



# Does alkali cation binding to aromatic ring retard the fluxional haptotropic migration? Evidences from density functional study

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**Abstract.** DFT calculations were performed on the sandwich complexes of naphthalene (MNC) with alkali metal cation ( $\text{Li}^+/\text{Na}^+/\text{K}^+$ ) on one  $\pi$  face and the tripodal  $\text{Cr}(\text{CO})_3$  moiety on the other with a view to explore the role of cation on haptotropic migration. Cation binding not only enhances the complex interaction energy but also delicately affects the fluxionality in the molecule by increasing the barrier to haptotropic shift of  $\text{Cr}(\text{CO})_3$ . The competing nature of the bifacial acids with sandwiched aromatic ring is established. In line with Pearson's HSAB principle, LiNC system with highest interaction energy is found to be the most stable one among all the systems under study.

**Keywords.** Cation- $\pi$  interactions; density functional theory; haptotropic rearrangements;  $\eta^6$ -naphthalene- $\text{Cr}(\text{CO})_3$  complexes.

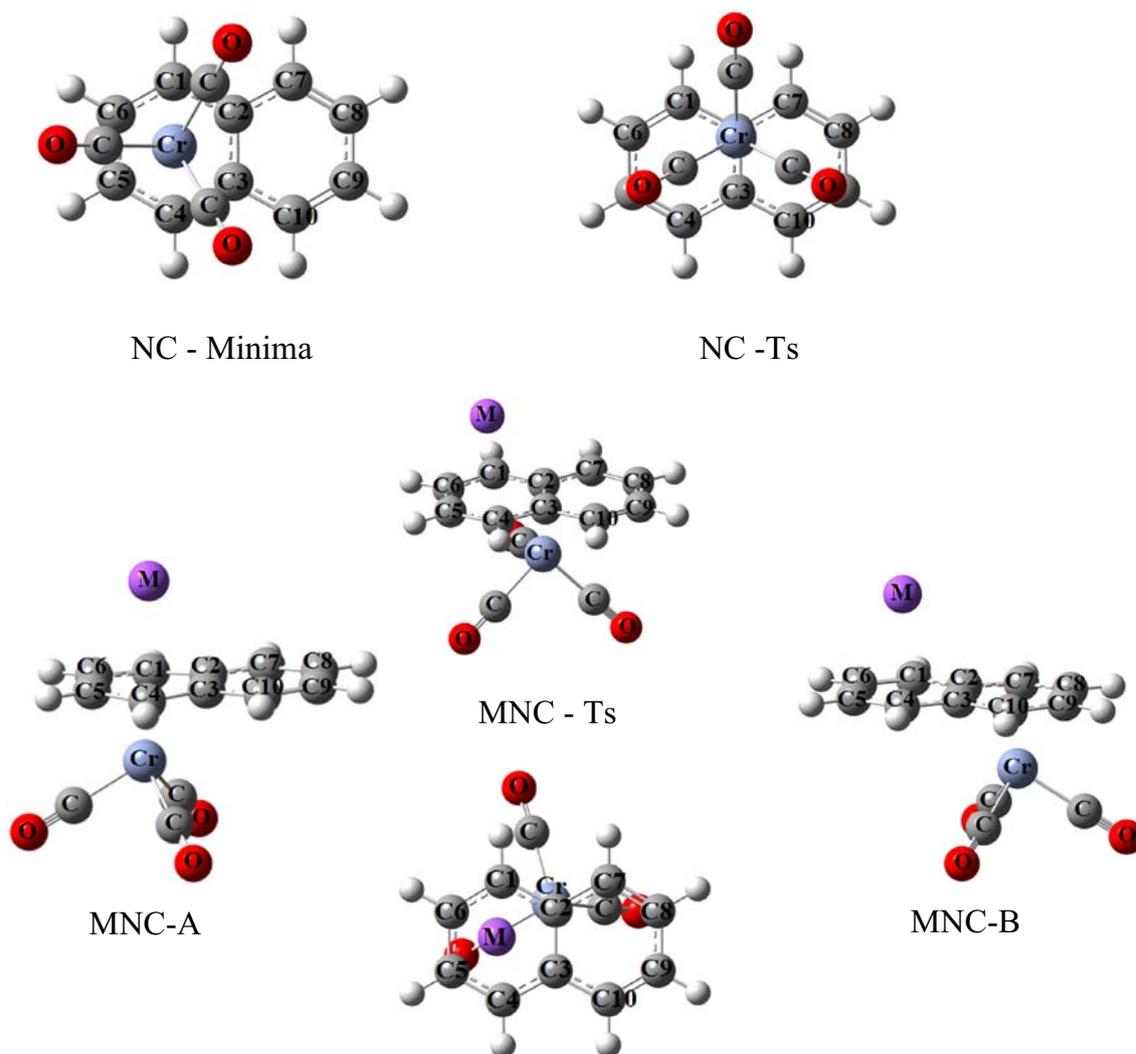
## 1. Introduction

The cation- $\pi$  interaction deserves to be called the most powerful interaction among the non-covalent interactions, and hence has wide range of applications in chemistry, material science and biology.<sup>1–5</sup> Cation- $\pi$  interactions are electrostatic in origin and occurs when a cation interacts with the negatively charged  $\pi$ -electron cloud of an arene system. The strength of cation- $\pi$  interactions can be tuned over a long range by altering the factors such as nature of the cation and  $\pi$  system, size of the  $\pi$  system, nature of the substituents present in the  $\pi$  system, etc., and it is this variability that underlies the utility of cation- $\pi$  interactions.<sup>5–7</sup> Wide range of experimental and theoretical investigations have been reported on these cation interactions on many types of aromatic systems.<sup>5–10</sup>

$\eta^6$ -arene- $\text{Cr}(\text{CO})_3$  systems are the most extensively studied half-sandwich complexes.<sup>11–19</sup> Many experimental and theoretical investigations have extensively explored the conformational biasing, barrier to tripodal rotation, aromaticity, structural and energetics of such complexes.<sup>11–19</sup> Exclusively, the  $\pi$ -complexes of polycyclic aromatics with metal moiety has the ability to undergo haptotropic rearrangements. There are two ways in which haptotropic rearrangements may

proceed; (i) when the metal moiety changes its  $\pi$ -coordination to the arene ligand within the same ring (intra-ring haptotropic) and (ii) when it involves migration of metal moiety from one of the aromatic ring to the other (inter-ring haptotropic).<sup>20</sup> In an inter-ring haptotropic rearrangement (IRHR), the  $\pi$ -coordinated  $\text{ML}_n$ -unit ( $M$  = metal,  $L$  = coligand) changes its connectivity by migrating between different rings of polycyclic aromatics which is a ligand with multicoordinate site possibilities.<sup>21</sup> Haptotropic shifts play significant role in transition metal catalysed processes and in designing organometallic switches.<sup>22,23</sup> Exhaustive studies have been done on haptotropic shifts in complexes with aromatic polycyclic ligands, like naphthalene, anthracene where the metal ion moves across the rings.<sup>20,24–26</sup> The simplest system in which haptotropic rearrangement takes place was  $\eta^6$ -naphthalene- $\text{Cr}(\text{CO})_3$  and its derivatives, which was first reported by Deubzer.<sup>27</sup> Also, qualitative study on haptotropic rearrangements in aromatic ligands with many transition metals such as Mo, W, Rh, Pd, Ir, Ni, Mn, Fe, Zr, Ru and Os have been reported.<sup>20</sup> The mechanistic pathway for the metal moiety [ $\text{Cr}(\text{CO})_3$ ] migration in the naphthalene system was proposed by Albright et al.<sup>28</sup> and they suggested that the metal-coligand unit migrates along the periphery of the naphthalene ligand with a  $\text{Cr}(\text{CO})_3$ - $\eta^4$ -coordinated trimethylenemethane transition state complex, i.e., the Cr is approximately located above the C2 (or C3) atom rather than above the center of the C2-C3 bond (cf.

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**Figure 1.** Geometry optimized structures of the  $M^{n+} - \eta^6$ -arene- $Cr(CO)_3$  complexes.

Figure 1). Later, kinetic study of the  $\eta^6 - \eta^6$ -haptotropic rearrangement in substituted naphthalene tricarbonyl chromium complexes have been reported.<sup>29-31</sup> Further, many experimental and theoretical studies have documented the haptotropic rearrangement of  $Cr(CO)_3$  complexes with a variety of arenes.<sup>20-40</sup> Molecular motion across the surfaces has significant importance in designing molecular machines such as molecular motors, brakes, switches, etc. and the past decade has been graced by a plethora of reports describing the design and function of such machines.<sup>41-43</sup> Generally, the haptotropic migration can be influenced by the incorporation of redox-, photo- or pH-sensitive functional groups in combination with a complementary substitution pattern in the metal moiety and the arene ligand and hence may facilitate the construction of a switchable device.<sup>23</sup>

And also, arene-chromium tricarbonyl compounds have attracted considerable attention for many years because of their potential applications in organic synthesis and in designing molecular switches/brakes, etc.<sup>41,43,44</sup> In our previous theoretical work we have reported the structural and electronic effects of cation binding to  $\pi$  system of  $\eta^6$ -benzene- $Cr(CO)_3$ .<sup>19</sup> Although many factors that affect the haptotropicity have been reported to the best of our knowledge, effect of cation binding on the aromatic ring on the haptotropic energetics and stability have not been explored. We consider it is worth exploring because we have already reported that the cation binding modulates the stability of the sandwich complex involving the Pearson's Hard and Soft Acid Base (HSAB) concept.<sup>19</sup> Therefore, assertively presuming the contribution of cation on fluxional haptotropic behaviour of  $Cr(CO)_3$

between the two rings of a simple naphthalene system bound to  $\text{Cr}(\text{CO})_3$ , we have intended to analyse the tuning effect of alkali metal cation on strength of the complexation energy, aromaticity, and most importantly on the fluxional behaviour of  $\text{Cr}(\text{CO})_3$  moiety in  $\eta^6$ -naphthalene- $\text{Cr}(\text{CO})_3$  systems.

## 2. Computational details

All calculations have been performed with the GAUSSIAN-09 program.<sup>45</sup> Geometry optimizations was carried out at B3LYP<sup>46,47</sup> method, 6-31G(d) basis set<sup>48</sup> was used for carbon, oxygen, hydrogen atoms and metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ). LANL2DZ basis set,<sup>49</sup> was used for the chromium atom in  $\text{Cr}(\text{CO})_3$ . All the optimized structures were characterized by frequency analysis. The haptotropic transition state is located and characterized by single imaginary frequency along the normal mode of the desired haptotropic shift. The transition state has been connected with the reactants MNCA and B through IRC calculations.<sup>50</sup> The interaction energies obtained were corrected for basis set superposition error (BSSE) using the counterpoise method described by Boys and Bernardi.<sup>51</sup> Natural bond orbital analysis (NBO)<sup>52-54</sup> and Nucleus-independent chemical shifts (NICS<sub>zz</sub>)<sup>55</sup> calculations have been done by B3LYP method using 6-31G(d) basis set<sup>48</sup> for carbon, oxygen, hydrogen atoms and metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) and LANL2DZ basis set,<sup>49</sup> for the chromium atom in  $\text{Cr}(\text{CO})_3$ . NICS<sub>zz</sub>(0) was calculated at the geometrical centres of the ring atoms, and also 1 Å above the ring NICS<sub>zz</sub>(1) using the gauge invariant atomic orbital (GIAO)<sup>56</sup> method.

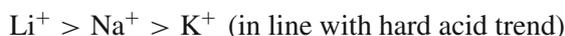
## 3. Results and Discussion

In the present study, the cation bound to the  $\pi$  cloud of one aromatic ring of naphthalene which is bound to the tripodal  $\text{Cr}(\text{CO})_3$  unit in  $\eta^6$  fashion has been considered [ $\text{M}^{n+} - \eta^6$ -naphthalene- $\text{Cr}(\text{CO})_3$  (MNC)] (Figure 1). Based on the location of the cation and  $\text{Cr}(\text{CO})_3$  there can be two isomers - **MNCA** (both metal cation and  $\text{Cr}(\text{CO})_3$  on the same ring) and **MNCB** (cation on one ring and  $\text{Cr}(\text{CO})_3$  on the other) (Figure 1). These isomers are fortunately interconvertible through the haptotropic shift of  $\text{Cr}(\text{CO})_3$  from one ring to another. The thermodynamic stability of the isomers **MNCA** and **B** are of interest since it would clarify the role of extended aromaticity in affecting the stability of the so called  $\pi$ -acid base interacting sandwich molecules (which has been explored in terms of role of cations in our earlier paper<sup>19</sup>). Also the subtle insights of role of cation- $\pi$  interaction in influencing the fluxional haptotropic behaviour is studied by locating the haptotropic transition state (**MNC-TS**) (Figure 1). For the sake of

comparison the **MN** (metal-cation bound naphthalene system) **MB** (metal-cation bound benzene system) analogues (without  $\eta^6$ - $\text{Cr}(\text{CO})_3$ ) and **MBC** (metal-cation bound  $\eta^6$ - $\text{Cr}(\text{CO})_3$ -benzene system) have also been included. The geometries of the minima and TS are presented in Figure 1.

### 3.1 Interaction energy

The BSSE corrected interaction energy (IE) calculated for all the  $\text{M}^{n+}$ -naphthalene- $\text{Cr}(\text{CO})_3$  (MNC) systems under study are given in Table 1. The Mulliken charges on different fragments (*viz.* metal-cation ( $\text{M}^{n+}$ ), ring (R) and  $\text{Cr}(\text{CO})_3$ ) are also presented in Table 1. The thermodynamic stability of the two isomers (MNC-A and MNC-B) could be compared by considering their interaction energies (Table 1). Although cation binding on the aromatic face of naphthalene- $\text{Cr}(\text{CO})_3$  system has sizeably altered their stability, it has very marginally differentiated MNCA and B by delicately stabilising B to A, immaterial of the metal ion. Now the prime intention of the paper is to focus on the role of cation on the stability of the isomers and on the haptotropic shift. The role of cations on the stability of the isomeric sandwich complexes are in line with HSAB (Hard and soft acid base) principle in which the aromatic cloud on one face acts as a hard base and consequently the stability is the highest for the hardest acid  $\text{M} = \text{Li}^+$  in MNCA and B and the trend goes as follows:



This is applicable for both the isomers. Yet another observation is that the interaction energies of all the MNCs are higher than their corresponding MN analogues. This is quite understandable as the former has two interactions with the  $\pi$  cloud of the aromatic unit on both faces and the latter has only cation- $\pi$  interaction. But the magnitude of interaction is less than the additivity of their individual interactions ( $\text{IE}_{\text{MNC}} < \text{IE}_{\text{MN}} + \text{IE}_{\text{NC}}$ ) (Table 1) signifying a competitive behaviour.

As this paper addresses the role of extended delocalisation, comparison of naphthalene systems with their corresponding benzene analogues is worth doing. The right end of the Table 1 presents the parameters for benzene analogues<sup>19</sup> for comparison purpose. It shows that benzene systems of Na and K (NaBC and KBC) have slightly higher interaction energy than their corresponding naphthalene analogues (NaNc and KNC). For Li, both naphthalene and benzene analogues have nearly equal energy. But it is worth noting that MN analogues are more stable than MB (increased interaction energy by nearly 2 kcal/mol). This can be explained

**Table 1.** Interaction energy (IE) (kcal/mol), Hardness ( $\eta$ ) (eV), Distance from the metal cation to centroid of one of the ring of Naphthalene ( $d_{M-\Omega}$ ) (Å) and from the chromium to centroid of one of the ring of Naphthalene ( $d_{Cr-\Omega}$ ) (Å), Mulliken charges (in au) of the cations, ring and Cr(CO)<sub>3</sub> computed for minimum energy structures in all the system (S).

S	MNCA			MNCB			Haptotropic shifts			MBC				
	IE <sup>a</sup>	$\eta$	$d_{M-\Omega}$	$d_{Cr-\Omega}$	Mulliken charges	Cr	$\frac{\Delta^{\ddagger}_{A \rightarrow B}}{\Delta E^{\ddagger}}$	$\frac{\Delta^{\ddagger}_{B \rightarrow A}}{\Delta E^{\ddagger}}$	IE <sup>a</sup>	$\eta$	$d_{M-\Omega}$	$d_{Cr-\Omega}$	Mulliken charges	Cr
			$\frac{M^{n+}}{R}$	$\frac{M^{n+}}{R}$	$\frac{M^{n+}}{R}$	$\frac{Cr}{Cr}$							$\frac{M^{n+}}{R}$	$\frac{Cr}{Cr}$
<b>N</b>	<b>-40.92</b>	<b>1.81</b>	<b>1.79</b>	<b>0.26</b>	<b>-0.26</b>		<b>19.70</b>	<b>0.41</b>	<b>-43.98</b>	<b>2.33</b>	<b>1.81</b>	<b>0.29</b>	<b>-0.29</b>	
<b>Li</b>	<b>-73.73</b>	<b>1.77</b>	<b>1.93</b>	<b>0.47</b>	<b>0.48</b>	<b>0.05</b>	<b>21.20</b>	<b>0.68</b>	<b>-73.77</b>	<b>2.18</b>	<b>1.85</b>	<b>1.72</b>	<b>0.59</b>	<b>1.28</b>
	-43.05	2.35	1.85	0.43	0.57		-40.17	3.48	-40.17	3.48	1.87		0.42	0.58
<b>Na</b>	<b>-60.84</b>	<b>1.70</b>	<b>2.29</b>	<b>0.66</b>	<b>0.37</b>	<b>-0.03</b>	<b>22.19</b>	<b>0.60</b>	<b>-62.28</b>	<b>1.89</b>	<b>2.28</b>	<b>1.78</b>	<b>0.66</b>	<b>0.35</b>
	-28.81	2.34	2.33	0.65	0.35		-26.66	3.12	-26.66	3.12	2.34		0.65	0.35
<b>K</b>	<b>-50.49</b>	<b>1.71</b>	<b>2.85</b>	<b>0.85</b>	<b>0.19</b>	<b>-0.04</b>	<b>21.90</b>	<b>0.61</b>	<b>-51.36</b>	<b>1.93</b>	<b>2.82</b>	<b>1.77</b>	<b>0.86</b>	<b>0.14</b>
	-18.42	2.38	2.84	0.84	0.16		-16.62	3.09	-16.62	3.09	2.82		0.84	0.16

Calculated parameters represented in bold (MNC/MBC<sup>19</sup>), plain (MN/MB<sup>19</sup>); <sup>a</sup>IE = BSSE corrected interaction energy (the inclusion of Grimme's dispersion corrections B3LYP-D3 & B3LYP-D3(BJ)<sup>57,58</sup> in interaction energy does not show any significant changes in our earlier related report<sup>19</sup>);  $\eta = [(E_{LUMO} - E_{HOMO})/2] \times 27.2116 \text{ eV}^{59}$ ;  $\eta = 2.41 \text{ eV}$  (naphthalene), 3.39 eV (benzene);  $\Delta E^{\ddagger}$  - Haptotropic energy barrier ( $E_{TS} - E_{\text{minima}}$ );  $\Delta \eta^{\ddagger} = \eta_R - \eta_{TS}$ ;  $IE_{MN+NC} = -83.97$  (Li),  $-69.73$  (Na),  $-59.34$  (K);  $IE_{MNCA-NC} = -32.81$  (Li),  $-19.92$  (Na),  $-9.57$  (K);  $IE_{MNCB-NC} = -33.16$  (Li),  $-19.55$  (Na),  $-9.69$  (K).

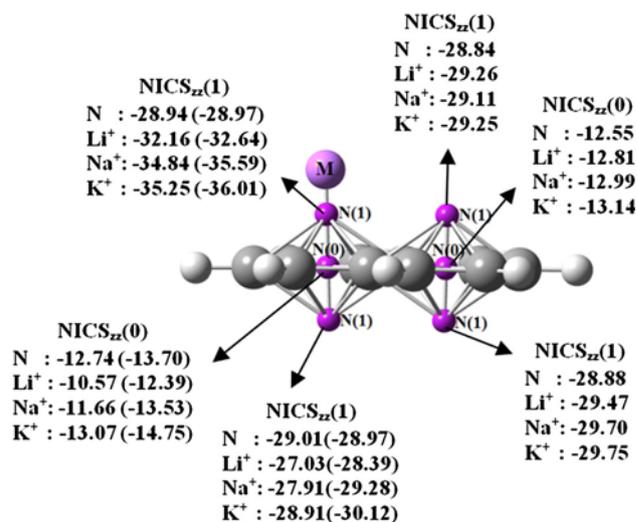
as follows: from the Mulliken charges (Table 1) it is found that both MB and MN carry nearly the same quantum of positive charge on metal and arene moiety but the stability of MN system could be attributed to the larger delocalisation of charges across both the rings of naphthalene in contrast to lesser delocalisation in benzene. Now revisiting the exactly reversed observation of MNC and MBC with the charge perspective, it is clear that in contrast to MN and MB cases the positive charge on aromatic moiety is increased due to the drain of electrons into  $\text{Cr}(\text{CO})_3$ . It is observed from the Table 1 that the  $\text{Cr}(\text{CO})_3$  moiety has (-0.03 (NaNc) and -0.04 (KNC)) units of electrons while it is just (-0.01) in the case NaBC/KBC. The excess of positive charge on the naphthalene ring of NaNc and KNC than those of their benzene counterparts probably explains the observation that interaction energy of MNC is slightly lower than MBC in the case of Na and K systems. LiNC behaves differently and has to be focussed separately because, in contrast to the above statement that MNCA/B have lower interaction than their MBC counterparts by nearly 2 kcal/mol, the LiNCA and B are almost equal LiBC. This can also be explained by looking at the charges on each moiety. In LiBC the positive charge on the ring is very high due to the transfer of electron to  $\text{Cr}(\text{CO})_3$  but both LiNCA and B have much less positive charge on aromatic ring (+0.48 and 0.64, respectively) than LiBC (+1.28) (Table 1). There is only a small difference between charge on  $\text{Cr}(\text{CO})_3$  in LiNCA and B. The former is slightly positive and the latter is slightly negative and probably this minuscule charge drain in the latter could have given a slightly more stability than the former and LiBC too!

### 3.2 Reactivity

The lower hardness values ( $\eta$ ) in the Table 1 reveals that the MN and MNC systems possess higher reactivity than their corresponding benzene counterparts (MB and MBC). And also,  $\text{Cr}(\text{CO})_3$  fragment present in MNC, enhances their reactivity when compared to MN complexes (Table 1). Also MNCA is slightly harder than MNCB but their stability is reverse. This is similar to our earlier reports that cation binding increases the interaction energy and reduces the hardness making the molecule more susceptible for reaction.

### 3.3 $d_{M-\Omega}$ and $d_{Cr-\Omega}$

From the Table 1, it is known that the  $\text{Li}^+$  complexes have minimum cation- $\pi$  distance and maximum interaction energy among all MNC complexes. A slight



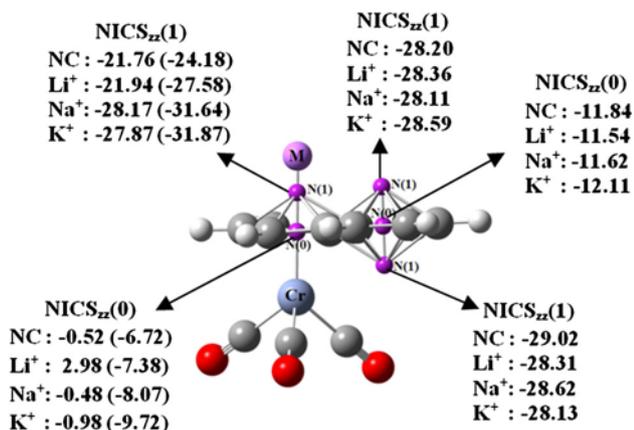
**Figure 2.**  $\text{NICS}_{zz}(0)$  and  $\text{NICS}_{zz}(1)$  (above and below the plane) values of MN (corresponding  $\text{NICS}_{zz}(0)$  and  $\text{NICS}_{zz}(1)$  values of benzene counterparts are shown in bracket).

decrease in  $M-\Omega$  distance of MN compared to MB, accounts for the slight higher interaction energy of the former. As the size of the  $\pi$ -system increases from MBC to MNC, the  $M-\Omega$  distance slightly increases in MNC systems, and it indicates the competitive interactions between the two acids (*viz.*, metal cation and  $\text{Cr}(\text{CO})_3$ ) with the common  $\pi$ -base (naphthalene ring). However, the perturbation of  $\text{Cr}-\pi/\text{cation}-\pi$  distances in MNC compared MN/NC systems were not in accordance with their corresponding IE trend. Thus cation- $\pi$  and  $\text{Cr}-\pi$  distance may not be the most appropriate structural parameters for determining the strength of binding of metal cation/ $\text{Cr}$  moiety.<sup>10</sup>

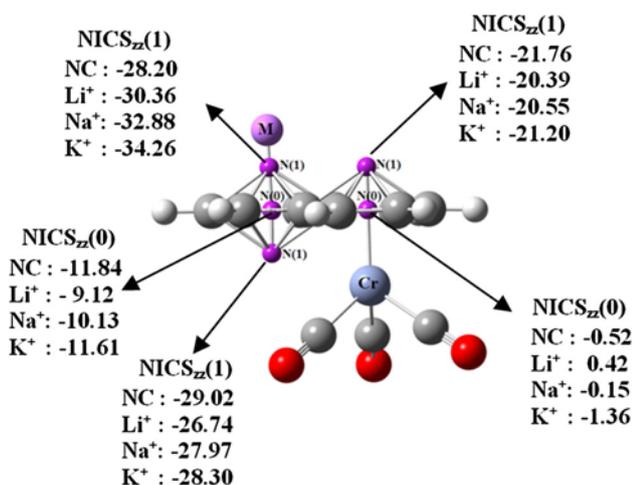
### 3.4 Aromaticity

The computed  $\text{NICS}_{zz}(0)$  and  $\text{NICS}_{zz}(1)$ <sup>15</sup> values of the cation bound naphthalene (MN) and cation bound naphthalene - chromium tricarbonyl complexes (MNCA and MNCB) are presented in Figures 2, 3 and 4, respectively. The  $\text{NICS}_{zz}(0)$  and  $\text{NICS}_{zz}(1)$  values of their corresponding benzene counterparts are also shown in Figures 2, 3 and 4 (in brackets), respectively, for the comparison purpose.

**3.4a Effect of size of  $\pi$ -system on aromaticity:** As the size of the  $\pi$ -system increases from metal cation bound benzene (MB) to metal cation bound naphthalene (MN) system (Figure 2) or from metal cation bound benzene-chromium tricarbonyl (MBC) to metal cation bound naphthalene-chromium tricarbonyl (MNCA and B) systems (Figures 3 and 4), both the  $\text{NICS}_{zz}(0)$  and (1) decreases.



**Figure 3.** NICS<sub>zz</sub>(0) and NICS<sub>zz</sub>(1) (above and below the plane) values of MNCA (corresponding NICS<sub>zz</sub>(0) and NICS<sub>zz</sub>(1) values of benzene counterparts are shown in bracket).



**Figure 4.** NICS<sub>zz</sub>(0) and NICS<sub>zz</sub>(1) (above and below the plane) values of MNCB (corresponding NICS<sub>zz</sub>(0) and NICS<sub>zz</sub>(1) values of benzene counterparts are shown in bracket).

**3.4b Effect of Cr(CO)<sub>3</sub> on aromaticity:** The effect of Cr(CO)<sub>3</sub> moiety could be observed by comparing the NICS<sub>zz</sub> values of simple naphthalene (N) with that of naphthalene-chromium tricarbonyl (NC) and metal cation bound naphthalene (MN) with that of metal cation bound naphthalene-chromium (MNCA and B) (Figure 2 with Figures 3 and 4) and it is inferred that the coordination of Cr(CO)<sub>3</sub> fragment to naphthalene or metal bound naphthalene system would reduce both NICS<sub>zz</sub>(0) and (1) aromaticity.

**3.4c Effect of metal cation on aromaticity:** The role of metal cation on aromaticity could be observed by comparing the NICS<sub>zz</sub> values of simple naphthalene (N) with that of metal bound naphthalene system (MN) (Figure 2) and naphthalene-chromium tricarbonyl (NC)

with that of metal bound naphthalene-chromium tricarbonyl (MNCA and B) (Figures 2 and 3). The binding of metal cation to naphthalene or naphthalene-chromium system reduces the NICS<sub>zz</sub>(0) aromaticity but increases NICS<sub>zz</sub>(1) aromaticity of the particular ring to which it is bound in naphthalene of MN and MNC systems.

### 3.5 Effect of cation on haptotropic shift

Cation interaction with both rings of naphthalene-Cr(CO)<sub>3</sub> yields two isomers A and B which are interconvertible by the haptotropic shift of Cr(CO)<sub>3</sub> from one ring to another. It is clear from the Table 1 that the barrier to haptotropic shift has increased upon cation binding in general. Especially the barrier to convert B to A is around 2 kcal/mol higher lying than that for A to B interconversion. This establishes that the thermodynamic and kinetic stability go hand in hand with one another. A noteworthy observation is that unanimously all the cations exert same effect on haptotropic shift of Cr(CO)<sub>3</sub> and thereby there is no differentiating effect which can be related to hard acid (Pearson's concept) as has been discussed for interaction energy. The activation hardness presented in Table 1 shows that cation binding has increased the  $\Delta\eta^\ddagger$  and it is in line with the observed haptotropic barrier (especially  $\Delta_{A \rightarrow B}^\ddagger$  than  $\Delta_{B \rightarrow A}^\ddagger$ ). This signifies that haptotropic event is Frontier orbital controlled. Therefore, the barrier enhancement during fluxional haptotropicity may be considered as an immediate effect of cations on Frontier orbitals. Frontier orbital energies listed in the Table 2 show that HOMO and LUMO of cation bound naphthalene chromium

**Table 2.** Energy of Frontier molecular orbitals (HOMO and LUMO) in atomic units computed for all the systems under study.

System	HOMO	LUMO
NC	-0.201	-0.068
NC-TS	-0.192	-0.089
N	-0.212	-0.035
LiNCA	-0.340	-0.210
LiNCB	-0.334	-0.222
LiNC-TS	-0.319	-0.239
LiN	-0.384	-0.211
NaNCA	-0.328	-0.203
NaNCB	-0.321	-0.209
NaNC-TS	-0.306	-0.225
NaN	-0.367	-0.195
KNCA	-0.315	-0.189
KNCB	-0.310	-0.192
KNC-TS	-0.294	-0.213
KN	-0.354	-0.179

tricarbonyl complexes and their transition states are stabilised than their counterparts without cations. Therefore during this dynamic haptotropy the role of cation is clearly that of any unit positive charge depreciating the electron density of the aromatic ring and thereby imparts a large barrier to the fluxional shift than the ones without cation binding.

#### 4. Conclusions

Cation- $\pi$  interaction with the fused aromatic ring system,  $\eta^6$ -naphthalene- $\text{Cr}(\text{CO})_3$  has enhanced both the interaction energy and reactivity (decreased hardness). The interaction energy is linearly related to Pearson's hard acid nature of the binding cation, with LiNC having maximum interaction energy. But the interaction between the bifacial acids (*viz.*  $\text{M}^{n+}$  on one face and  $\text{Cr}(\text{CO})_3$  on the other) towards the sandwiched aromatic naphthalene unit is rather competitive than cooperative. Further the fluxional migration of  $\text{Cr}(\text{CO})_3$  to both the ring centres become is less facile in the presence of cation in general and no specific differentiating influence is afforded by the alkali cations as in the case of interaction energies.

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