation size increases, but they fail to obtain the correct *in/out* preference, probably due to an insufficient estimation of dispersive effects.

According to our results, migration of Li^+ on the concave face (inside) is virtually free, especially at the MP2 level, with a very small energy barrier between the two minima, in-5 and in-6. For the interaction with the convex face (outside), rather small interconversion barriers were found, being smaller as the cation size increases. The transformation from a structure with concave interaction to a structure with convex interaction is clearly a more costly process, especially when this transformation takes place through migration of the cation across the edge of corannulene. However, when the process happens through bowl-to-bowl inversion, barriers are only moderately high. In general, MP2 barriers are slightly higher than DFT ones, but important differences were not found.

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