

# A comparison of diamino- and diamidocarbenes toward dimerization

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**Abstract** In this study, we compare the dimerization of N,N'-diamidocarbene with that of N-heterocyclic carbene (NHC). Less interaction occurred between the filled lone pair of nitrogen and the unfilled lone pair of the carbenic center for a N,N'-diamidocarbene than did in a saturated NHC because of the resonance between the lone pair of nitrogen and a carbonyl group. Therefore, a N,N'-diamidocarbene exhibits less singlet-triplet splitting. The less singlet-triplet splitting in a heterocyclic carbene containing nitrogen, the more exothermic the dimerization, which is consistent with the conclusion of Thiel et al. (Chem Phys Lett 217:11–16, 1994).

**Keywords** Dimerization · N,N'-diamidocarbene · Resonance · Singlet-triplet splitting

## Introduction

Carbenes were extensively used as reaction intermediates until 1991 [1], when Arduengo et al. synthesized the first crystalline carbene (Scheme 1, 1) [2]. Various quantum chemical calculations have since been used to examine the peculiar stability of these Arduengo-type carbenes, which are also referred to as N-heterocyclic carbenes (NHCs) [3–10]. These studies have indicated that the cyclic delocalization or resonance ( $6\pi e^-$ ) in the imidazole ring is not a dominant factor for stabilizing Arduengo-type carbenes [3–10]. Arduengo et al. synthesized a corresponding saturated carbene in 1995 (Scheme 1, 2) [11]; however, NHCs tend toward dimerization [12–18]. Theoretical investigations have indicated that the dimerization of NHC is a low-barrier process. For example, the B3LYP results show that the activation energies ( $E_a$ ) for

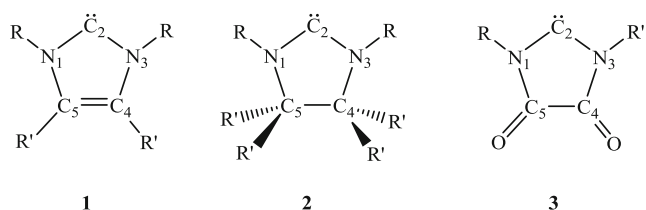
imidazol-2-ylidene and imidazolin-2-ylidene are 21 kcal mol<sup>-1</sup> and 11 kcal mol<sup>-1</sup>, respectively. The carbenes with  $6\pi e^-$  delocalizations (Scheme 1, 1) have larger activation energies toward dimerizations than non-aromatic carbenes (Scheme 1, 2) [10]. Based on the DFT results, Poater et al. rationalized that the thermodynamic tendency of a given NHC to dimerize has a relationship with its steric and singlet-triplet splitting ( $E_{ST}$ ). The  $E_{ST}$  can be defined as the energy difference between the  $S_0$  and  $T_1$  states, i.e.,  $E(T_1)-E(S_0)$  [18].

N-heterocyclic carbenes play a vital role in various chemical reactions [19]. For example, stable NHCs have become a crucial class of ligands in homogeneous catalysis [19, 20], because the  $\sigma$ -symmetric lone pair on the carbenic carbon facilitates strong  $\sigma$ -coordination bonds between the NHCs and transition metals. Although they are known for their exceptional  $\sigma$ -donor abilities [21], several recent studies have indicated that  $\pi$ -interactions affect the bonds between NHCs and transition metals [22–27]. Hobbs et al. prepared NHCs with reduced-energy lowest unoccupied molecular orbitals (LUMOs) to examine the importance of  $\pi$ -interactions between carbenes and transition metals [28]. By introducing an oxalamide into the heterocyclic backbone (Scheme 1, 3), researchers discovered that the resulting carbene possessed a higher electrophilicity than normal NHCs.

The filled nitrogen 2p orbitals in NHCs strongly interact with the unoccupied carbenic 2p orbital (Scheme 2), but the resonance structures from the insertion of the oxalamide fragment into the heterocyclic backbone reduced such orbital interactions. The resonance is represented in Scheme 3, 3. The oxalamide moiety in the heterocyclic backbone should influence other factors in addition to the electrophilicity of the heterocyclic carbenes.

In this study, we examined the difference in the relative kinetic stabilities of NHCs with respect to N,N'-diamidocarbenes. The dimerizations were chosen as prototypes for these comparisons, and a high barrier indicated a high level of carbene stability.

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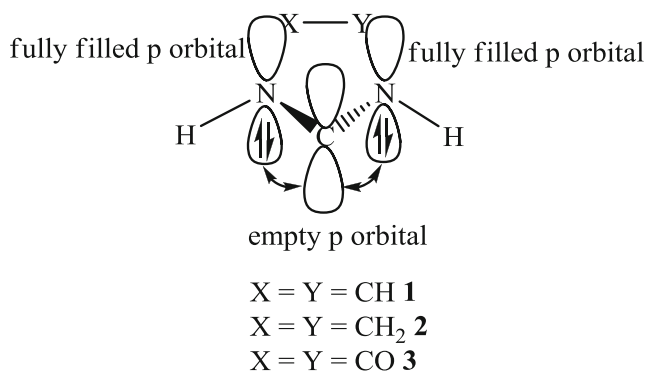


**Scheme 1** Structural representations of diamino- and diamidocarbenes **1**, **2**, and **3**

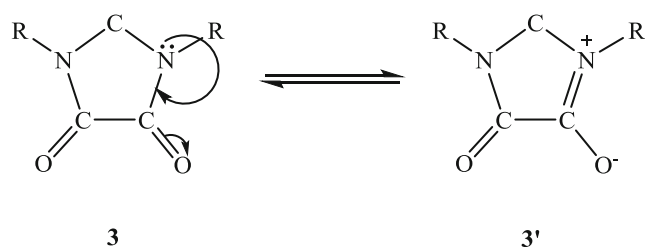
### Theoretical aspects

All calculations were performed using the Gaussian 09 program [29]. The results of the M06-2X/cc-pVTZ theoretical level showed the smallest derivation compared with those of the BD(T)/cc-pVQZ theoretical level in our previous study of the 1,2-H shifted reaction of imidazol-2-ylidene [30]. Therefore, we propose that the M06-2X/cc-pVTZ theoretical level is suitable for describing the stability or reactivity of a carbene and used it to examine the dimerizations of carbenes **1–3** in this study. Carbene **4** (Scheme 4) was considered to provide a systematic comparison. All R and R' in Schemes 1–4 are H to exclude the steric effect.

We examined carbenes **1–4**, their corresponding transition states (TSs), and dimers. All the stationary points were positively identified as equilibrium structures [numbers of imaginary frequency (NIMAG=0)] or TSs (NIMAG=1). The motions corresponding to the imaginary frequencies were visually checked for the TSs and the energetic values were corrected for zero point energies. The tendency of a NHC to dimerize is commonly regarded as related to its  $E_{ST}$  [18]. Moreover, the corresponding triplet state ( $T_1$ ) is fully optimized by the unrestricted version of M06-2X/cc-pVTZ (i.e., UM06-2X/cc-pVTZ). Although unrestricted calculations can be performed, their wavefunctions are no longer eigenfunctions of the total spin  $\langle S^2 \rangle$  [31]; thus, certain errors, such as spin contamination, may emerge during the calculation. The expected values of  $S^2$  for carbenes **1**, **2**, **3**, and **4** in



**Scheme 2** The schematic representation of the orbital interaction between the filled p orbital of nitrogen and the unfilled p orbital of the carbenic center



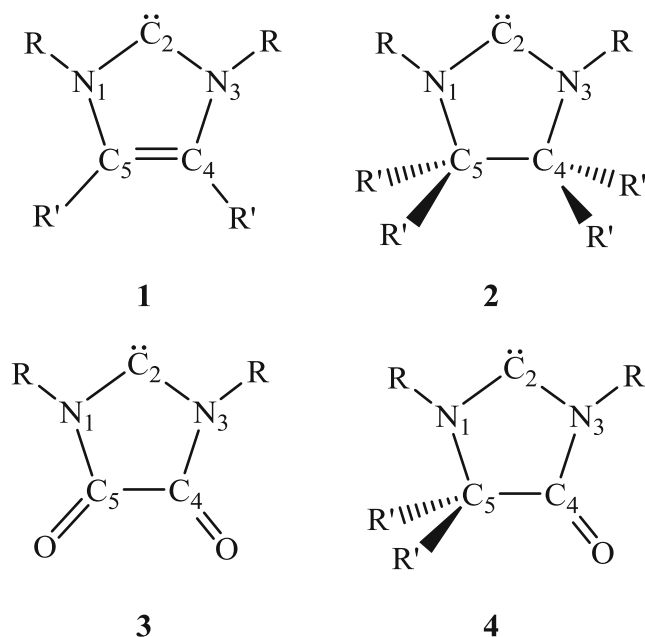
**Scheme 3** Resonance structures for carbene **3**

the triplet manifold were 2.009, 2.000, 2.001, and 2.000, respectively. These values indicate that spin contamination was not a serious factor in this study. The natural bond orbital (NBO) analysis was performed using NBO 5.9, which was implemented in Gaussian 09 [32]. The NBOs represent orthogonal sets of localized maximal occupancy orbitals that describe the molecular bonding pattern of electron pairs, yielding an accurate Lewis-like description of the total N-electron density.

### Results and discussion

#### Comparing carbenes **1–4**

We compared the electronic properties and optimized geometries of carbenes **1–4**. The selected geometrical parameters of carbenes **1–4** are summarized in Table 1. Previous data are included to enhance the comparison [9, 28]. Carbene **4** includes an amino-type and an amido-type nitrogen. These forms of nitrogen have distinct C-N bond lengths with the



**Scheme 4** The structures of carbenes **1–4**

carbenic center. The amido-type nitrogen forms a longer C-N bond with the carbenic center than does the amino-type. A comparison of the previous results for carbenes **1** and **2** indicated that the M06-2X functional provided a shorter C<sub>2</sub>-N<sub>1</sub> (or N<sub>3</sub>) bond length and a larger ∠N<sub>1</sub>-C<sub>2</sub>-N<sub>3</sub> bond angle than the B3LYP functional [9]. The optimized geometry of carbene **3** differs from the experimental X-ray structural analysis of the potential NHC precursor 2-chloro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione [28]. Two factors influence the discrepancy between the calculated (1.366) and experimental (1.441) bond length in carbene **3**. First, the calculated value was based on the M06-2X/cc-pVTZ theoretical level, whereas the experimental value was based on the X-ray crystallographic study, and the structure of a molecule may differ in the gas and solid phases [33, 34]. Second, the previous X-ray crystallographic analysis was performed on the potential NHC precursor 2-chloro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione. In the experiment, chlorine and hydrogen atoms were attached to the carbenic center. To investigate the effect of resonance on the N<sub>1</sub>-C<sub>5</sub> bond length, the new and previously calculated values are listed in Table 1 [9, 28]. Comparing the N<sub>1</sub>-C<sub>5</sub> bond lengths in **2–4** (Table 1) shows that the resonance between the lone pair on N<sub>1</sub> and the carbonyl group shortens the N<sub>1</sub>-C<sub>5</sub> bond length by changing the N<sub>1</sub>-C<sub>5</sub> bond from σ to partial double.

Table 2 shows the NBO analyses performed on carbenes **1–4**. The insertion of an oxalamide into the heterocyclic ring lowered the Lewis basicity of the carbenic center. For example, the energy of the lone pair of the carbenic carbon changed from -0.3114 eV in carbene **2** to -0.3530 eV in carbene **4**. The more negative the energy of the lone pair of the carbenic carbon, the less basic the carbene. A further change occurred from -0.3530 eV in carbene **4** to -0.3900 eV in carbene **3**. Furthermore, the addition of an oxalamide decreases the bond

**Table 1** The selected geometrical parameters of carbenes **1–4** (bond length in Å, bond angle in °)

	r[C <sub>2</sub> -N <sub>1</sub> (or N <sub>3</sub> )]	∠N <sub>1</sub> -C <sub>2</sub> -N <sub>3</sub>	r[N <sub>1</sub> -C <sub>5</sub> (N <sub>3</sub> -C <sub>4</sub> )]
1	1.360	100.4	1.385
	1.387 <sup>a</sup>	99.40 <sup>a</sup>	1.405 <sup>a</sup>
2	1.343	104.4	1.469
	1.365 <sup>a</sup>	103.8 <sup>a</sup>	1.499 <sup>a</sup>
3	1.366	104.2	1.390
	1.441 <sup>b</sup>	102.5 <sup>b</sup>	1.373 <sup>b</sup>
4	1.333 <sup>c</sup>	103.5	1.452 <sup>c</sup>
	1.377 <sup>d</sup>		1.388 <sup>d</sup>

<sup>a</sup> The previous B3LYP results in ref [9]

<sup>b</sup> X-ray structural analysis data for **1a** from ref [28]

<sup>c</sup> The C<sub>2</sub>-N<sub>1</sub> and N<sub>1</sub>-C<sub>5</sub> bond lengths in **4**, please see the atomic designation in Scheme 4

<sup>d</sup> The C<sub>2</sub>-N<sub>3</sub> and N<sub>3</sub>-C<sub>4</sub> bond lengths in **4**, please see the atomic designation in Scheme 4

**Table 2** The NBO analyses on carbenes **1–4**

	Bond order of C <sub>2</sub> -N <sub>1</sub> (or N <sub>3</sub> ) <sup>a</sup>	Bond order of N <sub>1</sub> -C <sub>5</sub>	Bond order of N <sub>3</sub> -C <sub>4</sub>	Hybrids of the lone pair on C <sub>2</sub>	Energy of the lone pair on C <sub>2</sub> <sup>b</sup>
1	1.286	1.129	1.129	sp <sup>1.03</sup> d <sup>0.00</sup> f <sup>0.00</sup>	-0.3289
2	1.315	0.9546	0.9547	sp <sup>1.20</sup> d <sup>0.00</sup> f <sup>0.00</sup>	-0.3114
3	1.214	1.046	1.046	sp <sup>1.02</sup> d <sup>0.00</sup> f <sup>0.00</sup>	-0.3900
4	1.385 <sup>c</sup> 1.160 <sup>d</sup>	0.9697	1.077	sp <sup>1.09</sup> d <sup>0.00</sup> f <sup>0.00</sup>	-0.3530

<sup>a</sup> The Wiberg bond index matrix in the NAO basis is adopted

<sup>b</sup> The values are in eV

<sup>c</sup> The C<sub>2</sub>-N<sub>1</sub> bond order in **4**, please see the atomic designation in Scheme 4

<sup>d</sup> The C<sub>2</sub>-N<sub>3</sub> bond order in **4**, please see the atomic designation in Scheme 4

order between C<sub>2</sub> and N<sub>1</sub> (or N<sub>3</sub>). For example, the bond order of C<sub>2</sub>-N<sub>1</sub> (or N<sub>3</sub>) decreased from 1.315 in carbene **2** to 1.160 in carbene **4**. This decrease can be explained by the resonance structure in Scheme 3, which hinders the strong interaction between the filled nitrogen 2p orbitals and the unoccupied carbenic 2p orbital (Scheme 2). Conversely, this resonance increases the bond order of the N<sub>3</sub>-C<sub>4</sub> or N<sub>1</sub>-C<sub>5</sub> bond (Table 2). The bond order is based on the method developed by Wiberg [35].

#### Comparing carbenes **1–4** in the singlet and triplet states

We then compared carbenes **1–4** in the S<sub>0</sub> and T<sub>1</sub> states, and Table 3 lists the optimized geometry of carbenes **1–4** in both states. Both the C<sub>2</sub>-N<sub>1</sub> (or N<sub>3</sub>) bond length and ∠N<sub>1</sub>-C<sub>2</sub>-N<sub>3</sub> of the heterocyclic carbene increased as it was excited from the

**Table 3** The geometrical parameters of carbenes **1–4** in S<sub>0</sub> and T<sub>1</sub> states (bond length in Å, bond angle in °)

Carbene	State	r[C <sub>2</sub> -N <sub>1</sub> (or N <sub>3</sub> )]	∠N <sub>1</sub> -C <sub>2</sub> -N <sub>3</sub>
1	S <sub>0</sub>	1.363	100.6
	T <sub>1</sub>	1.405	112.5
2	S <sub>0</sub>	1.343	104.4
	T <sub>1</sub>	1.400	115.5
3	S <sub>0</sub>	1.366	104.2
	T <sub>1</sub>	1.313	110.7
4	S <sub>0</sub>	1.333 <sup>a</sup> 1.377 <sup>b</sup>	103.5
	T <sub>1</sub>	1.386 <sup>a</sup> 1.393 <sup>b</sup>	111.2

<sup>a</sup> The C<sub>2</sub>-N<sub>1</sub> bond length in **4**, please see the atomic designation in Scheme 4

<sup>b</sup> The C<sub>2</sub>-N<sub>3</sub> bond length in **4**, please see the atomic designation in Scheme 4

$S_0$  to the  $T_1$  state, except in carbene **3**. In carbene **3**, the  $C_2-N_1$  (or  $N_3$ ) bond length decreased as it was excited from the  $S_0$  to the  $T_1$  state, and the  $\angle N_1-C_2-N_3$  concurrently increased. When exciting carbenes **1–4** from their  $S_0$  to  $T_1$  states, the bond angles  $\angle N_1-C_2-N_3$  of carbenes **1–4** increased. This behavior can be explained by the qualitative molecular orbital theory [36–39], in which linear geometry is expected to result in a smaller HOMO-LUMO energy gap than a bent geometry for a carbene bearing six valence electrons. Thus, a small HOMO-LUMO energy gap favors the triplet state [40, 41].

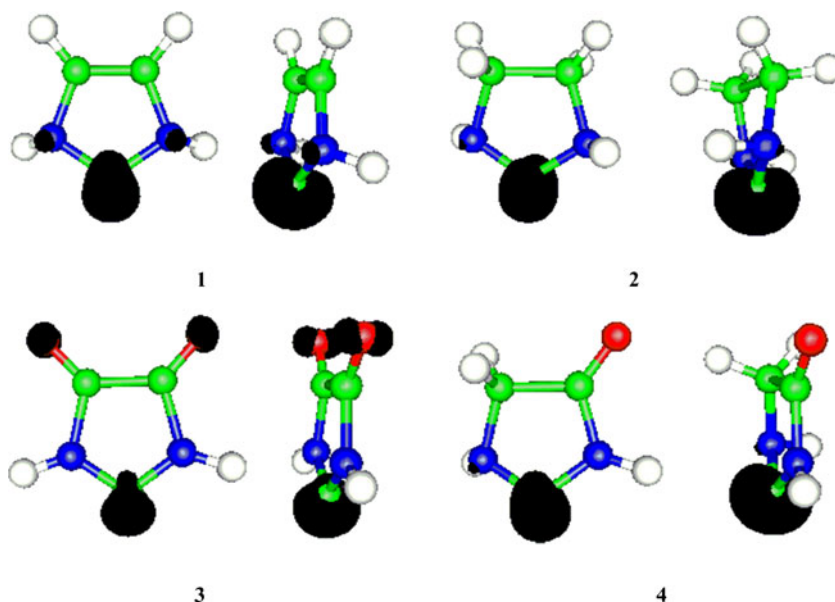
When including zero-point energy,  $E_{ST}$  is 83, 68, 43, and 66 kcal mol<sup>-1</sup> for carbenes **1**, **2**, **3**, and **4**, respectively. The M06-2X-calculated  $E_{ST}$  of **1** is consistent with the previous TCSCF, MP2, and B3LYP results [3, 7, 10]. Figure 1 shows the spin difference between the  $S_0$  and  $T_1$  states for the studied carbenes, indicating that the triplet states of the carbenes involve the transition from the  $\sigma$ -type lone pair of the carbenic centers to their  $\pi$ -type lone pair. The transition from the  $S_0$  to the  $T_1$  state in carbene **3** also involves the  $\pi$ -type p orbitals of the two oxygen atoms of the two C=O groups. Figure 1 shows that the maps were primarily developed using  $\pi$  orbitals. Our previous study of the thermodynamic stability of borylenes showed a similar trend: borylenes are isoelectronic to NHC [42]. Two possible low-lying unoccupied orbitals may involve the transitions from the  $S_0$  to  $T_1$  state for carbenes **1–4** (borylenes): the  $\pi$ -type lone pair of carbon (boron), and the delocalized  $\pi^*$  orbital around the five-membered ring. If the neighboring atom is a strong  $\pi$  donor (such as nitrogen), the  $\pi$ -type lone pair of carbon (boron) is lower in energy than the delocalized  $\pi^*$  orbital of the five-membered ring; then, the excitations of the carbenes (borylenes) from their  $S_0$  to  $T_1$  states involves the  $\sigma$ -type lone pair and  $\pi$ -type lone pair in carbon (boron).

## The dimerizations of carbenes **1–4**

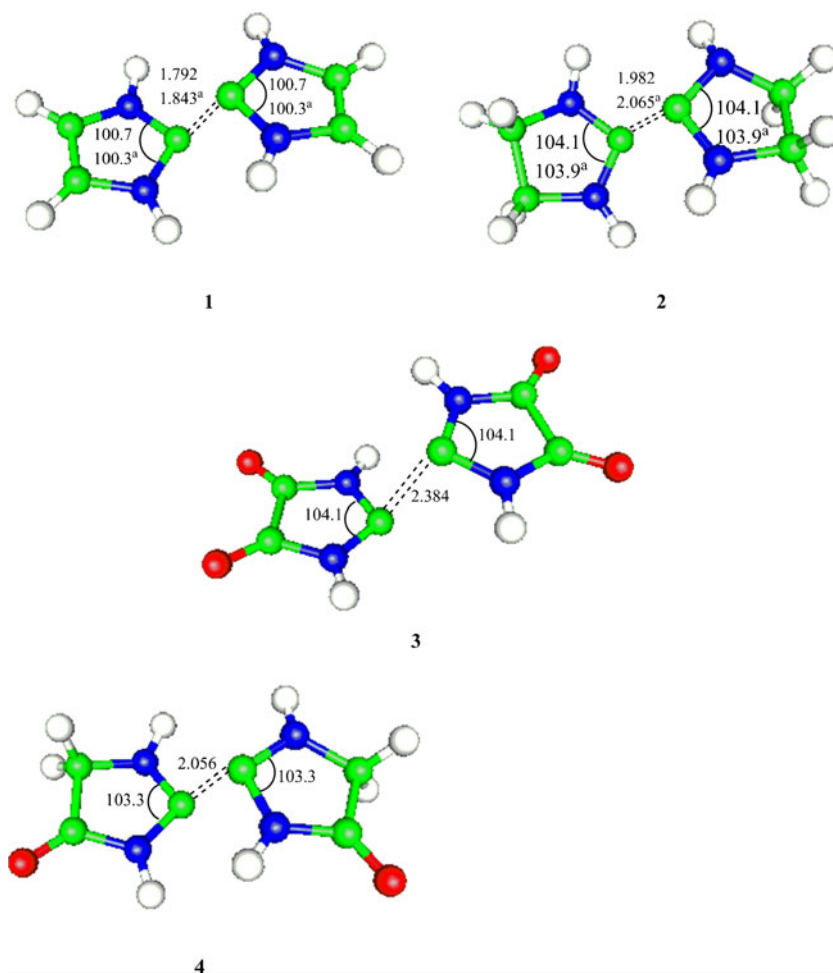
Figure 2 shows the optimized geometries of TSs for dimerizations of all examined carbenes. The previous B3LYP results of the TSs for carbenes **1** and **2** are included for comparison in Fig. 2 [10], which shows that the previous B3LYP results demonstrated longer C-C and C-N bond lengths for the TSs of the dimerization for carbenes **1** and **2** than the M06-2X results did.

Table 4 lists the converged geometrical parameters for the dimers of carbenes **1–4**, including the previous parameters for the dimers of carbenes **1–2** for comparison purposes [10]. The M06-2X-optimized bond order of the  $C_2-C_2'$  bond (Scheme 5) for carbenes **1–4** are summarized in Table 5. The Wiberg method indicates that the  $C_2-C_2'$  bonds for the dimers formed by carbenes **1–4** are all double-bonds [35]. The  $C_2-C_2'$  bond for the dimers formed by carbene **3** has the lowest bond order. Comparing the current M06-2X results and previous B3LYP results (Table 4) indicates that the M06-2X/cc-pVTZ theoretical level creates shorter bond lengths in the  $C_2-C_2'$  bonds of the dimers for carbenes **1** and **2**. However, both the M06-2X/cc-pVTZ and B3LYP/6-31G\* theoretical levels provide the same angles:  $\angle N_1-C_2-N_3$  ( $\angle N_1'-C_2'-N_3'$ ); further comparison shows that the dihedral angle  $\angle N_3-C_4-C_5-N_1$  calculated using the M06-2X functional for carbenes **1** and **2** shows a larger deviation from zero than does that calculated using B3LYP as they dimerize. The dimers formed in the studied carbenes deviated from planarity. In 1987, Trinquier et al. used simple valence bond modeling to show that the deviation from planarity of some double bonds is correlated with the singlet-triplet splitting of the interacting fragments forming the double bond [43]. Table 4 lists  $E_{ST}$  of all examined carbenes, showing that the distortions from

**Fig. 1** The spin difference maps for carbenes **1–4** in a triplet manifold (green for carbon, blue for nitrogen, and white for hydrogen; isodensity value=0.05)



**Fig. 2** The optimized geometries of TSS for four dimerization reactions (bond lengths in Å, bond angle in °). a. The previous B3LYP results [10]



planarity of the dimers are related to their  $E_{\text{ST}}$ s and the aromaticity of the five-membered rings.

**Table 4** The converged geometrical parameters and  $E_{\text{ST}}$ s for the dimers of **1**–**4**. (Bond length in Å, bond angle in °; the energetic values are in kcal mol<sup>-1</sup>)

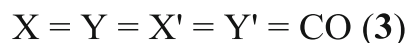
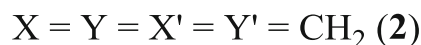
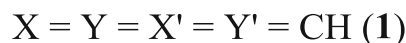
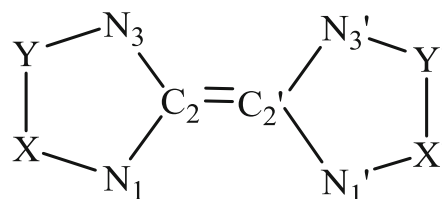
	$r(\text{C}_2\text{-C}_2')$ <sup>a</sup>	$\angle\text{N}_1\text{-C}_2\text{-N}_3$ $\angle\text{N}_1'\text{-C}_2'\text{-N}_3'$ <sup>a</sup>	$\angle\text{N}_1\text{-X-Y-N}_3$ $\angle\text{N}_1'\text{-X'-Y'-N}_3'$ <sup>a</sup>	Bond order of $\text{C}_2\text{-C}_2'$ <sup>b</sup>	$E_{\text{ST}}$
<b>1-1</b>	1.327 (1.341)	108.9 (108.9) 108.9 (108.9)	5.966 (-2.900) 6.005 (-2.900)	1.664	83
<b>2-2</b>	1.324 (1.337)	109.4 (109.4) 109.4 (109.4)	39.57 (0.0) 39.57 (0.0)	1.686	68
<b>3-3</b>	1.332	106.0 106.0	-4.928 -4.932	1.597	43
<b>4-4</b>	1.326	107.7 107.7	9.141 9.145	1.657	66

<sup>a</sup>Please see the atomic designations in Scheme 5

<sup>b</sup>The Wiberg bond index matrix in the NAO basis is adopted

<sup>c</sup>The values in parentheses are the previous B3LYP results in ref [10]

Table 5 shows the calculated barriers ( $E_a$ ),  $E_{\text{ST}}$ , and heats of complexation ( $\Delta E$ ) for all mentioned complexes, in addition to the previous B3LYP results [10], indicating that the current M06-2X results agree with previous results [10]. According to Hoffmann et al. [44], the dimerization of the simplest carbene,



**Scheme 5** The atomic designations for the dimers of carbenes **1**–**4**



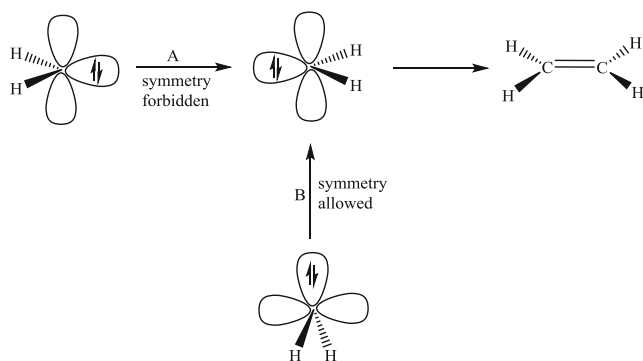
**Table 5** The calculated barriers ( $E_a$ ),  $E_{ST}$ , and the heats of dimerizations ( $\Delta E$ ; all in kcal mol<sup>-1</sup>), for all mentioned dimers

	$E_a$	$\Delta E$	$E_{ST}$
<b>1-1</b>	22	-12.0	83
	21 <sup>a</sup>	-9.2 <sup>a</sup>	82 <sup>a</sup>
<b>2-2</b>	9.6	-39	68
	11 <sup>a</sup>	-33	69 <sup>a</sup>
<b>3-3</b>	- <sup>b</sup>	-71	43
<b>4-4</b>	5.7	-47	66

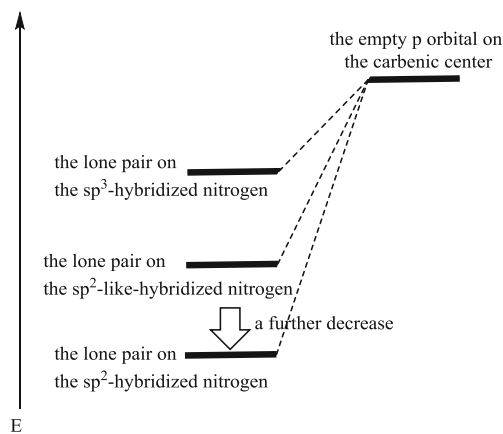
<sup>a</sup> The previous B3LYP results in ref [10]

<sup>b</sup> The barrier height is negligible

methylene, cannot proceed by a least motion pathway (A in Scheme 6). In 1985, Ohta and Morokuma found that the dimerization of a methylene in the triplet manifold proceeds without a barrier from either the least motion (A) or the nonleast motion (B) pathways; the dimerization of a methylene in the singlet state proceeding using either the A or B pathway may reach a Rydberg excited state of ethylene with the symmetry of the ground state [45]. Whereas the ground state in methylene is a triplet with  $E_{ST} \approx -9.0$  kcal mol<sup>-1</sup> [46], the species C(NH<sub>2</sub>)<sub>2</sub> and C(NMe<sub>2</sub>)<sub>2</sub> are found to be singlets in the ground state with an  $E_{ST}$  of 53 and 41 kcal mol<sup>-1</sup>, and their triplet states are not expected to participate in the dimerization process [47]. In agreement with these findings [44, 45, 47], Thiel et al. examined a series of NHCs, discovering that large  $E_{ST}$  values tend to be inert with respect to dimerization [7]. The results of the current study were consistent with those of Thiel et al. [7]; the smaller the  $E_{ST}$  of a heterocyclic carbene containing nitrogen, the more exothermic the dimerization. Our results are consistent with the Hammond postulate [48]: the larger the exothermicity of the dimerization, the lower the barrier height it must overcome. Table 5 shows that the insertion of an oxalamide fragment lowers  $E_{ST}$  of a heterocyclic carbene containing nitrogen. For example,  $E_{ST}$  of the carbene changes from 68 kcal mol<sup>-1</sup> to 66 kcal mol<sup>-1</sup> when carbene 2 changes to carbene 4. A further decrease is apparent in  $E_{ST}$ s as carbene 4 changes to carbene 3; this may result from the interaction between the filled nitrogen 2p orbitals and unoccupied carbenic 2p orbital, which is weakened by resonance (Scheme 3). Therefore, the calculated bond order of the N<sub>1</sub>-C<sub>5</sub>

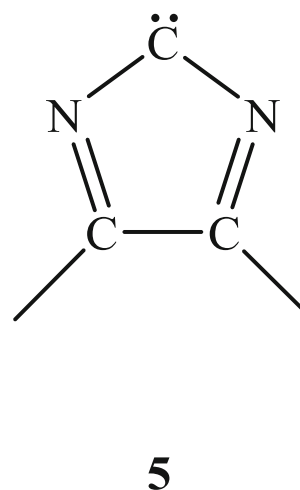


**Scheme 6** Least motion (a) and nonleast motion (b) pathways in the dimerization of two methylenes



**Scheme 7** The schematic representation of the energetic differences in the interaction between the empty  $p_\pi$  orbital of carbon and the full-filled  $p_\pi$  orbital of nitrogen in carbenes 2 and 3

(N<sub>3</sub>-C<sub>4</sub>) increases from 0.9546 in carbene 2 to 1.046 in carbene 3. Table 2 shows that the nitrogen element in an amino group is sp<sup>3</sup> hybridized (e.g., N<sub>1</sub> or N<sub>3</sub> in carbene 2), whereas the nitrogen element in an amido group is sp<sup>2</sup>-like hybridized (e.g., N<sub>1</sub> or N<sub>3</sub> in 3). The higher the s component in an atomic hybridized orbital, the lower the energy of that hybridized orbital. Scheme 7 shows that the lone pair on nitrogen in carbene 3 is lower in energy than is that in carbene 2, causing a weak orbital interaction between the nitrogen's lone pair and the empty carbenic lone pair. Furthermore, a decrease in the strength of the interaction should have occurred as the hybridization of N<sub>1</sub> or N<sub>3</sub> changed from sp<sup>2</sup>-like to sp<sup>2</sup>. Therefore,  $E_{ST}$  and the heat of the dimerization of a hypothesized carbene 5 (Scheme 8) was calculated for comparison with carbenes 2 and 3. Table 6 shows that  $E_{ST}$  of 5 is expected to be lower than that of carbenes 2 and 3 because the interaction between the filled lone pair of nitrogen (N<sub>1</sub> or N<sub>3</sub>) and the unfilled lone pair of carbon (C<sub>2</sub>) is the lowest among the three carbenes in 5; thus, the exothermicity of the dimerization for carbene 5 is the largest among the three carbenes.



**Scheme 8** The skeleton of the hypothesized carbene 5

**Table 6** The calculated  $E_{\text{ST}}$ s and the reaction enthalpies for dimerization (both in kcal mol<sup>-1</sup>) of **2**, **3**, and **5**

Carbene	$E_{\text{ST}}$	$\Delta E$
<b>2</b>	68	-39
<b>3</b>	43	-71
<b>5</b>	1.8	$-1.4 \times 10^2$

## Conclusions

The following conclusions can be drawn from the calculations on the dimerizations of the saturated NHC (carbene **2**) and N,N'-diamidocarbene (carbene **3**):

- (1) Inserting an oxalamide into the heterocyclic ring to form an N,N'-diamidocarbene lowers the Lewis basicity of the carbenic center.
- (2) Because of the resonance between the nitrogen's lone pair and the carbonyl group, the interaction between the filled lone pair on nitrogen and unfilled lone pair of the carbenic center is lower in the carbenes containing one or two amido groups (carbenes **3** and **4**) than it is in the NHC (carbene **2**). This weak orbital interaction causes the calculated bond order between N<sub>1</sub> (N<sub>3</sub>) and C<sub>2</sub> to decrease between carbene **2** and carbene **4**. A further decrease occurs as carbene **4** changes to carbene **3**.
- (3) Because the orbital interaction shown in Scheme 2 is lower in carbene **4** and carbene **3** than it is in carbene **2**, the singlet-triplet splitting of the carbene decreases as carbene **2** changes to carbene **4** or carbene **3**. Therefore, the barrier height of dimerization is lower for carbene **4** or carbene **3** than it is for carbene **2**. The exothermicity of dimerization is larger for carbene **4** or carbene **3** than it is for carbene **2**, which is in accordance with the Hammond postulate.

N,N'-diamidocarbenes have shown significant synthetic utility [49–52]. For example, Lee et al. discovered that N,N'-diamidocarbenes are ambiphilic and can behave as strong electrophiles and nucleophiles [49]. We suggest that our results provide rationalization for the reactivity of N,N'-diamidocarbenes.

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