

A theoretical study on the hydrogen adducts of diamidocarbenes and diaminocarbenes

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Abstract The hybrid-meta GGA DFT functional M06-2X was used to examine the potential of N,N'-diamidocarbenes for use as hydrogen storage materials. We previously discovered that borylene, which is isoelectronic with an Arduengo-type carbene, was a suitable candidate for a hydrogen storage material. We compared the capabilities of N,N'-diamidocarbenes and N-heterocyclic carbenes as hydrogen storage materials. The results indicate that diamidocarbenes are not suitable hydrogen storage materials because the removal of H₂ is more endothermic for diamidocarbenes than for diaminocarbenes.

Keywords Diaminocarbene · Diamidocarbene · Hydrogen adduct

Introduction

Carbenes have long been recognized as reaction intermediates [1]. In 1991, Arduengo and coworkers successfully synthesized the first crystalline carbene (1 in Scheme 1) [2]. These stable carbenes, referred to as N-heterocyclic carbenes (NHC), have played vital roles in various chemical reactions to date [3]. For example, stable NHCs have become an important class of ligands in homogeneous catalysis because the σ -symmetric lone pair on the carbenic carbon allows NHCs to form strong σ -coordination bonds with transition metals [3, 4]. Although they are typically known for their exceptional σ -donor abilities [5], π -interactions play a role in the bonding

between NHCs and transition metals, as indicated by recent studies [6–11]. Hobbs and coworkers focused on preparing NHCs with reduced-energy lowest unoccupied molecular orbitals (LUMOs) to determine the importance of π -interactions between carbenes and transition metals [12]. By introducing an oxalamide into the heterocyclic backbone (e.g., 2 in Scheme 1), they discovered that the resulting carbene, referred to as N,N'-diamidocarbene (NAC), possessed a higher electrophilicity compared with typical NHCs.

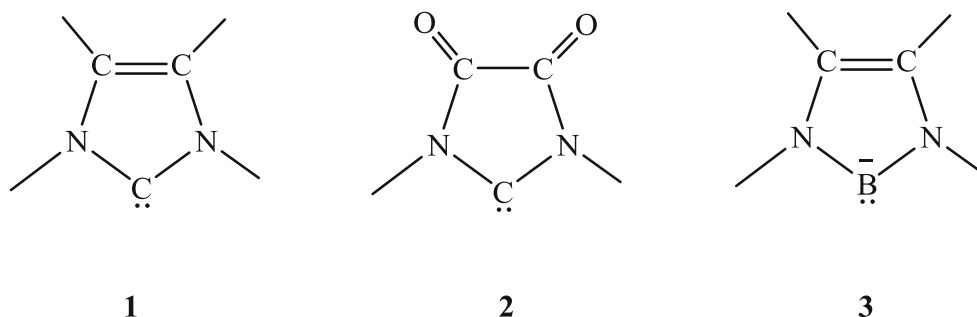
Various quantum chemical calculations were performed to examine not only the peculiar stability of NHCs but also their reactivity [13–20]. In 2006, Dixon and coworkers [20] discovered that NHCs may be suitable candidates for use as hydrogen storage materials by using a sophisticated theoretical level. Thereafter, we discovered that borylene (3 in Scheme 1), which is isoelectronic with an Arduengo-type carbene, is a suitable candidate for a hydrogen storage material [21]. In this study, we compared the capabilities of NACs with those of NHCs as hydrogen storage materials. These carbenes, and the hydrogenation reactions used in this study, are shown in Schemes 2 and 3. An NAC can exist as a five-membered, six-membered, or seven-membered ring [22–25]. Therefore, the effect of ring size on the ability of an NAC to store hydrogen was also examined in this study.

Computational details

All calculations were performed using the Gaussian 09 program [26]. In our previous study on the 1,2-H shift of imidazole-2-ylidene [27], results using the M06-2X/cc-pVTZ theoretical level showed the least deviation from results obtained using the BD(T)/cc-pVQZ theoretical level. Therefore, we posited that the M06-2X/cc-pVTZ theoretical level was suitable for describing the stability or reactivity of carbenes, and used this level to examine the hydrogen-storage

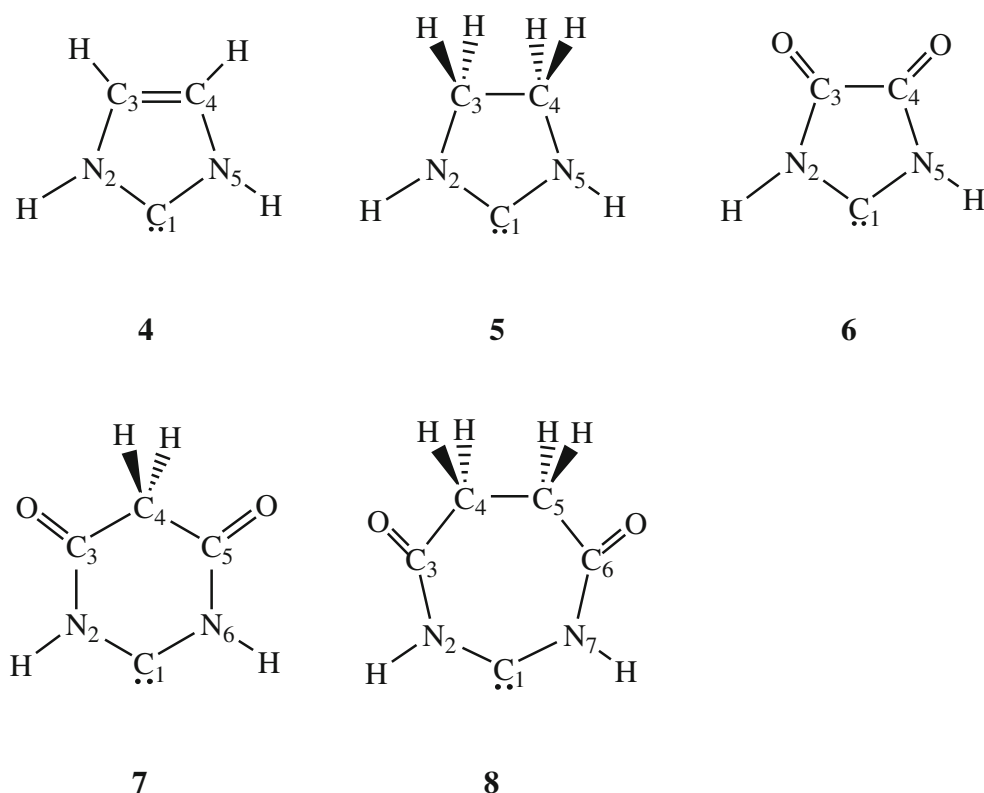
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Scheme 1 Skeletal representations of 1, 2, and 3

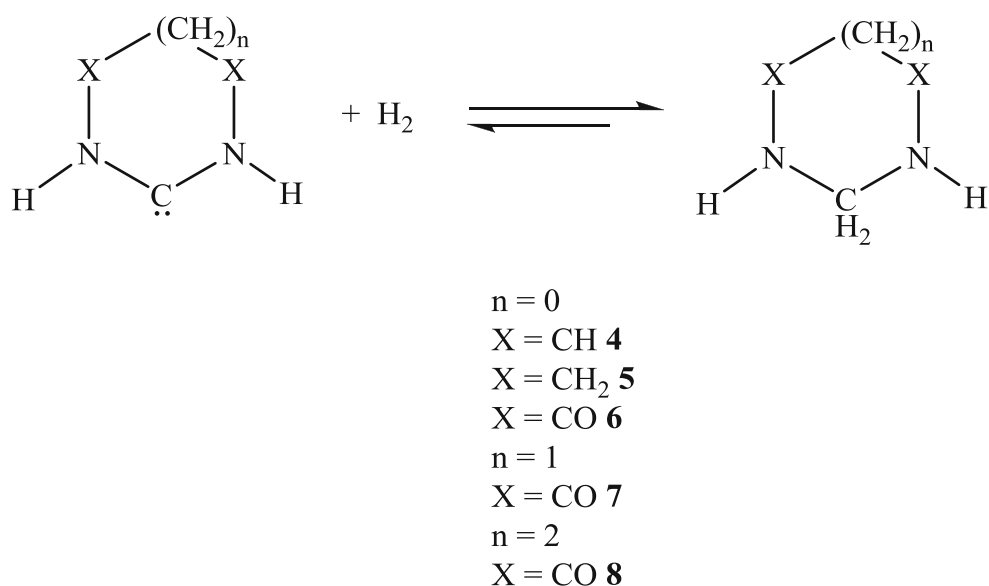
potential of carbenes. To confirm that this supposition was correct, the M06-2X-calculated formation enthalpies of 4H and 5H were compared with the previous CCSD(T) results [20]. Including zero-point energies, our M06-2X results were -14.7 and -31.5 kcal mol $^{-1}$ for 4H and 5H, respectively. These results deviated slightly from the previous CCSD(T) results. For a more quantitative comparison, the relative deviation (DE) from the previous CCSD(T) values was expressed as Eq. (1), and calculated as 1.494 % and 3.410 % for 4H and 5H, respectively [20].

$$DE = \frac{|\Delta H_f(M06-2X) - \Delta H_f(CCSD(T))|}{|\Delta H_f(CCSD(T))|} \times 100\% \quad (1)$$

Scheme 2 The carbenes discussed in this study

An average 2.452 % relative deviation with respect to the previous CCSD(T) results [20] was obtained using our M06-2X results [20]; therefore, we posited that the M06-2X/cc-pVTZ theoretical level, offering a balance between accuracy and available computational resources, could enable qualitative comparison of the potential of diaminocarbenes and diamidocarbenes to behave as hydrogen storage materials. Based on the CCSD(T)/CBS theoretical level, 4 in the singlet manifold (14) reacted with H $_2$ to result in an exothermic reaction of -14.9 kcal mol $^{-1}$, whereas 4 in the triplet state (34) reacted with H $_2$ to result in an exothermic reaction of -101 kcal mol $^{-1}$ [20]. In other words, a substantial amount of energy is necessary to make the hydrogen adduct 4H deplete into H $_2$ and 4 in the triplet manifold (34).

Scheme 3 Schematic representation of the formation reaction of the hydrogenation adducts 4H–8H



To investigate the influence of the solvation effect on the thermodynamics of the reaction, the DFT-CPCM method was used to calculate the reaction enthalpy and the Gibbs free energy of the following reaction [28]:



where the superscript *l* indicates that the species is in solution, and the superscript *g* indicates that the species is in the gas phase. To consider the effect of the polarity of the solvent on the reaction thermodynamics of Eq. (2), a nonpolar solvent (thiophene, $\epsilon=2.727$) and a polar solvent (acetonitrile, $\epsilon=35.69$) were considered in this study. In our previous study on the transnitrosation reaction ($\text{MeXNO} + \text{YMe}^- \rightarrow \text{MeYNO} + \text{XMe}^-$; X, Y=S, Se), the DFT-PCM results showed that these are concerted reactions, in sharp contrast to the two-step reaction pathways concluded in the gas phase [29]. Therefore, we believe that the solvent effect must be considered using full optimization in the appropriate environment. The solvent effects of the two solvents were thus considered by fully optimizing the reactants and corresponding products in this study.

All stationary points were positively identified as equilibrium structures [number of imaginary frequencies (NIMAG)=0]. All mentioned energetic values were corrected for zero-point energies. Natural bond orbital (NBO) analysis was performed using NBO 5.9, implemented in Gaussian 09 [30]. NBOs represent orthonormal sets of localized "maximum occupancy" orbitals that describe the molecular bonding pattern of electron pairs to yield the most accurate Lewis-like description of the total N-electron density.

Results and discussion

Comparison between five-membered diaminocarbenes and five-membered diamidocarbenes

We initially compared the electric properties and hydrogen storage abilities of carbenes 4–6. A summary of the optimized bond lengths of $\text{C}_1\text{--N}_2$, the forming C–H bond ($\text{C}_1\text{--H}$), and bond angle $\angle\text{N}_2\text{--C}_1\text{--N}_5$ for carbenes 4–6 is shown in Table 1. The previous values are also included in Table 1 for comparative purposes. The corresponding hydrogen adducts for carbenes 4–6 were designated 4H, 5H, and 6H. Because carbenes 4 and 5 are planar, but 4H and 5H are not, there are two types of hydrogen in 4H and 5H (one type is up to the molecular plane and the other is down to the molecular plane).

Table 1 Optimized bond lengths of $\text{C}_1\text{--N}_2$, $\text{C}_1\text{--H}$, and bond angle $\angle\text{N}_2\text{--C}_1\text{--N}_5$ for carbenes 4–6 (bond lengths in Ångstroms, bond angle in degrees)

	$R(\text{C}_1\text{--N}_2)$	$R(\text{C}_1\text{--H})$	$\angle\text{N}_2\text{--C}_1\text{--N}_5$
4	1.360 (1.366) ^a	–	100.4 (99.90) ^a
4H	1.467 (1.468) ^a	1.089 (1.087) ^a 1.105 (1.105) ^a	102.3 (102.0) ^a
5	1.342 (1.348) ^a	–	104.4 (104.1) ^a
5H	1.462 (1.464) ^a	1.093 (1.091) ^a 1.088 (1.087) ^a	108.0 (108.4) ^a
6	1.366	–	104.2
6H	1.444	1.093 1.093	101.6

^a Values in parentheses are the previous MP2/cc-pVTZ results [20]

Table 2 Charges of C₁ and N₂, the bond orders of C₁–N₂ and C₁–H for carbene 4–6 and their hydrogen adducts

	q(C ₁)	q(N ₂)	Bond order of C ₁ –N ₂ ^a	Bond order of C ₁ –H ^a
4	0.0886	–0.5682	1.286	–
4H	0.0042	–0.6353	0.9903	0.9281 0.9285
5	0.1860	–0.6417	1.315	–
5H	–0.0303	–0.6467	0.9969	0.9355 0.9202
6	0.2649	–0.6651	1.214	–
6H	0.0135	–0.6258	0.9885	0.9154 0.9154

^a The Wiberg bond index matrix in the natural atomic orbitals (NAO) basis was adopted

The two hydrogens in 4H and 5H have different C–H bond lengths to the carbenic center. Conversely, both 6 and 6H are planar, and the two hydrogens have the same C–H bond length to the carbenic center in 6H. NBO analyses were performed to examine further the electronic properties of the hydrogen adducts 4H, 5H, and 6H. The results of the NBO analyses are listed in Table 2. The calculation of bond orders was based on the method developed by Wiberg [31]; a larger calculated bond order means the bond is stronger. When the hydrogen adducts are formed, the decrease in electrophilic character on C₁ accompanies an increase in nucleophilic character on N₂. This may indicate that the ionic character of the C₁–N₂ bond increases and the covalent character decreases correspondingly as H₂ attaches to the C₁ atom, which is in agreement with the NBO results in Table 2. Furthermore, C₁ forms a single bond with each hydrogen in the hydrogen adducts. A summary of the formation enthalpies (ΔH_f^0) for 4H, 5H, and 6H is shown in Table 3. A further investigation was performed to determine whether corresponding carbenes in the triplet manifold (³4, ³5, ³6) participated in hydrogenation reactions. Our previous study found that singlet-triplet splittings equal to E(T₁) – E(S₀) of the tilted carbenes were 82.9, 67.8, and 43.0 kcal mol^{–1} for 4, 5, and 6, respectively [32]. Because ³6 was obtained the most easily, the UM06-2X/cc-pVTZ theoretical level was adopted to calculate the reaction enthalpy (ΔH) of ³6+H₂→6H. It was found that the

Table 3 Hydrogenation heats (ΔH), and Gibbs free energies (ΔG , both in kcal mol^{–1}) for 4–6

	4+H ₂ →4H	5+H ₂ →5H	6+H ₂ →6H
– ΔH (298 K)	14.7 14.9 ^a	31.5 32.6 ^a	49.8
– ΔG (298 K)	6.2	22.4	41.4

^a Values are based on the CCSD(T)/CBS theoretical level, please see [20]

Table 4 Geometrical parameters of both 4 and 4H in the gas phase (G), the thiophene solution (T), and the acetonitrile solution (A; bond length in Ångstroms, bond angle in degrees)

	R(C ₁ –N ₂)			R(C ₁ –H)			$\angle N_2$ –C ₁ –N ₂		
	G	T	A	G	T	A	G	T	A
4	1.360	1.359	1.358	–	–	–	100.4	100.7	100.9
4H	1.467	1.473	1.474	1.089 1.105	1.087 1.092	1.086 1.093	102.3	107.7	107.7

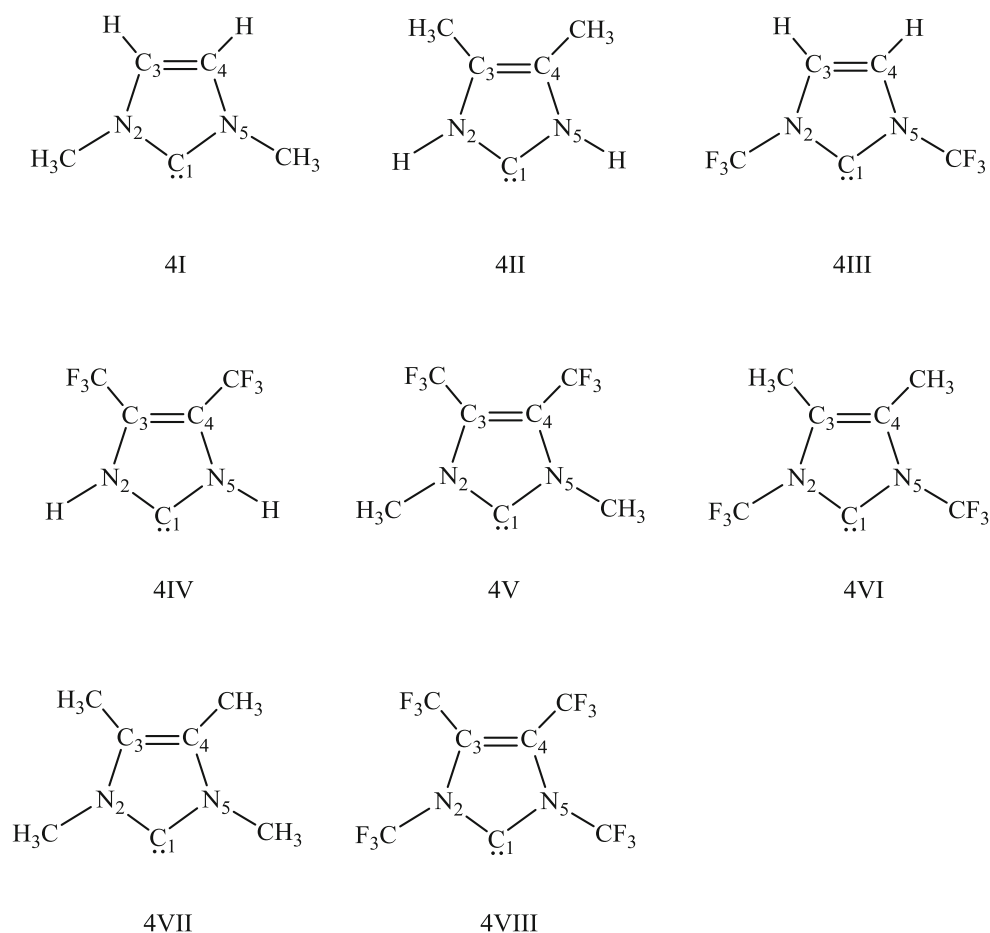
formation of 6H involving ³6 was a largely exothermic reaction with a ΔH of –92.9 kcal mol^{–1}. In accordance with previous results regarding 4, ³6 was excluded as a suitable candidate for hydrogen storage.

Table 3 shows that the reaction of a diamidocarbene (6) and H₂ is more exothermic than that of diaminocarbene (4, 5) and H₂. The formation free energies (ΔG_f^0) of the hydrogen adducts must be considered to ascertain whether diamidocarbenes are more suitable hydrogen storage materials than diaminocarbenes. The Gibbs free energies of formation for the hydrogen adducts 4H, 5H, and 6H are shown in Table 3. Accordingly, the additions of H₂ to carbenes 4–6 are all exothermic at 298.15 K. Conversely, the release of H₂ from the corresponding hydrogen adducts 4H–6H is highly endothermic. Carbenes 4–6 cannot serve as H₂ storage systems on their own because their enthalpies are not sufficiently favorable. Therefore, two factors affecting the formation enthalpies for the hydrogen adducts were considered in this study: the solvent effect, and the effect of the substituents on N₂, C₃, C₄, and N₅. As shown in Table 3, 4 was the most suitable hydrogen storage material candidate among the three carbenes (4, 5, and 6). Therefore, 4 was used as an example to demonstrate the effects of these two influential factors.

The fully optimized geometries of 4 and 4H in the gas phase, the thiophene solution, and the acetonitrile solution are listed in Table 4. As shown in Table 4, 4H is a nonplanar molecule, and its hydrogens have different bond lengths with the original carbenic center. Moreover, the converged geometries of both 4 and 4H are little influenced by thiophene, or acetonitrile as solvents. The enthalpies (ΔH_f) and Gibbs free energies (ΔG_f) for the hydrogenation of 4 in thiophene and acetonitrile are listed in Table 5. For comparison, both the ΔH_f

Table 5 Enthalpies, and Gibbs free energies (kcal mol^{–1}) for hydrogenation of carbene 4 in the gas phase, thiophene, and acetonitrile

4+H ₂ →4H	– ΔH (298 K)	– ΔG (298 K)
Gas phase	14.7	6.2
Thiophene	9.5	1.1
Acetonitrile	11.1	2.7

Scheme 4 Derivatives of 4 discussed in this study

and ΔG_f of the hydrogenation of 4 in the gas phase are also listed in Table 5. As shown in Table 5, 4 is more efficient at hydrogen storage when hydrogenated in thiophene and acetonitrile, and exhibits the least hydrogen-storing efficiency in the gas phase.

To consider the effects of the substituents attached to N_2 , C_3 , C_4 , and N_5 on the hydrogenation of 4, two substituents were considered. One is an electron-donating group, CH_3 , and the other is an electron-withdrawing group, CF_3 . The mentioned

derivatives of 4 in this study are listed in Scheme 4. The substituting effect on the geometry of 4 was investigated, and the converged geometries of 4I–4VIII are listed in Table 6. For comparison, the values corresponding to 4 are also listed in Table 6. As shown in Table 6, neither CH_3 nor CF_3 significantly influenced the geometry of 4. The thermodynamic data from 4I–4VIII are listed in Table 7. For comparison, data from 4 are

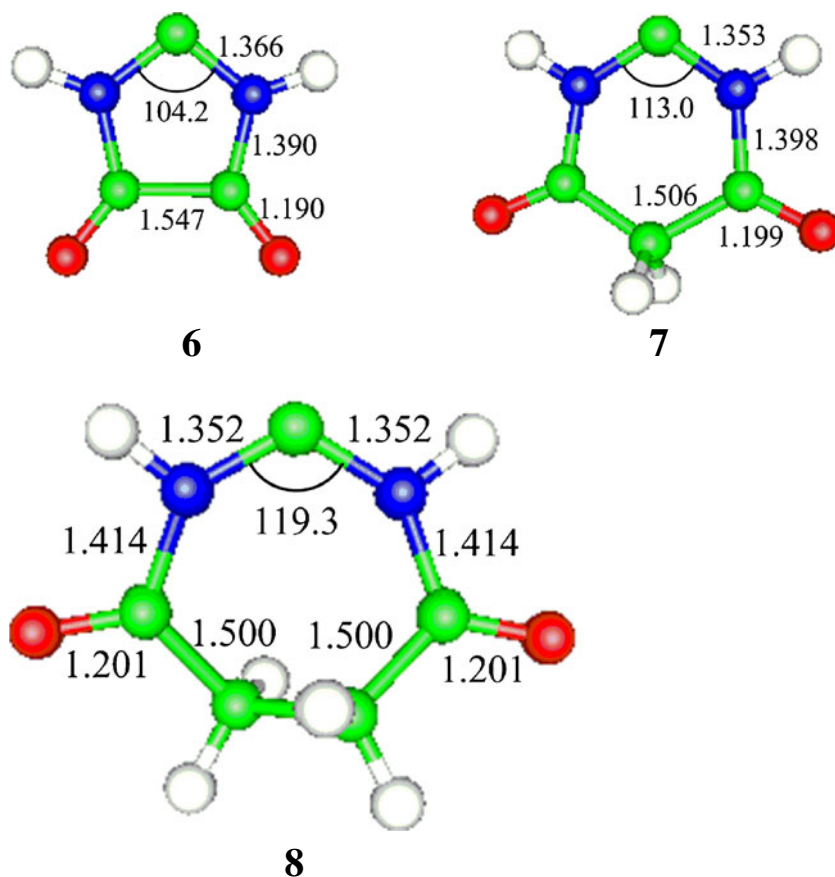
Table 6 Geometrical parameters of 4I–4 VIII (bond length in Ångstroms, bond angle in degrees)

	$R(C_1-N_2)$	$\angle N_5-C_1-N_2$
4	1.360	100.4
4I	1.360	101.8
4II	1.358	100.2
4III	1.358	100.3
4IV	1.358	100.3
4 V	1.358	102.7
4VI	1.358	100.3
4VII	1.359	101.7
4VIII	1.357	101.5

Table 7 Hydrogenation heats, and Gibbs free energies (both in kcal mol^{-1}) for 4I–4VIII

	$-\Delta H(298 \text{ K})$	$-\Delta G(298 \text{ K})$
4+H ₂ →4H	14.7	6.2
4I+H ₂ →4IH	15.0	5.4
4II+H ₂ →4IIH	16.6	7.3
4III+H ₂ →4IIIIH	31.8	22.5
4IV+H ₂ →4IVH	21.0	12.3
4 V+H ₂ →4VH	17.0	7.9
4VI+H ₂ →4VIH	31.3	23.6
4VII+H ₂ →4VIIH	14.4	4.8
4VIII+H ₂ →4VIIIH	33.9	25.6

Fig. 1 M06-2X-optimized geometries of 6, 7, and 8 (bond length in Ångstroms, bond angle in degrees)



also listed in Table 7. As shown in Table 7, the ability of 4H to provide H₂ can be increased by substituting electron-donating groups like CH₃ on both N₂ and N₅. The application of Le Chatelier's principle suggests that the ability of hydrogen adducts 4H–6H to provide H₂ can be enhanced by pumping. The results here further suggest that pressuring with H₂ is useful for regenerating the H₂ storage system. Therefore, we anticipated that diamidocarbene would be less efficient as a hydrogen storage system because the removal of H₂ from the hydrogen adduct 6H was more endothermic.

Effect of ring size on the ability of a diamidocarbene to behave as a hydrogen storage material

The optimized geometries of five-, six-, and seven-membered ring diamidocarbene adducts are shown in Fig. 1. The figure indicates that the converged structures of 6, 7, and 8 are nearly planar molecules except for the H₂C–CH₂ fragment in 8. It is well known that the filled nitrogen 2p orbital interacts strongly with the unoccupied carbon 2p orbital in an NHC [33]. However, this type of orbital interaction is weakened when

Scheme 5 Resonance structures for 6

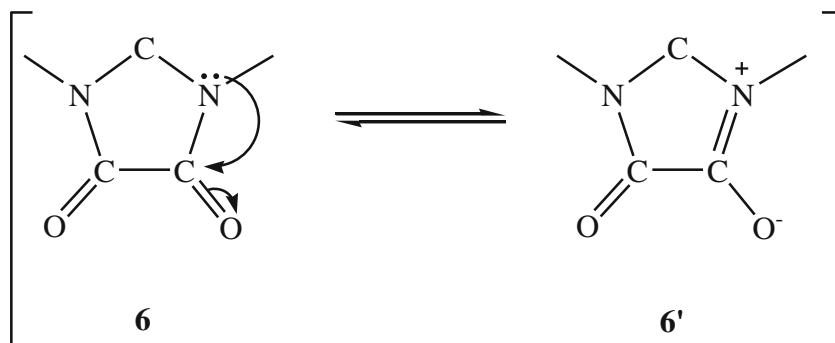


Table 8 Calculated energies (Hartree), optimized dipole moments (Debye), rotational constants (GHz), unscaled frequencies (cm^{-1}), bond orders of the C–O, and C–N bonds in 6, 7, and 8

	6	7	8
Electronic energy	−375.371249	−414.669848	−453.938189
Dipole moment	2.369	0.2005	1.255
Rotational constants	3.953, 3.928, 1.970	4.091, 1.913, 1.314	3.456, 1.328, 1.001
κ	0.9748	−0.5686	−0.7336
Bond order of the C ₃ –O bond	1.858 1.834	1.786 1.785	1.785 1.785
Bond order of the C ₃ –N ₂ bond	1.051 1.049	1.029 1.030	1.002 1.002
Interaction strength between the lone pair of N ₂ and the π^* orbital of C ₃ –O	55.1	55.9	50.1

inserting an oxalamide fragment into a heterocyclic backbone to form a diamidocarbene because a resonance (in Scheme 5) exists between the filled nitrogen 2p orbital and the carbonyl group. This resonance can simultaneously reduce the bond order of the C₃–O (C₄–O) bond and increase the bond order of

Table 9 Hydrogenation heats and Gibbs free energies (both in kcal mol^{-1}) for 6–8

	6+H ₂ →6H	7+H ₂ →7H	8+H ₂ →8H
$\Delta H(298\text{ K})$	−49.8	−45.0	−49.8
$\Delta G(298\text{ K})$	−41.4	−36.1	−41.3

the C₃–N₂ (C₄–N₅) bond in 6. Similar bond order changes occurred in 7 and 8. A summary of the zero-point-energy (ZPE) corrected energies (in Hartree), optimized dipole moments (in debye), rotational constants (in GHz), and bond orders of C–O and C–N bonds of 6, 7, and 8, is listed in Table 8. The asymmetric parameter (κ) was obtained based on the calculated rotational constants. If $\kappa=1$, the molecule will be an oblate symmetric top. In contrast, if $\kappa=-1$, the molecule will be a prolate symmetric top.

$$\kappa = \frac{(2B-A-C)}{(A-C)} \quad (3)$$

As shown in Table 8, both 7 and 8 are prolate symmetric tops, but 6 is an oblate symmetric top.

According to second perturbation theory, the interaction strength between a lone pair of nitrogen (LP_N) and

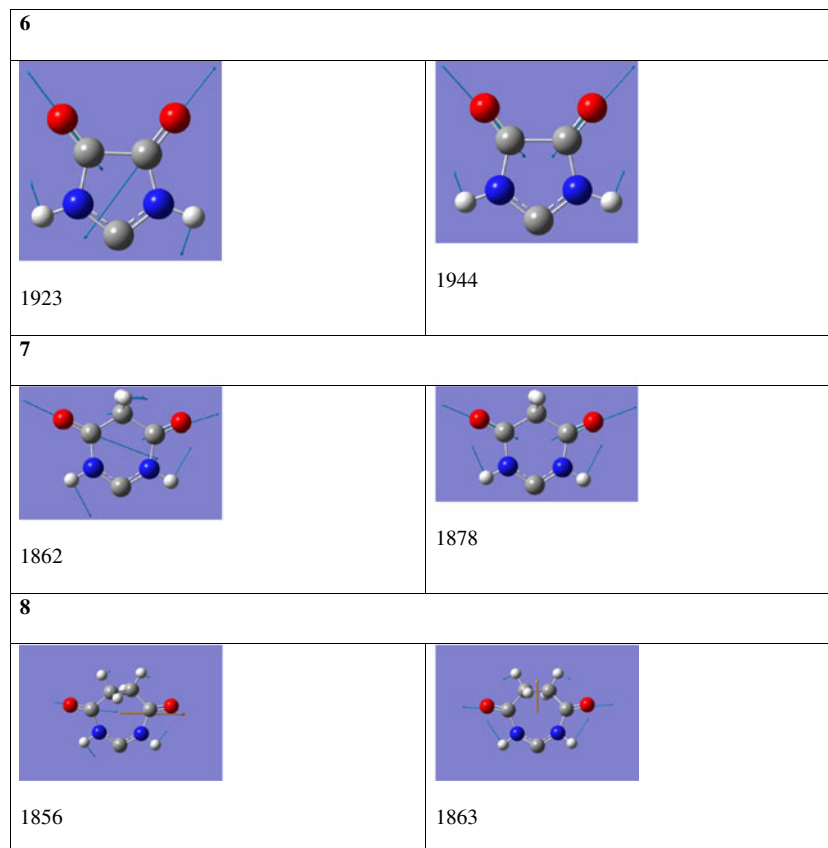
Fig. 2 Uncorrelated stretching frequencies (in cm^{-1}) and displacement vectors of the C=O stretching mode in 6, 7, and 8

Table 10 Results of the natural bond orbital (NBO) analyses for 6–8 and their corresponding hydrogen adducts 6H–8H

	6	6H	7	7H	8	8H
q(C ₁)	0.2649	0.0135	0.2438	−0.0087	0.2389	−0.0182
q(N ₂)	−0.6650	−0.6258	−0.6574	−0.6446	−0.6705	−0.6468
Bond order of C ₁ –N ₂ ^a	1.214	0.9885	1.253	0.9830	1.273	0.9918
Bond order of C ₁ –H ^a	–	0.9154	–	0.9287	–	0.9175
q(C ₃)	0.5915	0.5873	0.7058	0.7028	0.7086	0.7027
q(O)	−0.4813	−0.5605	−0.5512	−0.6037	−0.5548	−0.6128

^a The Wiberg bond index matrix in the NAO basis was adopted

π^* orbital of a carbonyl group ($\pi^*_{C=O}$) can be calculated using Eq. (4):

$$E^{(2)} = \frac{\langle LP_N | H | \pi^*_{C=O} \rangle^2}{E(\pi^*_{C=O}) - E(LP_N)} \quad (4)$$

where $E(X)$ is the energy of orbital X . A summary of the calculated interaction strength between LP_N and $\pi^*_{C=O}$ for 6, 7, and 8 is shown in Table 8. As shown in Table 8, strong interactions exist between LP_N and $\pi^*_{C=O}$ (> 50.0 kcal mol^{−1}) in 6, 7, and 8.

Moreover, 6, 7, and 8 are all polar molecules and their polarity shows a trend: $6 > 8 > 7$ (see Table 8). The stretching frequencies of the two carbonyl groups were 1923 and 1944 cm^{−1} for 6, 1862 and 1878 cm^{−1} for 7, and 1856 and 1863 cm^{−1} for 8. The displacement vectors of the corresponding normal modes are shown in Fig. 2. Figure 2 indicates that a coupling exists between the two stretching normal modes of the two C=O bonds. In the experiments, the C=O stretching frequency was 1670–1820 cm^{−1} for a carbonyl group, whereas the C–O stretching frequency was 1050–1150 cm^{−1} for alcohol [34]. The stretching frequencies of the two carbonyl groups were obtained using the scaling factor on the M06-2X/aug-cc-pVTZ theoretical level (0.985) [35]: 1894 and 1915 cm^{−1} for 6, 1834 and 1850 cm^{−1} for 7, and 1828 and 1835 cm^{−1} for 8. Therefore, the resonance effect between the nitrogen and carbonyl groups in 6, 7, and 8 (e.g., Scheme 5) should not significantly reduce the bond order between carbon and oxygen. The bond orders of the two carbonyl groups in 6, 7, and 8 were near 2, in accordance with the results of the Wiberg bond index matrix for 6, 7, and 8.

A summary of the enthalpies and Gibbs free energies of formation of the hydrogen adducts for 6H, 7H, and 8H is shown in Table 9. As mentioned above, the diamidocarbenes in triplet states (³6, ³7, ³8) are not considered herein. Table 9 indicates that all of the NACs were less suitable as hydrogen storage materials compared with NHCs, because the removal of H₂ from the hydrogen adducts 6H–8H was

more endothermic. Table 9 indicates that the spontaneity of the formation for the hydrogen adducts exhibited the trend 6H ≈ 8H > 7H. The efficiency of the carbene to act as a suitable hydrogen storage material can be simply viewed as $-\Delta G$ of its hydrogen adduct. The abilities of carbenes 6, 7, and 8 to act as hydrogen storage materials form the trend $7 > 8 \approx 6$. A comparison of the electronic properties of 6–8 and their hydrogen adducts 6H–8H is shown in Table 10. The positively charged characteristic of C₁ decreases as hydrogen is added. For example, the charge carried by C₁ changes from 0.2649 to 0.0135 as 6H is formed by 6. Because all of the calculated C=O bond lengths are similar, the natural population analyses show that the polarity of the C=O bond is the largest in 8 among the three NACs. The polarity of the C=O bond among the three NACs exhibits the trend: $8 > 7 > 6$. In all three NACs, the polarities of the C=O bonds increase as H₂ attaches to the C₁ center.

Conclusions

The results presented here allow the following conclusions to be drawn regarding the abilities of NHCs and NACs, as shown in Scheme 2, to behave as hydrogen storage materials:

- (1) According to the M06-2X results, NACs are poor candidates for use as hydrogen storage materials because the removal of H₂ from 6H–8H is more endothermic than from NHCs.
- (2) In the NACs shown in Scheme 2, the bond orders of the carbonyl groups were not influenced significantly by the resonance between LP_N and the carbonyl groups.
- (3) The ability of the hydrogen adduct 4H to behave as a hydrogen storage material is enhanced with the use of the solvents thiophene and acetonitrile.
- (4) The ability of the hydrogen adduct 4H to store hydrogen is also enhanced with the substitution of electron-donating groups on N₂ and N₅.

N,N'-diamidocarbenes have been demonstrated to have significant synthetic utility [36–39]. For example, Lee et al. [36] discovered that N,N'-diamidocarbenes are ambiphilic and can behave as electrophiles and nucleophiles. We believe that our results can provide a basis for rationalizing more appropriately the effect of the insertion of an oxalamide into the heterocyclic ring of an NHC.

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