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ARTICLE

## Cation-assisted interactions between N-heterocycles and CO<sub>2</sub>

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Cation-assisted interactions between N-containing heterocycles (NHCs) and CO<sub>2</sub> have been systematically studied by using density functional theory (DFT). For neutral and anionic (non-carbenoid) NHCs, the effects of monovalent cations (i.e., alkali metal ions) are moderate to small (the NHC-CO<sub>2</sub> binding energy change,  $\Delta BE$  usually < 25 kJ/mol). However, for NHC carbenes, due to their strong basicity, the effects are strong ( $\Delta BE > 60$  kJ/mol) and the monovalent cations play a critical role in the single carboxylation of dicarbenes with CO<sub>2</sub>. In comparison, divalent alkali earth metal cations, due to both their smaller sizes and higher formal charges, exhibit much stronger influence ( $\Delta BE > 100$  kJ/mol). Divalent cations should be incorporated in the next generation CO<sub>2</sub> capture reagents. Other aspects including the reaction potential energy surface (PES), orbital-based analyses of interactions, substitution effects, and the reactivity descriptors (cation size, reacting N lone pair orbital energy, etc) have been discussed in detail as well.

### 1. Introduction

Nitrogen-containing heterocycles (NHCs) either as anions<sup>1-5</sup> or carbenes (including normal<sup>6-10</sup>, abnormal<sup>11, 12</sup>, and anionic dicarbenes<sup>13</sup>), can chemically bond with CO<sub>2</sub> through the electron lone pair of the N or C (carbene) atoms, making them suitable for postcombustion CO<sub>2</sub> capture.<sup>14, 15</sup> NHCs have been successfully introduced into ionic liquids (ILs)<sup>1-6</sup> and metal-organic frameworks (MOFs)<sup>16-20</sup>. It is well-known that anionic NHCs (non-carbenes) dominate the reactions with CO<sub>2</sub>, while the charge balancing cations only exhibit limited secondary effects.<sup>4, 15, 21-27</sup>

However, in some cases, the cation effects are indispensable. Very recent experiments by He and Dai groups have revealed that the weakly basic salts composed of lithium or potassium and organic bases can nearly 1:1 stoichiometrically react with CO<sub>2</sub> by forming stable zwitterionic carbamate adducts through multidentate coordination between the metal cation and organic base.<sup>28, 29</sup> Moreover, even though neutral NHCs (except carbenes) display only weak physical interactions with CO<sub>2</sub><sup>30</sup>, their behavior together with metal cations, commonly seen in NHC-grafted MOFs, are recently shown by Neaton group to be very different, whose calculations prove that the linker NHC ligands with metal centers can cooperatively and strongly bond with CO<sub>2</sub>.<sup>31, 32</sup> Additionally, for carbenes, there is a lack of

understanding of their interaction with CO<sub>2</sub> in co-existence with charged species in general. For example, lately, anionic dicarbenes derived from imidazol-2-ylidene core reported by Vogt et. al. selectively react with equal moles of CO<sub>2</sub> at the abnormal carbene position (C4), mysteriously leaving the reactive normal carbene position (C2) vacant.<sup>13</sup>

Thus, there is a clear need for a systematic survey of the cation effects on the interactions between NHCs (neutral, anionic, and carbenoid) and CO<sub>2</sub>. More importantly, the acquired knowledge can be extended beyond the NHC architecture to other CO<sub>2</sub> capture materials that may have similar functionality but at lower costs. Here, we try to answer the question by employing the density functional theory (DFT)-based calculations. To focus on the nature of the interactions, we choose a number of simple and representative NHCs (Figure 1) and cations (alkali and alkaline earth metals) to minimize complex steric effects. We start with one of the simplest NHCs, i.e., the neutral pyridine and explore its reaction potential energy surface (PES) with CO<sub>2</sub> assisted by Li<sup>+</sup>. Next, we discuss more NHCs in the presence of metal cations like Li<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, etc. Then we identify a structure-specific descriptor to quantitatively account for the different reactivities of NHCs at the presence of the same metal cation (e.g. Li<sup>+</sup>). Finally, we use the Li<sup>+</sup>-bound carbene model to explain the single carboxylation of dicarbenes. This study provides complementary insights of the cation effects on NHC-based CO<sub>2</sub> capture reagents like ILs and porous materials.

### 2. Computational methods

All calculations were performed with the Gaussian 09 suite of programs.<sup>33</sup> The geometries of all reported structures were optimized without symmetry constraints at the B3LYP<sup>34</sup> level of DFT in conjunction with the standard 6-311++G(d,p)<sup>35</sup> basis

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set for all atoms except alkali and alkaline earth metals, for which the SDD<sup>36</sup> basis sets were employed. This model chemistry has been proven to be very efficient and accurate for similar NHC systems.<sup>1-4, 12, 13, 15, 28, 29</sup> Frequency analyses were conducted at the same level of theory to verify the stationary points as the energy minima. The binding energy between CO<sub>2</sub> and NHCs is defined in the following equation:

$$E_{\text{binding}} = E_{\text{sorbent-CO}_2} - (E_{\text{sorbent}} + E_{\text{CO}_2})$$

$E_{\text{sorbent-CO}_2}$ ,  $E_{\text{sorbent}}$  and  $E_{\text{CO}_2}$  denote the electronic energies of the complex, the pure sorbent and CO<sub>2</sub>, respectively.

To understand the nature of the CO<sub>2</sub>-NHC-cation interactions, the relaxed scan of the N-C distance ( $d_{\text{N-C}}$ ) was performed, in which only  $d_{\text{N-C}}$  was fixed and incrementally varied at 0.01 Å intervals and the rest were allowed to relax. Energies reported for the scan were electronic energies. The same methods were used for natural resonance theory (NRT)<sup>37-39</sup>, natural bond orbital (NBO), and NBO charge calculations, implemented in the NBO 6 program.<sup>40, 41</sup>

### 3. Results and discussions

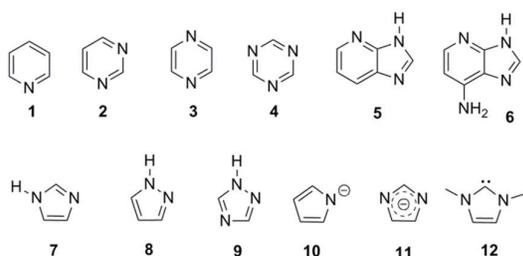


Figure 1. NHCs studied in this work.

We choose a group of conjugated NHCs, including neutral single-ringed structures (six-membered **1-4** and five-membered **7-9**), neutral double-ringed structures (imidazopyridine **5** and imidazopyridamine **6**), anions (pyrrolidine **10** and imidazolidine **11**), and a neutral carbene (imidazol-2-ylidene **12**). Using these simple structures, we hope to minimize other factors like steric effects and focus on their interactions with simple cations (e.g. Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, etc).

#### 3.1 Reaction mechanism

We first examined the reaction mechanism between pyridine (**1**) and CO<sub>2</sub> at the presence of Li<sup>+</sup>. We scanned the reaction PES (Figure 2) by reducing the distance between N (pyridine) and C (CO<sub>2</sub>). Initially, when CO<sub>2</sub> is far away from the NHC sorbent, Li<sup>+</sup> complexes strongly with pyridine at the N position by forming a Li-N bond of 1.92 Å (Figure 2, a) and the binding energy is -198.2 kJ/mol. With the approaching of CO<sub>2</sub>, the system experiences complex energy and configuration changes. Through a few key intermediate states (Figure 2, c-f) at the N-C distance of around 2.6-2.2 Å, CO<sub>2</sub> eventually inserts in between the NHC and Li atom by breaking the Li-N bond

(Figure 2, g). The newly formed N-C bond (1.50 Å) and the bidentation of the two O atoms to Li (1.97 Å) help bend the ∠OCO to 128.0°. The reaction energy is -25.7 kJ/mol and the overall barrier is ~ 100 kJ/mol, which may be greatly reduced by adding proper solvents to weaken the cation-NHC interaction and to facilitate the CO<sub>2</sub> insertion, like in the case of adding functionalized polyethylene glycol to the Li/K-organic base salts to improve the CO<sub>2</sub> absorption.<sup>28, 29</sup> In contrast, the interactions between the neutral pyridine and CO<sub>2</sub> reported by Vogiatzis et. al.,<sup>30</sup> are just weak physical bindings (-11.8 kJ/mol) and the most stable configuration is also a coplanar of the two molecules with the N atom (pyridine) facing the C atom (CO<sub>2</sub>), but at a much longer distance of 2.85 Å and only a slight bending with ∠OCO = 176.3°. While for anionic NHCs (e.g. **10**) or carbenes (e.g. **12**), their reactions with CO<sub>2</sub> are a much simpler direct Lewis base to acid complexation, experiencing a very small or even zero barrier.<sup>42, 43</sup>

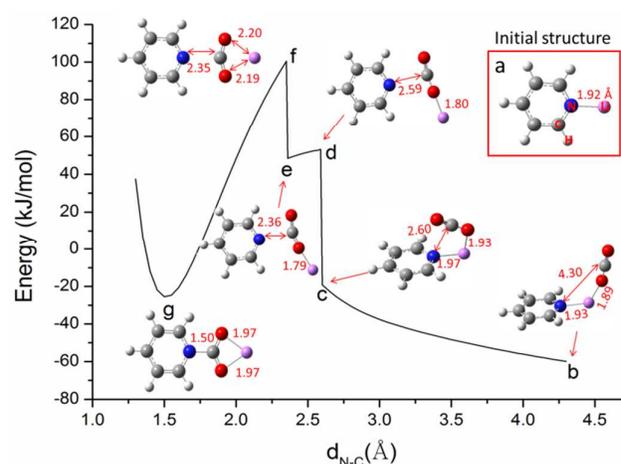


Figure 2. PES of the Li<sup>+</sup>-assisted pyridine and CO<sub>2</sub> reaction. Key structures are plotted. The energy reference point is chosen when the (NHC-Li<sup>+</sup>) complex and CO<sub>2</sub> are at infinite distance. (a) The reference complex of (NHC-Li<sup>+</sup>). (b) The initial binding of CO<sub>2</sub> to Li. (c) The simultaneous binding of CO<sub>2</sub> to Li and NHC. (d) and (e) The replacement of Li by CO<sub>2</sub>. (f) The transition state of CO<sub>2</sub> insertion. (g) The CO<sub>2</sub> inserted complex.

We carried out the NBO and NRT analyses of the (1-CO<sub>2</sub>-Li<sup>+</sup>) complex to explore the nature of the interaction. The N-C bond is a double bond (Figure 3a). Unlike the case of anionic NHCs<sup>43</sup>, where the N-C σ bond is formed by the donation of the N lone pair to one of the π\*<sub>C-O</sub> orbitals, the σ bond here is constructed by overlapping one *sp*<sup>2.56</sup> orbital from N (NBO orbital occupancy 1.33 *e*) and one *sp*<sup>2.61</sup> orbital from C (NBO orbital occupancy 0.65 *e*), respectively. While the π bond between the N and C atoms is formed by the donation of the N lone pair now in the *p*<sub>z</sub> orbital (NBO orbital occupancy 1.38 *e*) to that of the C atom (NBO orbital occupancy 0.13 *e*). The under populated π bond (NBO orbital occupancy 1.51 *e*) is a result of the electron withdrawing effect of the cation (Li<sup>+</sup>, NBO charge +0.965 *e*), which also facilitates its formation.

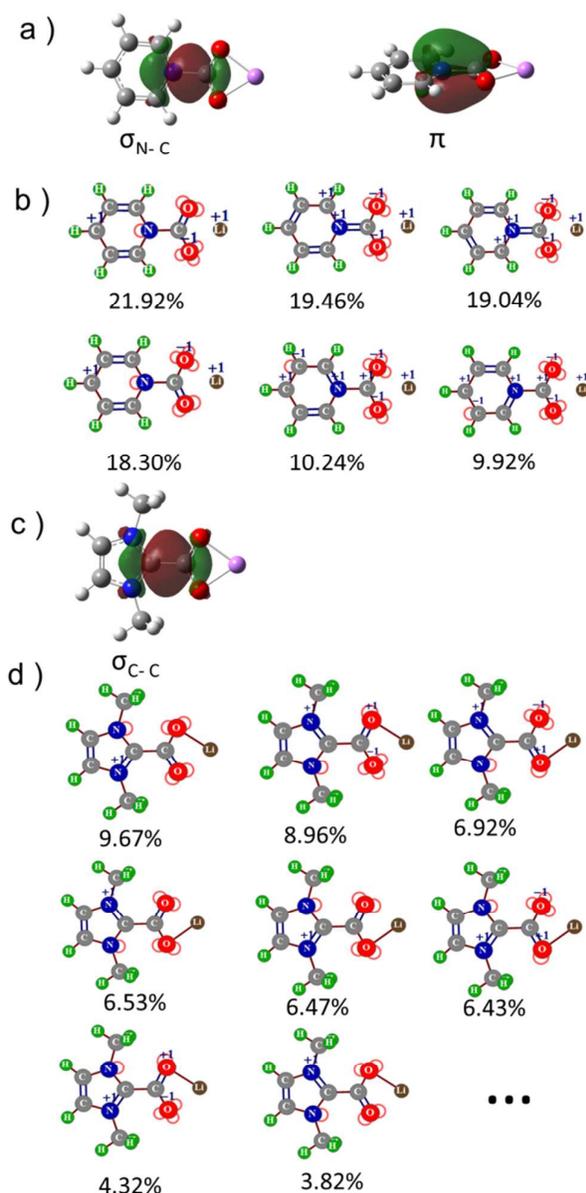


Figure 3. NBO and NRT analyses of selected (NHC-CO<sub>2</sub>-Li<sup>+</sup>) complexes. (a) and (c) NBO decomposition of the N/C-C bond of (1-/12-CO<sub>2</sub>-Li<sup>+</sup>), respectively. (b) and (d) Leading Lewis resonance structures and their abundance of the corresponding complexes. Each half circle represents a pair of electrons. Formal charges are placed above the corresponding atoms.

The NRT analyses produce a number of resonance structures (Figure 3b). The main Lewis structure contributes over 20% abundance and features a N-C single bond. The next two structures together possessing nearly 40% resonance weight present the N-C as a double bond. The following three significant structures again show the N-C as a single bond. The partial N-C double bond feature is echoed in its NBO covalent bond order of 1.4, much less than the ideal value of 2.0. Moreover, all structures exhibit various conjugations in part of

the ring, reflecting the high degree of electron delocalization within the molecule. However, no bond between Li<sup>+</sup> and CO<sub>2</sub> is observed (NBO bond order 0.0). A highly localized positive charge on Li implies less stability of the whole complex.

For comparison, we studied the interaction between carbenes (**12**) and CO<sub>2</sub> along with Li<sup>+</sup>. Like the interactions between anionic NHCs and CO<sub>2</sub> without cation, the carbene donates its lone pair to CO<sub>2</sub> by forming a C-C  $\sigma$  single bond (Figure 3c). There is no  $\pi$  bond observed between the carbene and CO<sub>2</sub>, which is further verified by the NRT structures (Figure 3d). Additionally, a single bond is formed between Li<sup>+</sup> and O(CO<sub>2</sub>) in all the leading NRT structures, which is a pure ionic bond and the bond order is 0.46. The positive charge on Li<sup>+</sup> is transferred to the ring *via* the extensive conjugation of the complex, reflecting the super strong basicity of carbenes and suggesting the complex to be more stable. The interactions between NHC anions (e.g. **10**) and CO<sub>2</sub> along with Li<sup>+</sup> are analogous to carbenes (for the NBO and NRT analyses, see the Supporting Information, SFigure 1). However, it is noted that the ionic Li-O bond order is 0.41, less than that of carbene **12**, indicating a less stable complex compared to the one with carbene.

### 3.2 Li<sup>+</sup>-assisted NHC-CO<sub>2</sub> interaction

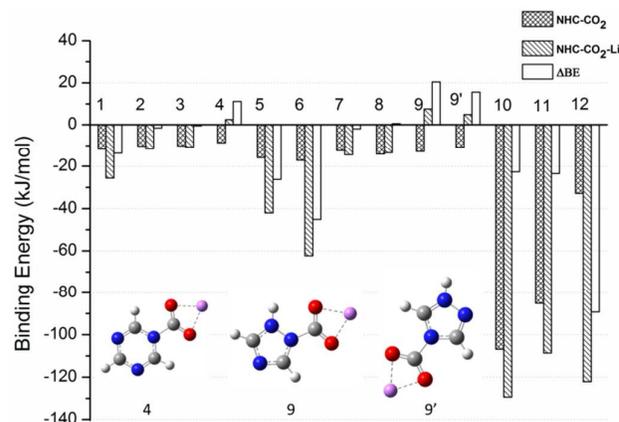


Figure 4. Binding energies between CO<sub>2</sub> and NHCs alone or with Li<sup>+</sup>. The binding energy differences are represented by unfilled bars. For **5** and **6**, the reaction sites are on the pyridine ring. Insets: the configurations of CO<sub>2</sub> bound to **4**, **9**, and **9'** assisted by Li<sup>+</sup>. Similar results are obtained using other computational methods (STable 1 in SI).

We calculated other (NHC-CO<sub>2</sub>-Li<sup>+</sup>) complexes and compared their CO<sub>2</sub> binding energies with those of the cases without Li<sup>+</sup> (Figure 4). Overall, the Li<sup>+</sup> cation presents limited influences over the binding and the difference (either increase or decrease) in binding energies is usually smaller than 25 kJ/mol, agreeing with the previous studies.<sup>4, 15, 21-26</sup> The distinctive exceptions include some neutral double-ringed structures (**5** and **6**) and carbenes (**12**). When comparing **6** to **5**, the additional electron donating group of NH<sub>2</sub> on the pyridine ring moderately enhances the binding (more in the substitution effects part). In turn, when comparing **5** to **1**, the imidazole ring may be viewed as substitutions to the pyridine

ring with electron donating nature, thus leading to a stronger interaction between **5** and CO<sub>2</sub>. The binding energy difference for carbene is far greater than that of other NHCs, which stems from the extremely strong electron donating capability of carbenes (Figure 3). It is also worth noting that for single-ringed structures with either five or six atoms, the enhancement of binding by Li<sup>+</sup> reduces gradually with the increasing number of nitrogen atoms, which are more electronegative than carbon. When three N atoms are in one ring, like **4**, **9** and **9'** (a different binding position, Figure 4, insets), the binding is actually weakened by the cation.

### 3.3 Substituent effects

We calculated the CO<sub>2</sub> binding energies of neutral NHCs (**1** and **7**) and anionic NHC (**10**) with either an electron-donating (NH<sub>2</sub>) or an electron-withdrawing (NO<sub>2</sub>) group on the ring (Figure 5, insets). Compared with the binding energy of unsubstituted structures, the interaction strengths are weakened by the electron-withdrawing group and enhanced by the electron-donating group on a similar level, similar as in the case of the neutral carbenes.<sup>44</sup> A single substitution like NH<sub>2</sub> or NO<sub>2</sub> can bring ~ 20-30 kJ/mol change in binding energy. Evidently, the stronger binding by 20.1 kJ/mol of **6** compared to **5** comes from the NH<sub>2</sub> group. Moreover the imidazole ring of **5** is equivalent to adding a NH<sub>2</sub> to **1**, whose binding energies are -42.1 and -45.5 kJ/mol for (6-CO<sub>2</sub>-Li<sup>+</sup>) and (1-NH<sub>2</sub>-CO<sub>2</sub>-Li<sup>+</sup>), respectively. The already electron rich anionic system (**10**) is more sensitive to electron-withdrawing than electron-donating.

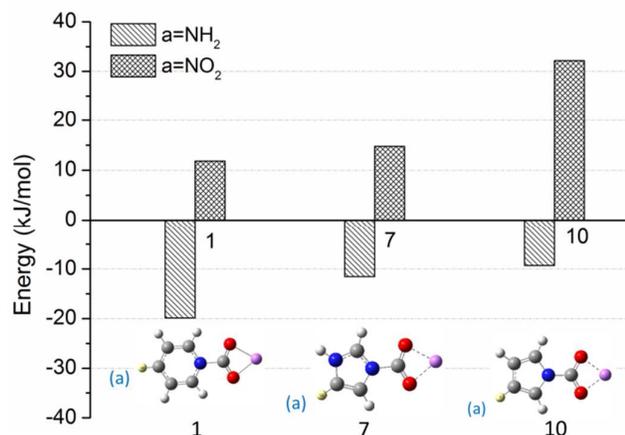


Figure 5. Substitution effects on binding energy of Li<sup>+</sup>-assisted NHC-CO<sub>2</sub> interaction. All energies are referenced to their unsubstituted parent molecules. The substitution position is labeled by letter "a".

### 3.4 Correlation between structure and binding energy

Now we take a closer look at how different core structures of NHCs affect their binding with CO<sub>2</sub> and we leave the variation of metal cations to a later part. The most important factor must be the number of N atoms in the ring. Since the reaction is in nature the base-acid adduction, the NBO nitrogen lone pair orbital energy or NBO charge on the

reacting N atom may be used as descriptors for reactivity.<sup>43</sup> We first focus on six-membered rings and explore the correlation between their Li<sup>+</sup>-assisted CO<sub>2</sub> binding energies and the NBO lone pair orbital energies of the reacting N atom (Figure 6).

The N atom lone pair orbital energy drops quickly and linearly with the increase of N atoms and the rise of binding energy (less exothermic). The decrease of the lone pair orbital energy indicates its weaker donating capability and lower reactivity as a base, which is a natural result of the increasing competition among the growing number of N atoms for the electron density. Substitutions with electron-donating or withdrawing groups fits well into this linear correlation, as the conjugated ring allows them to efficiently influence the electron density distribution. In contrast, the NBO charge on the reacting N atom exhibits much less linearity with the binding energy (SI, SFigure 2), again reflecting complex electron dynamics in a highly conjugated system during reaction. As the five-membered NHCs have a different energy reference point, the corresponding linear correlation is shown in a separate plot (SI, SFigure 3).

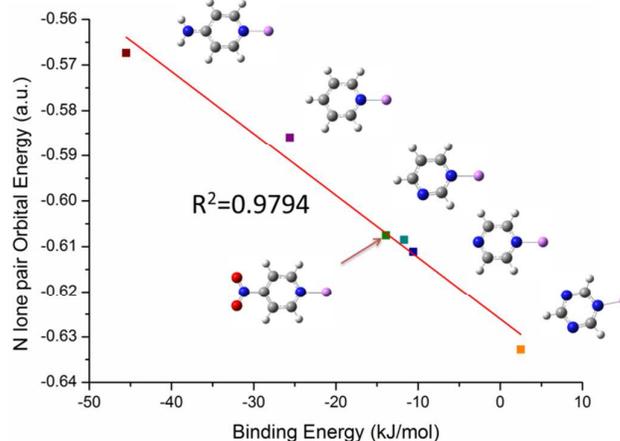


Figure 6. Binding energy of neutral six-membered NHCs and CO<sub>2</sub> with Li<sup>+</sup> versus the NBO orbital energy of the lone pair of the reacting N atom.

### 3.5 Other metal cation-assisted NHC-CO<sub>2</sub> interactions

To gain a more comprehensive view of the cation effects, we investigated the NHC-CO<sub>2</sub> interaction with other alkali and alkaline earth metals. The NHC-CO<sub>2</sub> binding energy at the presence of a divalent cation (alkaline earth metal ions) is far greater than that of monovalent ones (alkali metal ions, Figure 7). The enhanced interactions are more of an electrostatic nature, which is caused by the smaller sizes and higher charges of the divalent cations. For example, the C-N bond and ∠OCO are 1.45 Å and 122° in (1-CO<sub>2</sub>-Ca<sup>2+</sup>) compared to those of 1.51 Å and 128° in (1-CO<sub>2</sub>-Li<sup>+</sup>). The binding strength can be linearly correlated to Goldschmidt's ionic radii<sup>45</sup> for monovalent and divalent metal cations, respectively (Figure 7b). Again, for the

same cation, the higher number of N atoms in the ring reduces its stabilization effects on the binding (1-4).

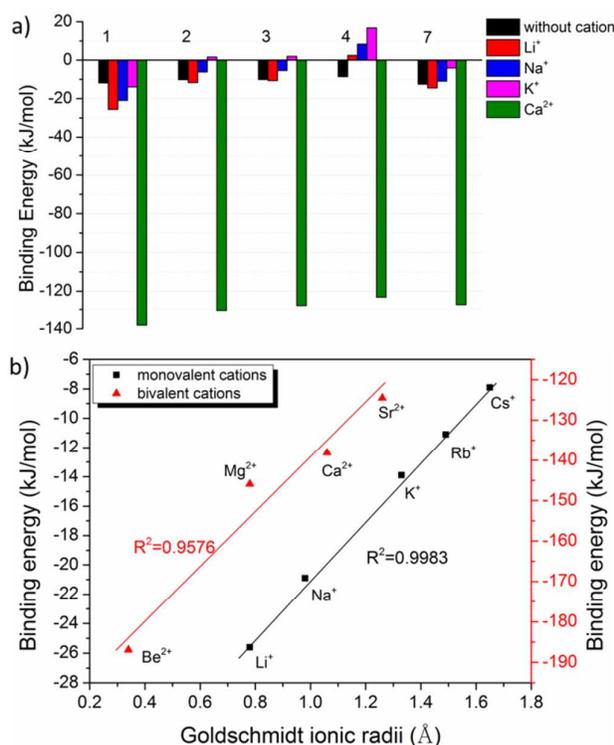


Figure 7. (a) The NHC-CO<sub>2</sub> binding energy at the presence of selected monovalent and divalent cations. (b) The correlation between the NHC-CO<sub>2</sub> binding energy of pyridine (1) and Goldschmidt's ionic radii.

### 3.6 Li<sup>+</sup>-assisted CO<sub>2</sub> capture by dicarbenes

Since the binding between carbene and CO<sub>2</sub> is very sensitive to cations, we now revisit the case of CO<sub>2</sub> capture by anionic NHC dicarbenes, where only one CO<sub>2</sub> binding occurred at C4 and the second expected carboxylation at the C2 carbene center was missing.<sup>13</sup> Herein, we try to explain these observations by incorporating the effects of metal cations (Figure 8). The energetics of the reaction between the dicarbene and CO<sub>2</sub> without any cation is shown in the yellow rectangle. The CO<sub>2</sub> binding energies at C2 and C4 are -136.8 and -178.7 kJ/mol, respectively, suggesting C4 as the first favored binding site, agreeing with the previous theoretical and experimental results.<sup>13</sup> Then a following CO<sub>2</sub> absorption at C2 has a binding energy of -85.2 kJ/mol and a bent  $\angle\text{OCO}$  of 134°, both indicating a chemical bond. However, the second CO<sub>2</sub> absorption was not observed.

The blue area presents the reaction energetics with the assistance of the stoichiometric 1:1 Li<sup>+</sup> cation. At C4, the Li<sup>+</sup> binding energy is -650.4 kJ/mol, 50 kJ/mol lower than that at C2, indicating C4 as the preferred cation coordination position. Then, binding energies of CO<sub>2</sub> at C4 with the Li<sup>+</sup> and at the empty C2 are -208.8 and -63.3 kJ/mol, respectively, clearly favouring the former position. After that, the second CO<sub>2</sub> binding at C2 only has a very weak binding energy of -26.1 kJ/mol, whose absorption is below 0.01 mol CO<sub>2</sub>/mol

dicarbene at ambient conditions (0.1 MPa and room temperature)<sup>43</sup>, virtually undetectable in experiment.<sup>13</sup> However, by introducing Li salts into the system, an extra Li<sup>+</sup> can bind to the dicarbene at C2 very exothermically (-276.9 kJ/mol, in the champagne pink area) and the second CO<sub>2</sub> binding energy at this position is now lowered to -98.5 kJ/mol, which should be well observed in experiment.

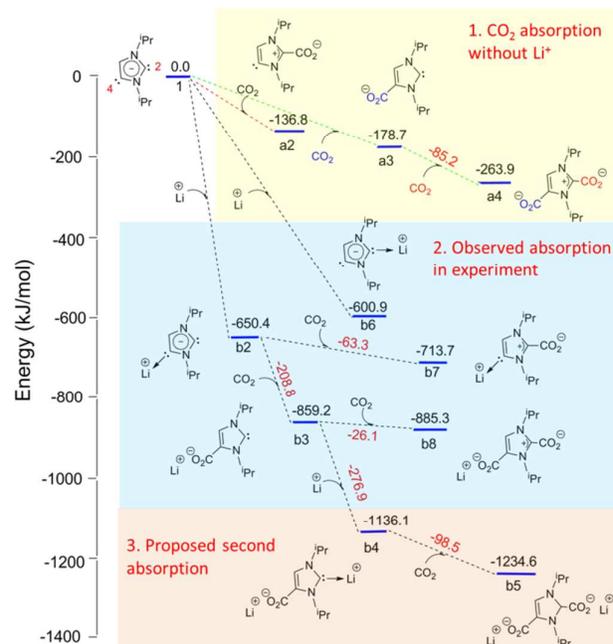


Figure 8. Reaction energetics of the dicarbene and CO<sub>2</sub> with or without Li<sup>+</sup>. <sup>i</sup>Pr is the isopropyl group. Red numbers label the energy change in two adjacent steps.

## 4. Conclusions

Using DFT calculations, we have systematically studied the cation effects on the interactions between a group of highly conjugated N-containing heterocycles (NHCs) including neutral, anionic, and carbenoid species and CO<sub>2</sub>. A few key observations are summarized below.

- (1) The cation-assisted NHC-CO<sub>2</sub> reaction goes through a more complex mechanism compared with the cases without cation. CO<sub>2</sub> inserts into the NHC-cation complex by forming a bidentate coordination of the two O atoms to the metal ion and a C(CO<sub>2</sub>)-N(NHC) double bond. The C-N bond is different from the physical interactions between neutral NHCs and CO<sub>2</sub> and also unlike the single bond between anionic or carbenoid NHCs and CO<sub>2</sub>.
- (2) A single monovalent cation shows moderate to small effects on the binding energy (< 25 kJ/mol enhancement or reduction) for most NHCs (neutral and anionic), but it promotes the binding between carbenes and CO<sub>2</sub> substantially by over 60 kJ/mol. This is due to the extremely high basicity of carbene, which makes the charge transfer from the NHC ring to the cation and eventually stabilizes the complex.

(3) Electron-donating substituents enhance the NHC-CO<sub>2</sub> binding strength, while the electron-withdrawing groups reduce it.

(4) The divalent cations have a much larger effect on promoting the binding of NHCs to CO<sub>2</sub> by over 100 kJ/mol. Very recently, for acyclic amines and CO<sub>2</sub>, similar strong influences by divalent cations have been observed and utilized to achieve high CO<sub>2</sub> uptake in diamine-appended MOFs (M = Mg, Mn, Fe, Co, Zn).<sup>46</sup>

(5) The cation enhancement of the NHC-CO<sub>2</sub> binding linearly drops with the increasing radii for both monovalent and divalent cations.

(6) For the same cation, the NHC-CO<sub>2</sub> binding energy can be linearly correlated with the nitrogen lone pair NBO energy of the reacting N atom, reflecting the base-acid reaction nature.

(7) The Li<sup>+</sup> assisted CO<sub>2</sub> absorption model successfully explains the single carboxylation at the abnormal carbene position (C4) of anionic NHC dicarbenes observed in experiment. We propose by adding charged species (e.g. Li salts), the second carboxylation at the normal carbene position (C2) can take place.

In summary, our study provides comprehensive and complementary information of the cation effects on NHC-based CO<sub>2</sub> capture, which should be very useful for design the next generation CO<sub>2</sub> capture materials.

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