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Ab initio study on anomalous structures of anionic [(N-heterocycle)-CO₂]⁻ complexes

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Several unusual anionic complexes between carbon dioxide (CO₂) and N-heterocycles (NHCs) possessing a significantly positive adiabatic electron affinity over 0.7 eV were studied by density functional theory calculations (UB3LYP/6-311++g(d,p)). Unlike all previously reported [NHC-CO₂]⁻ anions with a coplanar structure that ensures full delocalization of the negative charge through extended π -conjugation, this new class of anionic [NHC-CO₂]⁻ complexes has a strongly non-coplanar geometry and no π -bond character between CO₂ and NHC. Despite the fundamental differences in chemical bonding between all prior cases and the new class of [NHC-CO₂]⁻ complexes, we found that the CO₂ moiety in the latter still has a large negative charge (~ 0.4 e) and a strongly bent geometry (O-C-O angle of $\sim 140^\circ$) just like in the former. This seemingly anomalous case was explained by a simple model based on the torsional steric effect and the electron affinities of the constituent moieties. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4979576>]

I. INTRODUCTION

CO₂ is one of the most quintessential triatomic molecules with exceptional stability. Adding an electron to it is not an energetically favored process, signified by a negative adiabatic electron affinity (AEA) of $-0.60(\pm 0.20)$ eV.¹⁻³ Therefore, a stable form of CO₂⁻ does not exist in the gas phase, and only a metastable form with a predicted geometry of bent structure has been detected with a lifetime of ~ 100 μ s.¹ The interaction between CO₂ and neutral molecules is weak and they can form only a weakly bound van der Waals (vdW) complex at low temperatures. Electron attachment to such CO₂-containing clusters can often result in a stabilized CO₂⁻ anion or a new anion core such as (C₂O₄)⁻ produced from [(CO₂)_n(ROH)] (R = H, CH₃) neutral clusters.⁴⁻⁷

If, on the other hand, the electron attachment is done on a neutral cluster between CO₂ and a certain N-heterocycle (NHC) molecule such as pyridine (Py), the newly introduced negative charge brings the two moieties together to form a chemical bond that results in a totally new anionic core [Py-CO₂]⁻,⁸ with a theoretically predicted covalent C-N bond length and a considerable negative charge (≥ 0.5 e) on the CO₂ moiety. The presence of the covalent C-N bond in [Py-CO₂]⁻ was later verified by Kamrath *et al.* using vibrational predissociation spectroscopy.⁹

In this covalently bound anion core, the two moieties were expected to be nearly coplanar (with the dihedral angle between the two molecular planes nearly 0°) to maximize the π -conjugation for the most stable structure. In the case of [Py-CO₂]⁻, the calculated torsional barrier around the central C-N

bond (680 meV) comes from the energy difference between the orthogonal and coplanar structures and is an order of magnitude larger than that of the neutral [Py \cdots CO₂] complex (53 meV).⁸

Because both CO₂ and Py have a negative AEA,^{1-3,10} the fact that their complex accepts an electron was initially very striking. The only chemically sound model would be to accept that the extended π -conjugated system that forms over the entirety of the complex allows the accommodation of the extra electron. One may be reminded that the π system of benzene has a large negative AEA (-1.12 eV), but becomes less negative (-0.19 eV) in naphthalene, and ultimately becomes even slightly positive ($+0.53$ eV) in anthracene, as the π -conjugation becomes more extended in space.

Since our first discovery of [Py-CO₂]⁻ in 2000, all subsequent studies on [NHC-CO₂]⁻ with NHCs of pyrazine, pyridazine, pyrimidine and even NHCs with a positive electron affinity such as triazine (AEA = 0.03 eV)¹¹ or quinoline (Qn, AEA = 0.16 eV)¹² have found unequivocally coplanar structures as their relaxed geometry.^{13,14}

In the condensed phase, even a neutral complex between a neutral molecule and CO₂ could possess an intermolecular bond with a significant covalent bond character. Schossler and Regitz synthesized neutral complexes between N-heterocyclic carbenes (NHCars) and CO₂ ([NHCars-CO₂]), with a covalent bond between the two moieties.¹⁵ It was found by X-ray crystallography and *ab initio* studies that the CO₂ moiety has a considerable negative charge and the O-C-O bond is strongly bent in the [NHCars-CO₂] complex.¹⁶⁻¹⁹ Even though carbene is neutral, its high-lying highest occupied molecular orbital (HOMO) allows NHCars to donate an electron to the lowest unoccupied molecular orbital (LUMO) of CO₂. The unique properties of the strongly bound [NHCars-CO₂] complex have

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been applied to CO₂ capture and CO₂ reduction.^{20–24} Meanwhile, Van Ausdall *et al.* found by X-ray crystallography that both orthogonal and coplanar geometries are possible in the [NHC_{ar}-CO₂]⁻ complex, depending upon the steric bulkiness of the substituent imidazolyliene derivatives.¹⁸

In this paper, we report a novel case of anionic [NHC-CO₂]⁻ complexes that display non-coplanar geometries, in contrast to all known previous examples. A simple model was proposed to account for the seemingly anomalous structures that were based on the torsional steric effect and the electron affinities of the constituent moieties.

II. COMPUTATIONAL METHODS

All optimized structures presented in this study were obtained using analytical gradients with full geometry optimization at the level of unrestricted B3LYP/6-311++g(d,p) without any constraint. In this optimization, we checked for the absence of imaginary vibrational frequencies to verify that the structures obtained were stable ones. The B3LYP functional was selected because it has been widely used in various systems including organic molecules,^{2,25,26} while the 6-311++g(d,p) basis set was chosen because its diffuse functions were deemed appropriate for the calculation of anionic molecules.⁹ At this level of theory, the values of AEA and vertical detachment energy (VDE) were calculated by the following equations without zero point vibrational energy (ZPE) correction:

$$\text{AEA}(X) = E(X) - E(X^-),$$

$$\text{VDE}(X^-) = E_a(X) - E(X^-),$$

where $E(X)$ and $E_a(X)$ stand for the calculated absolute energy of species X in its relaxed neutral geometry and in its optimized anion geometry, respectively.²⁷ We obtained reliable theoretical estimates for several NHCs and [NHC-CO₂]⁻ complexes, which were verified to be in good agreement with previously reported photoelectron spectroscopy results as shown in Table I. All of the partial negative charges obtained in this study were determined using the natural bond orbital (NBO) analysis.^{28,29}

We also carried out density functional theory (DFT) calculations at the level of unrestricted ω B97XD/aug-cc-pVTZ as a double check to determine the structure for the anionic complexes of a bicyclic system, following the earlier study by

TABLE I. Calculated (UB3LYP/6-311++g(d,p)) and experimental values of adiabatic electron affinity (AEA) and vertical detachment energy (VDE) of pyridine (Py), quinoline (Qn), and their anionic [NHC-CO₂]⁻ complexes.

	AEA _{cal} (eV)	AEA _{exp} (eV)	VDE _{cal} (eV)	VDE _{exp} (eV)
Py	-0.52	-0.48 ^a		
[Py-CO ₂] ⁻			1.50	1.2 ^b
Qn	0.19	0.16 ^c		
[Qn-CO ₂] ⁻			1.80 ^d	1.8 ^d

^aReference 10.

^bReference 8.

^cReference 12.

^dReference 14.

the Bowen group for Qn and [Qn-CO₂]⁻.^{12,14} All of the calculations in this study were performed using the Gaussian 09 software package.³⁰

III. RESULTS AND DISCUSSION

A. Orthogonal structures of [NHC-CO₂]⁻ and the origin of the anomaly

The NHC molecules of interest we chose in this study were 6H-pyrrolo[2,3-c]pyridazine (NHC1), pyrido[2,3-c]pyridazine (NHC2), and 3H-pyrazolo[3,4-b]pyridine (NHC3), which all share a common structural motif (-N¹-N²-C-N³-) spanning over both rings of the purine-like bicyclic 6- and 5-membered rings or Qn-like bicyclic 6-membered rings. For comparison with these species, we also employed 3,4-dihydropyrrolo[2,3-c]pyrazole (NHC4) that shares the same (-N¹-N²-C-N³-) motif but on a bicyclic 5-membered ring structure.

Figure 1 shows the structures of [NHC_x-CO₂]⁻ that forms a covalent bond between CO₂ and N^y of NHC. Each species is distinct in their NHC identity (by x) and the site of the covalent bond (by y) and denoted as [NHC_x-CO₂]⁻_{N^y} ($x = 1-4$, $y = 1-3$). We learn from the figure that all [NHC_x-CO₂]⁻ species show a coplanar structure when the C-N covalent bond involves N¹ or N³ of NHC or when NHC is the bicyclic 5-membered ring ($x = 4$). On the other hand, when the CO₂ moiety binds to N² of NHC_x ($x = 1, 2, 3$), a highly non-coplanar

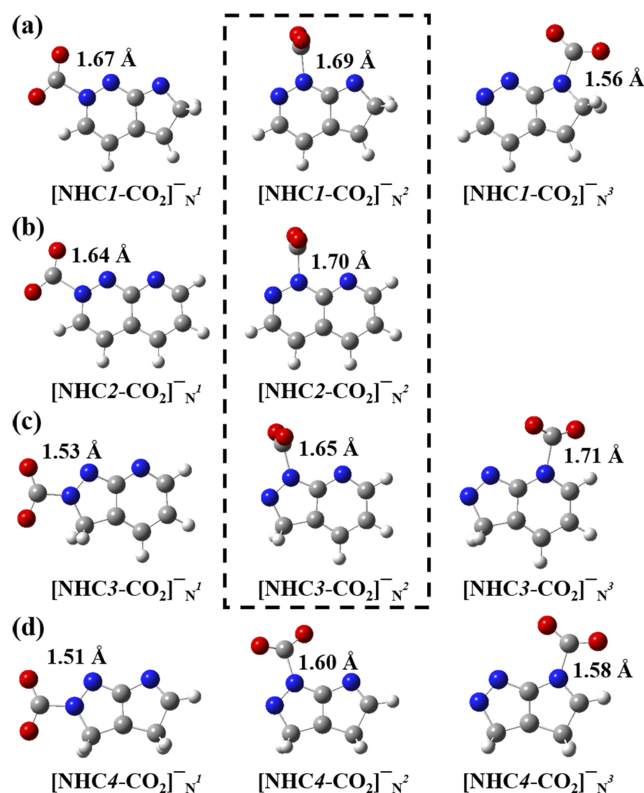


FIG. 1. Relaxed molecular structures obtained by DFT calculations (UB3LYP/6-311++g(d,p)). The C-N bond length is shown for anionic complexes (a) [NHC1-CO₂]⁻_{N^y} ($y = 1-3$), (b) [NHC2-CO₂]⁻_{N^y} ($y = 1, 2$), (c) [NHC3-CO₂]⁻_{N^y} ($y = 1-3$), and (d) [NHC4-CO₂]⁻_{N^y} ($y = 1-3$). The dashed box is used to emphasize the uniquely different dihedral angle of [NHC_x-CO₂]⁻_{N²} ($x = 1-3$) from the rest of the species.

structure is obtained, with the dihedral angle between the CO₂ and NHC planes nearly orthogonal. Calculations at different levels of theory (UB3LYP/6-311++g(d,p) vs. UωB97XD/aug-cc-pVTZ) yielded nearly the same dihedral angle (Table II). It is also to be noted that NHC x ($x = 1-3$) have much larger electron affinities than previously studied NHCs such as azabenzenes or Qn.

Although the three [NHC x -CO₂]⁻_{N ^{x}} ($x = 1-3$) complexes exhibit the anomalous non-coplanar structures, their strongly bent CO₂ moiety (with the O-C-O angle of 139°-141°) is a sign that they are still significantly negatively charged, just as in the more conventional coplanar complexes. In fact, our charge analysis shows that the CO₂ moiety in these complexes have a considerable anionic charge (0.42-0.45 e) (Table III). In contrast to the coplanar anionic complexes that endow the anionic charge to CO₂ via extended π -conjugation, it appears that a certain degree of charge transfer occurs from NHC x ⁻ ($x = 1-3$) to CO₂, which further stabilizes the [NHC x -CO₂]⁻_{N ^{x}} ($x = 1-3$) complexes. The bond dissociation energy (BDE) of [NHC-CO₂]⁻ complexes that dissociate into NHC⁻ and CO₂ can be obtained by the following equation without ZPE correction:

$$\text{BDE}([\text{NHC} - \text{CO}_2]^-) = \text{E}(\text{NHC}^-) + \text{E}(\text{CO}_2) - \text{E}([\text{NHC} - \text{CO}_2]^-),$$

where E(X) stands for the calculated absolute energy of species X in its relaxed geometry. The results are summarized in Table III, showing indeed a significant value of the BDE (0.25 eV).

The orthogonal structures have already been discovered in the neutral [NHCar-CO₂] complex as mentioned earlier, but the formation of similarly structured anionic [NHC-CO₂]⁻ complexes is considered still interesting. Unlike Py or Qn, singlet carbene of imidazolylidene derivatives commonly used in [NHCar-CO₂] is known to intrinsically possess a negligibly

TABLE II. Calculated values of dihedral angle and electron binding energies of [NHC x -CO₂]⁻_{N ^{y}} and NHC x ($x = 1-4$, $y = 1-3$).

	Dihedral angle 1 ^a (deg)	Dihedral angle 2 ^{a,b} (deg)	AEA of NHC (eV)	VDE of NHC ⁻ (eV)	VDE of [NHC-CO ₂] ⁻ (eV)
[NHC1-CO ₂] ⁻ _{N¹}	0.2	...	1.7	1.9	3.2
[NHC1-CO ₂] ⁻ _{N²}	89.1	89.2	3.1
[NHC1-CO ₂] ⁻ _{N³}	0.4	3.4
[NHC2-CO ₂] ⁻ _{N¹}	0.0	...	1.1	1.3	2.6
[NHC2-CO ₂] ⁻ _{N²}	89.5	89.3	2.4
[NHC3-CO ₂] ⁻ _{N¹}	28.1	...	0.8	1.1	3.0
[NHC3-CO ₂] ⁻ _{N²}	93.3	112.4	2.5
[NHC3-CO ₂] ⁻ _{N³}	21.3	2.2
[NHC4-CO ₂] ⁻ _{N¹}	0.0	...	0.5	0.8	2.8
[NHC4-CO ₂] ⁻ _{N²}	23.6	9.9	2.4
[NHC4-CO ₂] ⁻ _{N³}	0.0	2.1

^aDihedral angle is the angle between the molecular planes of CO₂ and NHC x in the anionic complex of optimized geometry.

^bExcept for dihedral angle 2 obtained at the level of UωB97XD/aug-cc-pVTZ, every quantity was calculated by UB3LYP/6-311++g(d,p).

TABLE III. Results of DFT calculations on [NHC x -CO₂]⁻_{N ^{y}} ($x = 1-3$, $y = 1-3$) (UB3LYP/6-311++g(d,p)).

	O-C-O angle (deg)	NBO charge of CO ₂	BDE (eV)
[NHC1-CO ₂] ⁻ _{N¹}	138.7	0.48 e	0.48
[NHC1-CO ₂] ⁻ _{N²}	140.2	0.43 e	0.25
[NHC1-CO ₂] ⁻ _{N³}	135.1	0.55 e	0.41
[NHC2-CO ₂] ⁻ _{N¹}	138.0	0.50 e	0.49
[NHC2-CO ₂] ⁻ _{N²}	140.7	0.42 e	0.25
[NHC3-CO ₂] ⁻ _{N¹}	134.9	0.58 e	0.80
[NHC3-CO ₂] ⁻ _{N²}	138.8	0.45 e	0.25
[NHC3-CO ₂] ⁻ _{N³}	140.3	0.43 e	0.15

weak overlap between its LUMO including the p-orbital at the carbene center and other systems like the filled d-orbitals of a metal.³¹⁻³⁵ Although strong destabilization against its coplanar geometry by sterically bulky substituents of carbene was proposed as a major driving force for the orthogonal geometry in the [NHCar-CO₂] complexes,¹⁸ it cannot be ignored that the negligible π -bond character in its intermolecular bond allows CO₂ to internally rotate around the molecular plane of carbene and form an orthogonal geometry. On the other hand, the orthogonal structures in the anionic [NHC-CO₂]⁻ complexes appear highly anomalous because all of the energy minimum structures of [NHC-CO₂]⁻ previously reported show an unequivocally coplanar geometry. It is totally unexpected that an orthogonal geometry without a π -bond character in the C-N bond was found in the [NHC-CO₂]⁻ complex, since the delocalization of an extra negative charge through the entire molecular frame by an extended π -conjugated system has been regarded to be essential for stabilizing the anionic core of [NHC-CO₂]⁻.

To understand what drives the stabilization of the orthogonal [NHC-CO₂]⁻ complexes, we investigated what makes [NHC x -CO₂]⁻_{N ^{x}} ($x = 1-3$) in the coplanar geometry unstable. First, the simple steric factor may play a role. In [NHC x -CO₂]⁻_{N ^{x}} ($x = 1-3$) with a coplanar geometry, the C-N² bond would have to be considerably extended to avoid a significant overlap not only between the lone pair (LP) electrons of O (denoted by O_{LP}) of the CO₂ moiety and (N¹)_{LP} of the NHC moiety but also between O_{LP} of CO₂ and (N³)_{LP} of NHC. Sufficient destabilization of the coplanar structure would result in an orthogonal geometry as the minimum-energy structure. Indeed, the C-N² bond is longer in the intended coplanar structure of [NHC3-CO₂]⁻_{N²} (1.68 Å) than that in the orthogonal structure (1.65 Å), where the coplanar structure was obtained using optimization by fixing the dihedral angle at 0°. It is also to be noted that although NHC4 shares the same local structural motif (-N¹-N²-C-N³-) with NHC x ($x = 1-3$), it has no isomeric form of the orthogonal structure in its relaxed geometry, unlike [NHC x -CO₂]⁻_{N ^{x}} ($x = 1-3$). Since a 5-membered ring has smaller bond angles than a 6-membered ring, it would lead to a slight decrease in steric hindrance between CO₂ and NHC in the coplanar geometry of [NHC4-CO₂]⁻_{N²}. This is supported by the dihedral angle-dependent torsional barrier in [NHC x -CO₂]⁻_{N ^{x}} ($x = 3, 4$) (67 meV for $x = 3$, 59 meV for $x = 4$) as shown in Fig. 2. On the contrary, in the [NHC x -CO₂]⁻_{N ^{x}}

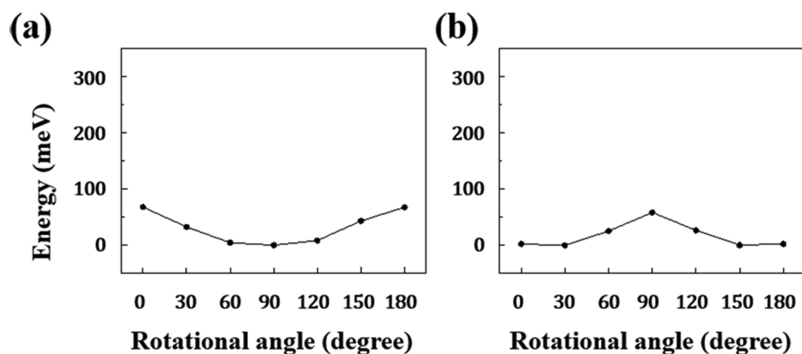


FIG. 2. Rotational barrier as a function of the dihedral angle. Internal rotation barrier was shown for (a) anionic $[\text{NHC3-CO}_2]^-_{\text{N}^2}$ complex with orthogonal geometry (90°) as its energy minimum structure and (b) anionic $[\text{NHC4-CO}_2]^-_{\text{N}^2}$ complex with coplanar geometry (0°) as its energy minimum structure.

($x = 1-3$) anionic complex, a smaller degree of steric destabilization toward the coplanar structure is expected than that in $[\text{NHC}x-\text{CO}_2]^-_{\text{N}^2}$ ($x = 1-3$) to reduce the electron cloud overlap between only one O_{LP} of the CO_2 moiety and $(\text{N}^2)_{\text{LP}}$ of NHC, leading to a coplanar geometry as its relaxed structure and a rather large torsional barrier (Fig. 3).

B. Additional structure-determining factor for anionic $[\text{NHC-CO}_2]^-$ arising from electronic stabilization

$\text{NHC}x$ ($x = 1-3$) that form an orthogonal geometry with CO_2 in the anion are also unique in their electronic properties. Their large positive AEA (over 0.7 eV) may result from the strong local electrostatic charge polarization by the three adjacent N atoms that create a sufficiently electron-deficient region to accommodate an additional electron.¹¹ The relatively large ring size of these bicyclic compounds may also facilitate the delocalization of the extra negative charge. Based on these electronic properties, we suggest that there may be another factor that favors the anomalous orthogonal geometry.

First, in order to understand the dependence of the minimum energy structures of $[\text{NHC-CO}_2]^-$, whether coplanar or not, upon its electronic features, DFT calculations were carried out at the level of UB3LYP/6-311++g(d,p) for the selected anionic complexes in which steric effects could be ignored. More specifically, the relationship between the electron affinity of NHCs and the torsional barrier of the CO_2

moiety around the C-N bond in $[\text{NHC-CO}_2]^-$ was investigated for such simple and well-known molecules as Py and Py derivatives including pyrimidine (Pmd), pyrazine (Pz), 1,3,5-triazine (s-Tz), 1,2,4-triazine (Tz), and 1,2,3,5-tetrazine (Tez). As shown in Fig. 4, they appear to possess similarly insignificant steric effects in their optimized geometry of $[\text{NHC-CO}_2]^-$. Since there is no experimental information about the internal rotation of $[\text{NHC-CO}_2]^-$ in the literature, to confirm the calculation method we first performed a calculation on the rotational barrier by internally rotating the methyl moiety around the plane of benzene in a benzylic radical, which is an analogous system to $[\text{NHC-CO}_2]^-$ in that the internal rotation leads to the dissociation of the π -bond in the rotational axis for both $[\text{NHC-CO}_2]^-$ and benzylic radical. The rotational barrier of the benzylic radical was calculated to be 0.61 eV (14.0 kcal/mol), which is in good agreement with the experimental value of $13.4(\pm 1)$ kcal/mol obtained by electron spin resonance.³⁶

For the above six pyridine derivatives, we found certain generic trends for the partial charge on NHC, the O-C-O bond angle, the C-N bond length, and the rotational barrier as a function of AEA (Fig. 5). The trends look reasonable and self-consistent, as NHC with a larger electron affinity would prefer the extra negative charge more localized to the NHC moiety than delocalized over the entire molecular frame (Fig. 5(a)), leading to a less strongly bent CO_2 because of a smaller charge on it (Fig. 5(b)) and a weaker and longer C-N bond (Fig. 5(c)), which facilitates the internal rotation of the CO_2 moiety

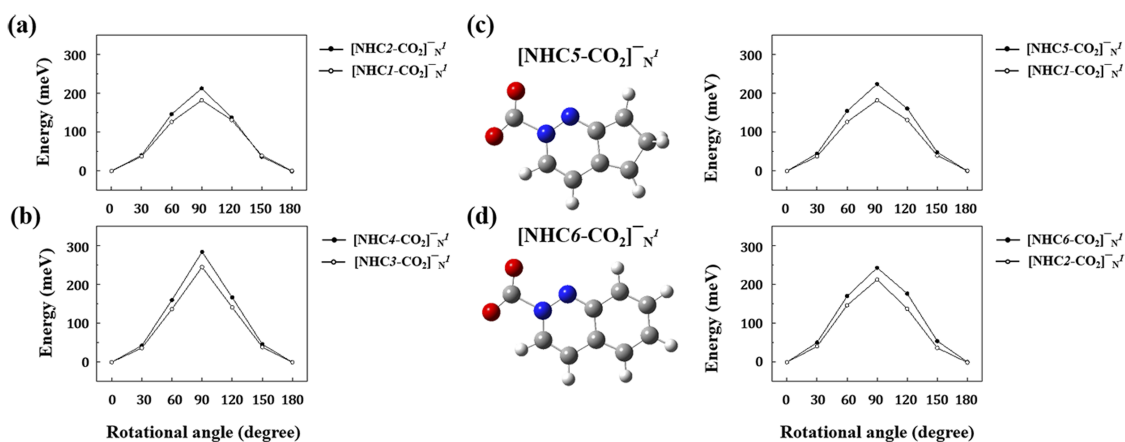


FIG. 3. Rotational barrier as a function of the dihedral angle. The barrier for internal rotation of (a) $[\text{NHC1-CO}_2]^-_{\text{N}^1}$ and $[\text{NHC2-CO}_2]^-_{\text{N}^1}$, (b) $[\text{NHC3-CO}_2]^-_{\text{N}^1}$ and $[\text{NHC4-CO}_2]^-_{\text{N}^1}$, (c) $[\text{NHC1-CO}_2]^-_{\text{N}^1}$ and $[\text{NHC5-CO}_2]^-_{\text{N}^1}$, and (d) $[\text{NHC2-CO}_2]^-_{\text{N}^1}$ and $[\text{NHC6-CO}_2]^-_{\text{N}^1}$, where each pair with a similar local structure around CO_2 but different overall electronic characteristics, was chosen for comparison.

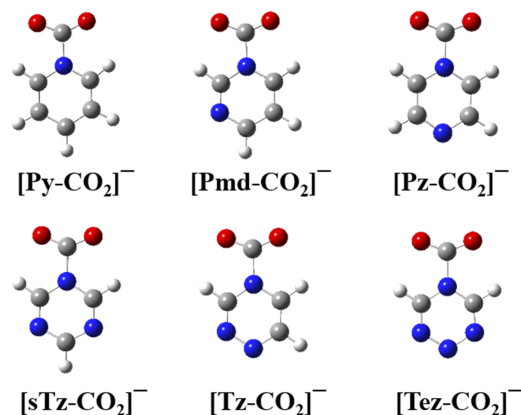


FIG. 4. Molecular structures obtained by DFT calculations (UB3LYP/6-311+g(d,p)) for Py and its derivatives (pyrimidine (Pmd), pyrazine (Pz), triazine (Tz), tetrazine (Tez)) that were used to consider the relation between the electron affinity of NHC and the rotational barrier in its anionic complex with CO₂.

around the NHC molecular plane with a lower torsional barrier (Fig. 5(d)).

In order to examine whether such an electronic effect could be applied to NHCs in bicyclic species as well, we investigated the rotational barrier of the [NHC x -CO₂]⁻ ($x = 1-4$) complexes in which similar steric repulsions are expected. As presented in Figs. 3(a) and 3(b), the comparison between [NHC1-CO₂]⁻ and [NHC2-CO₂]⁻ with a 6-membered ring bonded to CO₂ and that between [NHC3-CO₂]⁻ and [NHC4-CO₂]⁻ where a 5-membered ring has an intermolecular bond with CO₂ show that, just like in the above monocyclic Py derivative systems, the increase in the AEA of NHC leads to the reduced stability of the coplanar geometry and the resultant decrease of the rotational barrier in the anionic complexes (see also Table II). In addition, we further examined the rotational barrier as a function of the dihedral angle for 6H-cyclopenta[c]pyridazine (NHC5), which is analogous to NHC1 but has a smaller AEA (1.3 eV) than NHC1 (AEA = 1.7 eV), and cinnoline (NHC6), which is analogous to NHC2 but has a smaller AEA (0.7 eV) than NHC2 (AEA = 1.1 eV). The relaxed geometry of [NHC5-CO₂]⁻ and [NHC6-CO₂]⁻ is shown on the left side of Figs. 3(c)

and 3(d). The similar correlations as seen in Figs. 3(a) and 3(b) are obtained in the comparison of the rotational barriers between [NHC1-CO₂]⁻ and [NHC5-CO₂]⁻ as well as between [NHC2-CO₂]⁻ and [NHC6-CO₂]⁻ (Figs. 3(c) and 3(d)).

Since the rotational barrier in the anionic complexes is changed not as much as the AEA of NHC (Figs. 3 and 5 showing the change in the rotational barrier over the range of ~ 0.1 eV while the change in the AEA being over the range of ~ 1 eV), the steric effect should be the major factor that determines the minimum energy structure of [NHC x -CO₂]⁻ ($x = 1-3$) to be the orthogonal geometry. However, we should keep in mind that the decrease in electronic stabilization toward its coplanar geometry caused by a large positive AEA of NHC x ($x = 1-3$) allows the CO₂ moiety to rotate internally around the C-N bond more readily. Furthermore, a dramatic conversion of optimized geometry may be possible in an anionic complex with a small rotational barrier. For example, the small barrier over the orthogonal geometry of the [NHC4-CO₂]⁻ complex (59 meV) would decrease even more in an anionic complex containing NHC with a larger electron affinity such as NHC3. Because the gap between the AEA of NHC3 (0.8 eV) and NHC4 (0.5 eV) is not very much, the difference in their relaxed geometries is mainly caused by the steric effect. But a significant increase in the AEA by introducing more N atoms or substituents to the molecular frame of NHC4 may even lead to the change in the minimum energy structure to an orthogonal geometry, although such an [NHC-CO₂]⁻ complex has similar steric repulsions to those of [NHC4-CO₂]⁻.

Meanwhile, several NHCs with imidazole in their molecular frame have been applied to CO₂ capture and reduction in zeolitic imidazolate frameworks (ZIFs) or ionic liquids.³⁷⁻⁴⁰ Generally, in ZIFs the active sites for CO₂ capture or reduction are only metal ions, but organic frames could also be used for the active site by introducing bicyclic systems including imidazole or proper functionals.³⁷⁻³⁹ In these cases, most of the organic frames previously studied do not include adjacent nitrogen atoms.^{37,38} Additionally, NHCs with more than three nitrogen atoms were rarely reported in ionic liquids for CO₂ uptake.^{41,42} Based on our work, however, the interaction between CO₂ and NHC containing the local structural

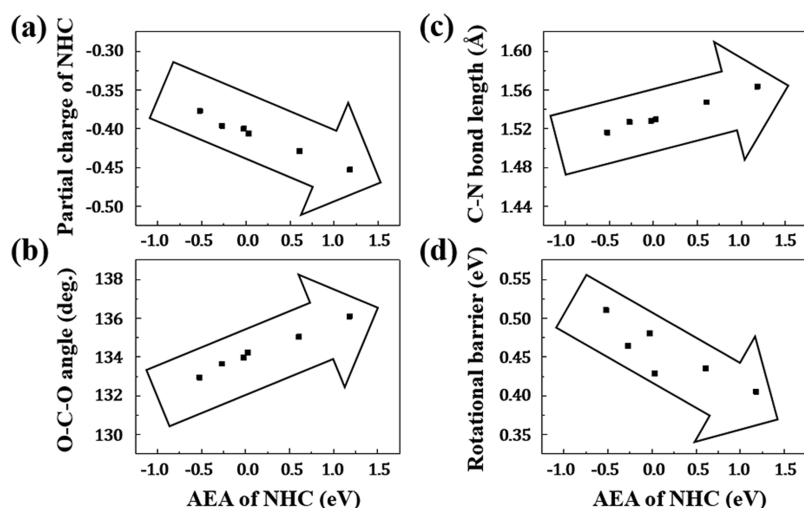


FIG. 5. Relation between the AEA of NHC and (a) the partial negative charge of the NHC moiety obtained by the NBO analysis, (b) the O-C-O angle of the CO₂ moiety, (c) the intermolecular C-N bond length, and (d) the rotational barrier in the anionic complex [NHC-CO₂]⁻ (NHC = Py, Pmd, Pz, s-Tz, Tz, and Tez). General tendency of their relation is shown by an arrow in each graph.

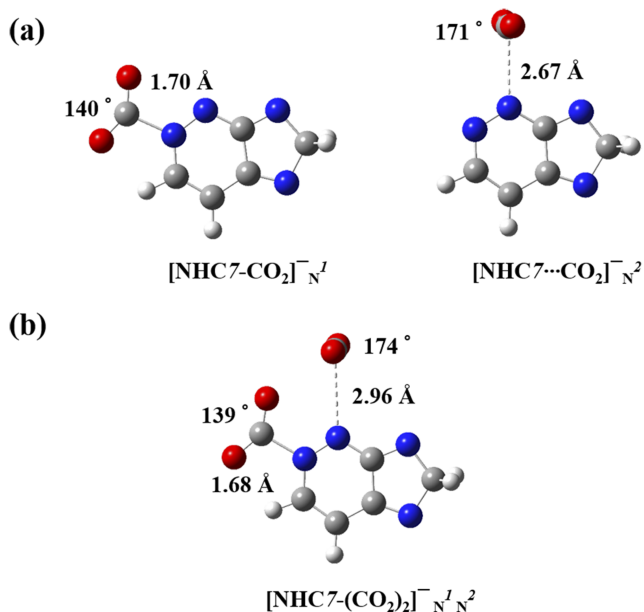


FIG. 6. Molecular structures obtained by DFT calculations (UB3LYP/6-311++g(d,p)) for (a) $[\text{NHC7-CO}_2]^- \text{N}^1$ with a covalent bond character in the C–N bond and $[\text{NHC7}\cdots\text{CO}_2]^- \text{N}^2$ with an ion-molecule interaction and (b) $[\text{NHC7-(CO}_2)_2]^- \text{N}^1 \text{N}^2$. The intermolecular C–N bond length and the O–C–O angle are shown for each complex.

motif of $-\text{N}^1-\text{N}^2-\text{C}-\text{N}^3-$ is expected to be applicable toward increasing the number of possible active sites for CO_2 capture. Figure 6 presents the relaxed geometry of complexes between CO_2 and NHC7 analogs with 4 nitrogen atoms (8H-imidazo[4,5-c]pyridazine, NHC7). NHC7 containing the imidazole ring is suggested as an active material for CO_2 capture in ZIFs. Two of the nitrogens in NHC7 are shown to interact with CO_2 through a covalent bond or longer intermolecular bond (2.67 Å), while the other two nitrogen atoms in the imidazole ring coordinate to the metal ions in ZIFs. Although too many nitrogen atoms in NHC would decrease the nucleophilicity of NHC^- , increasing the number of active sites to interact with CO_2 , whether through chemical or physical adsorption, may provide an opportunity for raising the efficiency of CO_2 uptake.⁴²

IV. SUMMARY

We studied several anionic complexes between CO_2 and NHCs with a positive AEA of over 0.7 eV by DFT calculations (UB3LYP/6-311++g(d,p)). These anionic $[\text{NHC-CO}_2]^-$ complexes have an anomalous isomeric structure with a dihedral angle of $\sim 90^\circ$, in contrast to any previously reported $[\text{NHC-CO}_2]^-$ anions that are coplanar as a result of stabilization by the delocalization of an extra negative charge through an extended π -conjugated framework. Our NBO analysis and geometry optimization showed that these novel types of anionic complexes have a CO_2 moiety with a considerable negative charge and a strongly bent O–C–O angle, just as in the coplanar structures. Instead of charge acquisition through delocalization, a certain degree of charge transfer is expected to occur in these orthogonal complexes. The seeming anomaly was explained by the simple steric effect as its major governing factor, and to a lesser degree, by the unique

electronic properties of the constituent NHC species that lead to the decrease in the electronic stabilization effect toward the structure with a dihedral angle of $\sim 0^\circ$. Such an electronic effect was supported by demonstrating the correlation between the internal rotation barrier and the electron affinity for several $[\text{NHC-CO}_2]^-$ complexes that have negligible steric effects. The results of our work are expected to be applicable to designing NHCs to increase the CO_2 uptake by allowing adjacent nitrogen atoms of NHC to be utilized for CO_2 capture.

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- R. N. Compton, P. W. Reinhardt, and C. D. Cooper, *J. Chem. Phys.* **63**, 3821 (1975).
- G. L. Gutsev, R. J. Bartlett, and R. N. Compton, *J. Chem. Phys.* **108**, 6756 (1998).
- K. Takahashi, S. Sawamura, N. M. Dimitrijevic, D. M. Bartels, and C. D. Jonah, *J. Phys. Chem. A* **106**, 108 (2002).
- M. J. DeLuca, B. Niu, and M. A. Johnson, *J. Chem. Phys.* **88**, 5857 (1988).
- T. Tsukuda, M. A. Johnson, and T. Nagata, *Chem. Phys. Lett.* **268**, 429 (1997).
- T. Tsukuda, M. Saeki, R. Kimura, and T. Nagata, *J. Chem. Phys.* **110**, 7846 (1999).
- A. Muraoka, Y. Inokuchi, N. I. Hammer, J.-W. Shin, M. A. Johnson, and T. Nagata, *J. Phys. Chem. A* **113**, 8942 (2009).
- S. Y. Han, I. Chu, J. H. Kim, J. K. Song, and S. K. Kim, *J. Chem. Phys.* **113**, 596 (2000).
- M. Z. Kamrath, R. A. Relph, and M. A. Johnson, *J. Am. Chem. Soc.* **132**, 15508 (2010).
- S. Y. Han, J. K. Song, J. H. Kim, H. Bin Oh, and S. K. Kim, *J. Chem. Phys.* **111**, 4041 (1999).
- J. H. Kim, J. K. Song, H. Park, S. H. Lee, S. Y. Han, and S. K. Kim, *J. Chem. Phys.* **119**, 4320 (2003).
- A. M. Buytendyk, Y. Wang, J. D. Graham, A. K. Kandalam, B. Kiran, and K. H. Bowen, *Mol. Phys.* **113**, 2095 (2015).
- S. H. Lee, N. Kim, D. G. Ha, and S. K. Kim, *J. Am. Chem. Soc.* **130**, 16241 (2008).
- J. D. Graham, A. M. Buytendyk, Y. Wang, S. K. Kim, and K. H. Bowen, *J. Chem. Phys.* **142**, 234307 (2015).
- W. Schossler and M. Regitz, *Chem. Ber.* **107**, 1931 (1974).
- N. Kuhn, M. Steimann, and G. Weyers, *Z. Naturforsch., B: J. Chem. Sci.* **54**, 427 (1999).
- H. A. Duong, T. N. Tekavec, A. M. Arif, and J. Louie, *Chem. Commun.* **2004**, 112.
- B. R. Van Ausdall, J. L. Glass, K. M. Wiggins, A. M. Aarif, and J. Louie, *J. Org. Chem.* **74**, 7935 (2009).
- M. Vogt, J. E. Bennett, Y. Huang, C. Wu, W. F. Schneider, J. F. Brennecke, and B. L. Ashfeld, *Chem. - Eur. J.* **19**, 11134 (2013).
- L. Yang and H. Wang, *ChemSusChem* **7**, 962 (2014).
- F. Huang, G. Lu, L. Zhao, H. Li, and Z. X. Wang, *J. Am. Chem. Soc.* **132**, 12388 (2010).
- H. Zhou, W. Z. Zhang, C. H. Liu, J. P. Qu, and X. B. Lu, *J. Org. Chem.* **73**, 8039 (2008).
- W. Li, D. Huang, and Y. Lv, *RSC Adv.* **4**, 17236 (2014).
- S. N. Riduan, Y. Zhang, and J. Y. Ying, *Angew. Chem., Int. Ed.* **48**, 3322 (2009).
- J. Tirado-Rives and W. L. Jorgensen, *J. Chem. Theory Comput.* **4**, 297 (2008).
- D. Moran, A. C. Simmonett, F. E. Leach, W. D. Allen, P. V. R. Schleyer, and H. F. Schaefer, *J. Am. Chem. Soc.* **128**, 9342 (2006).

- ²⁷Y. Bouteiller, C. Desfrancois, and J. P. Schermann, *J. Chem. Phys.* **108**, 7967 (1998).
- ²⁸E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold, NBO version 3.1, University of Wisconsin, Madison, WI, 1995.
- ²⁹J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* **102**, 7211 (1980).
- ³⁰M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, GAUSSIAN 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.
- ³¹A. J. Arduengo III, *Acc. Chem. Res.* **32**, 913 (1999).
- ³²H. Jacobsen, A. Correa, C. Costabile, and L. Cavallo, *J. Organomet. Chem.* **691**, 4350 (2006).
- ³³D. Bourissou, O. Guerret, F. P. Gabbaï, and G. Bertrand, *Chem. Rev.* **100**, 39 (2000).
- ³⁴K. Chandra Mondal, S. Roy, and H. W. Roesky, *Chem. Soc. Rev.* **45**, 1080 (2016).
- ³⁵O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, and G. Bertrand, *Angew. Chem., Int. Ed.* **52**, 2939 (2013).
- ³⁶Z. Li, T. Bally, K. N. Houk, and W. T. Borden, *J. Org. Chem.* **81**, 9576 (2016).
- ³⁷A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O’Keeffe, and O. M. Yaghi, *Acc. Chem. Res.* **43**, 58 (2010).
- ³⁸H. Hayashi, A. P. Côté, H. Furukawa, M. O’Keeffe, and O. M. Yaghi, *Nat. Mater.* **6**, 501 (2007).
- ³⁹T. Jose, Y. Hwang, D. W. Kim, M.-I. Kim, and D. W. Park, *Catal. Today* **245**, 61 (2015).
- ⁴⁰S. Wang and X. Wang, *Appl. Catal., B* **162**, 494 (2015).
- ⁴¹S. Seo, M. Quiroz-Guzman, M. A. Desilva, T. B. Lee, Y. Huang, B. F. Goodrich, W. F. Schneider, and J. F. Brennecke, *J. Phys. Chem. B* **118**, 5740 (2014).
- ⁴²M. Ramdin, T. W. de Loos, and T. J. H. Vlugt, *Ind. Eng. Chem. Res.* **51**, 8149 (2012).