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Substituted six-membered ring carbenes: the effects of amino and cyclopropyl groups through DFT calculations

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ABSTRACT

DFT calculations are employed to compare and contrast six-membered ring carbenes including 1,3-dimethyltetrahydropyrimidin-2-ylidene (**1a**), 1-methyl-3-cyclopropyltetrahydropyridine-2-ylidene (**2a**), and 1,3-dicyclopropylcyclohexane-2-ylidene (**3a**) as well as their unsaturated analogues **1b**, **2b**, **3b**, and **2c**. The amino groups exert singlet–triplet energy separation (ΔE_{s-t}) of 60.9 kcal/mol to **1a** while cyclopropyls induce a ΔE_{s-t} of 14.8 kcal/mol to **3a**. The simultaneous presence of amino and cyclopropyl in **2a** leads to a ΔE_{s-t} of 43.3 kcal/mol. Unsaturation slightly increases the ΔE_{s-t} of **1a** and **3a** but not that of **2a**. Our thermodynamic, kinetic, and reactivity results are compared with those of synthetic five-membered ring *N*-heterocyclic carbenes.

1. Introduction

The electronic structure of carbenes[1] is affected by the mesomeric and/or inductive effects of substituents attached to the divalent carbon.[2] Two kinds of substituents, which were mainly employed in the synthesis of carbenes are amino and alkyls. Due to the stabilization of the carbene center by the π-electron donating and σ-electron accepting effects of two adjacent amino groups, the first stable singlet *N*-heterocyclic carbene (NHC) was synthesized in 1991.[3] Since then, the usage of strong π-donor groups has become a common strategy for the stabilization of singlet carbenes.[4] However, through a literature survey, one can find characterization of a singlet dialkylcarbene prior to the birth of NHCs. In 1989, Ammann et al. reported the spectroscopic characterization of dicyclopropyl carbene generated from the irradiation of dicyclopropyldiazirine in a matrix of N_2 at 6 K.[5] This singlet carbene is stabilized via the interaction of the occupied Walsh orbitals with the empty carbene *p* orbital.[6–8] However, in comparison with the interaction of amino lone pair with the carbene center in NHCs, the cyclopropyl group can logically be considered as a weak π-electron donor group. On the other hand, the studies of Bertrand et al. on cyclic aminoalkylcarbenes (CAAC) showed that only one amino group is sufficient for the stabilization of a singlet carbene center.[9] Also, applying bulky substituents, such as cyclohexyl group at the α position of the carbene center provides compounds with stabilities comparable to those of common NHCs. Our recent computational study showed that replacing the cyclopropyl by cyclohexyl in the routine CAACs engenders singlet state with higher stabilization.[10] This creates a unique combination between two distinct π-electron donor groups, a strong amino group on one side and a weak cyclopropyl group on the other, that prompted us to design a study, which covers diaminocarbenes, aminocyclopropyl carbenes, and dicyclopropylcarbenes. On the other hand, due to the importance of the divalent angle in the determining of multiplicity and stability of carbenes,[11,12] it is valuable to pay more attention to carbenes with ring sizes other than typical five-membered ones.[13] Hence, the six-membered 1,3-dimethyltetrahydropyrimidin-2-ylidene (**1a**) ring, synthesized by Bertrand et al.,[13] is selected as the parent diaminocarbene and extended to the corresponding aminocyclopropyl and dicyclopropylcarbenes (**2a**, **3a**, **1b**, **2b**, **3b**, and **2c**) (Scheme 1).

The thermodynamic and kinetic stabilities as well as reactivities of the species will be discussed through appropriate criteria using DFT calculations. A brief comparison is also made among these results with those of some stable synthesized NHCs A–E (Scheme 2).

2. Computational methods

Full geometry optimizations are accomplished without any symmetry constraints using hybrid functional B3LYP[14–16] and the 6-31+G* basis set, employing the Gaussian 98 code.[17] The applied basis set is comprised of Pople's well known 6-31G* basis set[18,19]

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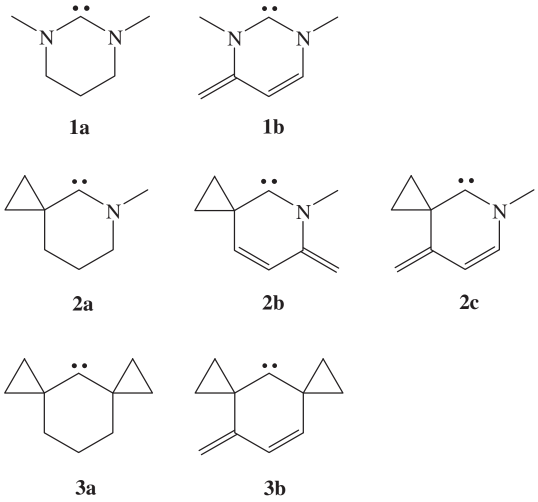
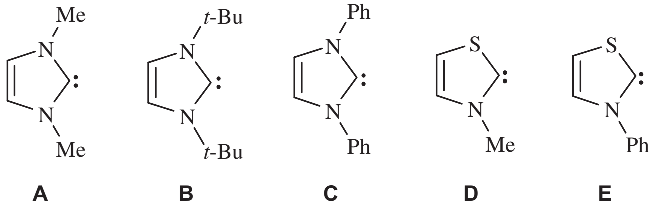


Scheme 1.



Scheme 2.

and an extra plus due to the importance of diffuse functions.[20,21] To obtain more accurate energetic data, single point calculations are performed at B3LYP/AUG-cc-pVTZ.[22] Vibrational frequencies are calculated to establish the nature of obtained stationary points as true minima.[23] Also, the NBO[24] population analysis on optimized structures is accomplished at B3LYP/6-311++G**.

The nucleophilicity index, N, which was recently introduced by Domingo et al.,[25] is calculated as $N{=}E_{\mathrm{HOMO(Nu)}}{-}E_{\mathrm{HOMO(TCNE)}}$, where tetracyano ethylene (TCNE) is chosen as the reference. The global electrophilicity, ω,[26] is also calculated following the expression, $\omega{=}(\mu^2/2\eta)$, where μ is the chemical potential ($\mu\approx(E_{\mathrm{HOMO}}+E_{\mathrm{LUMO}})/2$) and η is the chemical hardness ($\eta{=}E_{\mathrm{LUMO}}{-}E_{\mathrm{HOMO}}$).[27]

3. Results and discussion

1,3-Dimethyltetrahydropyrimidin-2-ylidene (**1a**), 1-methyl-3-cyclopropyltetrahydropyridine-2-ylidene (**2a**), and 1,3-dicyclopropyl cyclohexan-2-ylidene (**3a**) (Scheme 1) are selected as the representative carbenes to compare and contrast thermodynamic and kinetic stabilities as well as reactivities of these species. The same discussions is also made among their corresponding unsaturated counterparts (**1b**, **2b**, **3b**, and **2c**).

3.1. Thermodynamics

3.1.1. Singlet–triplet energy separations through optimized geometries. The first carbene structures studied are diaminocarbenes **1a** and **1b**. A typical tetrahydropyrimidine shows a chair conformation, N–C bonds of 1.457 Å (R_{CN}), N–C–N angle of 111.89° (α) and pyramidalization angle (γ, Table 1)[28] of 25.57°. Singlet (s) and triplet (t) states of **1a**, carbenes derived from tetrahydropyrimidine, have two adjacent amino groups, which are well known for significant singlet state stabilization through π-donating/σ-accepting interactions (Scheme 3).

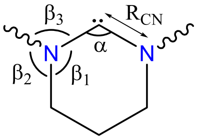
Like tetrahydropyrimidine, the optimized structure of **1a**(t) is a chair conformation with a plane of symmetry bisecting the structure. However, the R_{CN} decreases to 1.393 Å (Table 1) indicating partial π-bonding (i.e., triplet stabilization through the amino group!). It should also be noted that our calculated data on the N–C bond length (R_{CN}) and N–C–N divalent angle (α) of **1a**(s) are consistent with those in the crystal structure of a comparable carbene structure, 1,3-diisopropyl-3,4,5,6-tetrahydropyrimid-2-ylidene in a dimeric form of its potassium complex ($R_{\mathrm{CN}}{=}1.345$ Å, $\alpha{=}116.3°$[29]).

The divalent angle of 120.45° is consistent with the nature of a triplet state. Eventually, the pyramidalization angle γ of **1a**(t) reduces to 19.83°. As stated by Alder, the smaller γ is, the more effective nitrogen's lone pair interaction with the carbene ($n\rightarrow p$) is.[28] The geometry of **1a**(s) significantly deviates from that of tetrahydropyrimidine and adopts a half-chair conformation with a plane of symmetry, which places two amino groups and the carbene center in the same plane. Due to the decrease of γ to 0°, this geometry is anticipated to permit the highest possible interaction of the nitrogen lone pair with the empty carbene p orbital. The shortening of R_{CN} to 1.351 Å is accompanied with this prediction and shows the high $n\rightarrow p$ stabilization (Table 1). The stabilization of the carbene center by substituents can be revealed through its

Table 1
The principal geometry parameters of the singlet (s) and triplet (t) carbenes at B3LYP/6-31+G* (for abbreviations see Scheme 2)

Structure	Symmetry	R_{CN}, R_{CC}	α	γ[c]
1a(s)	C_2	1.351	115.84	0
1a(t)	C_2	1.393	120.45	19.83
1b(s)[a]	C_s	1.358 (1.360)	114.61	0 (0)
1b(t)[a]	C_1	1.378 (1.389)	118.76	8.24 (0)
2a(s)	C_1	1.321, *1.483*	115.66	0
2a(t)	C_1	1.383, *1.464*	122.27	14.93
2b(s)	C_s	1.334, *1.472*	115.50	0
2b(t)	C_1	1.378, *1.462*	123.07	1.90
2c(s)	C_s	1.332, *1.477*	114.88	0
2c(t)	C_1	1.362, *1.458*	124.05	1.80
3a(s)	C_s	*1.448*	115.59	
3a(t)	C_s	*1.455*	126.55	
3b(s)[b]	C_s	*1.445* (*1.446*)	115.15	
3b(t)[b]	C_1	*1.451* (*1.452*)	127.77	

[a] Two different nitrogens lead to two different values for R_{CN} and γ.
[b] Two different cyclopropyls lead to two different values for R_{CC}.
[c] Based on Alder's definition 'the pyramidalization on nitrogen is measured as $\gamma{=}360{-}(\beta_1{+}\beta_2{+}\beta_3)$: $\gamma{=}0$ indicates a planar nitrogen; the larger γ, the more pyramidalized nitrogen'.[28]



Scheme 3.

Table 2
Calculatedthermodynamic data (in kcal/mol) for the studied carbenes under studied at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G* and NBO atomic charges on the singlet and triplet carbenes at B3LYP/6-311++G**//B3LYP/6-31+G*

Structure	$\Delta E_{\mathrm{s-t}}$	ΔE_{dim}	$\Delta E^{\ddagger}$	$^1\mathrm{C}_{\mathrm{carbene}}$	$^3\mathrm{C}_{\mathrm{carbene}}$
1a	60.9	−13.6	—	0.161	0.360
1b	63.3	−16.0	—	0.188	0.336
2a	43.3	−36.0	27.2	0.068	0.253
2b	43.1	−43.9	22.8	0.090	0.289
2c	40.2	−50.5	18.7	0.088	0.320
3a	14.8	−86.5	9.7	0.002	0.194
3b	17.9	−89.3	6.8, *9.4*	0.016	0.214

more negative or less positive partial atomic charge.[30] The lower positive atomic charge on the carbene center of **1a**(s) compared to the corresponding triplet indicates its stabilization by two amino groups (0.161 vs 0.360) (Table 2).

In summary, we observe both singlet and triplet stabilization effects of the amino groups in **1a** with a more pronounced effect on the former. A close investigation of molecular orbitals of **1a**(s) reveals such interactions in HOMO-1 (HOMO and LUMO indicate the occupied σ and empty *p* orbitals of singlet carbene center, respectively) (Fig. 1).

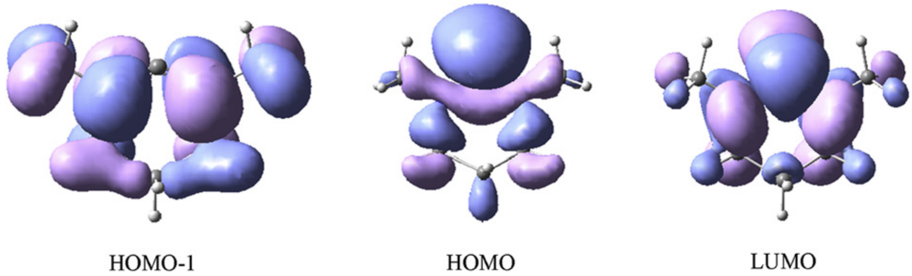


Fig. 1. The molecular orbitals of **1a**(s).

Therefore, these effects lead to the singlet–triplet energy separation ($\Delta E_{s-t}=E_t-E_s$) of 60.9 kcal/mol for **1a** (Table 2). Transforming **1a** to an unsaturated species necessitates introducing one endocyclic and one exocyclic double bond to the structure, resulting in planar **1b** (Table 1). The two different R_{CN} values of **1b**(s) appear longer than those of **1a**(s). This may convey the smaller stabilizing effect of amino groups in the former. The increase of the carbene atomic charge from 0.161 to 0.188 in **1a**(s) to **1b**(s) shows that the stabilizing effect of amino groups slightly decreases under the effect of unsaturation. This change is alongside the increase of R_{CN} that was already mentioned (Table 1). It is related to the conjugation of nitrogen lone pairs with double bonds, which leads to the slight decrease in $n \rightarrow p$ interaction.

The second carbene structures studied are aminocyclopropyl carbenes **2a**, **2b**, and **2c**. The inclusion of a cyclopropyl substituent leads to the stabilization of singlet carbenes possibly through the interaction of occupied Walsh orbital with the empty carbene *p* orbital ($W \rightarrow p$).[6] Consistent with this idea, the bond length of **2a**(s) is shorter than a typical single C–C bond (1.483 Å vs 1.540 Å). Moreover, this interaction is also observable in the HOMO-2 of **2a**(s) (Fig. 2).

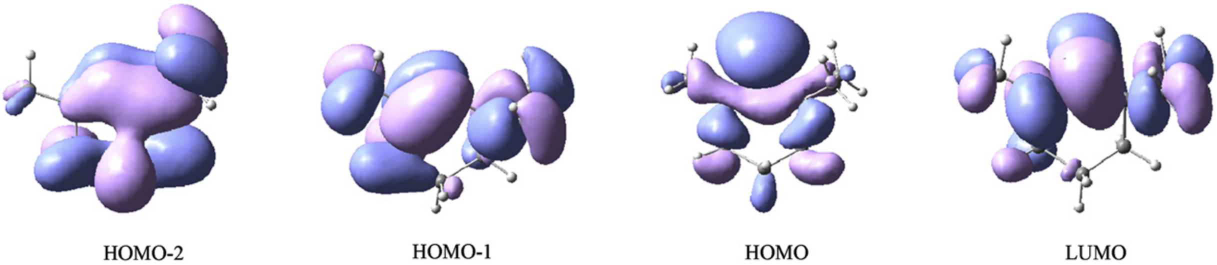


Fig. 2. The molecular orbitals of **2a**(s).

In the study of bond lengths, R_{CN} in **2a**(s) is shorter than **1a**(s) by 0.030 Å. It seems that the amino group has a higher stabilizing effect in the former compared to the latter. Consequently, addition of the second strong π-donor amino group reduces the stabilizing effect of the first one in **2a**(s) through so-called 'cross-conjugation'. Inspecting the HOMO-1 orbitals of **2a**(s) and **1a**(s) indicates more intense $n \rightarrow p$ interaction in the former (Fig. 2).

The electronic repulsion between the nitrogen's lone pair and carbene 2*p* solo electron in **2a**(t) leads to the lengthening of R_{CN} (1.383 Å vs 1.321 Å). This phenomenon is along with the shortening of R_{CC} (1.464 Å vs 1.483 Å), due to the lower repulsion of σ bonding orbitals of cyclopropyl compared to nitrogen's lone pair. Apparently, the absence of an electronegative nitrogen atom induces less positive atomic charges on the carbene centers of **2a**–**c**. Again unsaturation increases the atomic charge from 0.068 in **2a** to about 0.089 in **2b** and **2c**. This geometrical data results in the ΔE_{s-t} of 43.3 kcal/mol for **2a**, which is not affected by the unsaturation in **2b**. The other possible unsaturated **2c** shows R_{CN} and R_{CC} similar to those of **2b** but with a decreased ΔE_{s-t} of 40.2 kcal/mol.

The third carbene structures in this study are dicyclopropylcarbenes **3a** and **3b**. It seems that the substitution of two cyclopropyls at the α position to the carbene center increases the stabilizing effect of $W \rightarrow p$ interaction on singlet state (see HOMO-2 in Fig. 3) since the R_{CC} bond length of 1.483 Å in **2a**(s) is decreased to 1.448 Å in **3a**(s) (Table 1).

Also, the lower positive atomic charge on the carbene center of **3a**(s) compared to **3a**(t) indicates its stabilization by two cyclopropyl groups (0.002 vs 0.194) (Table 2). However, the overall stabilizing effect of two cyclopropyl on the singlet state appears in the ΔE_{s-t} of 14.8 kcal/mol. This moderate stabilization effect is near to that of characterized acyclic dicyclopropyl carbene (with ΔE_{s-t}=15.4 kcal/mol at the same level based on our calculations). The R_{CC} lengths do not considerably change during unsaturation, but an increase is observed in the calculated ΔE_{s-t} of 17.9 kcal/mol for **3b**.

3.1.2. *Stabilizing effects through isodesmic reactions.*

Different stabilizing factors are discussed in terms of isodesmic reactions, which are capable of distinguishing between singlet and triplet states. The effect of two amino groups on singlet (ΔE_s) and triplet (ΔE_t) carbene centers of **1a** is shown in isodesmic reaction 1 (Scheme 4).

Confirming the discussions made through geometry parameters, this reaction shows the stabilization of both singlet and triplet states with a much more pronounced effect on the former. On this basis, **1a**(s) and **1a**(t) are stabilized by 65.1 kcal/mol and 2.7 kcal/mol, respectively. This is in contrast to the suggestion of Nemirowski and Schreiner that the classical π-donor/σ-acceptor substituents, such as amino group, stabilize the singlet and destabilize the triplet states of a carbene.[30] Nevertheless, the high structural similarities in two sides of our isodesmic reactions make them

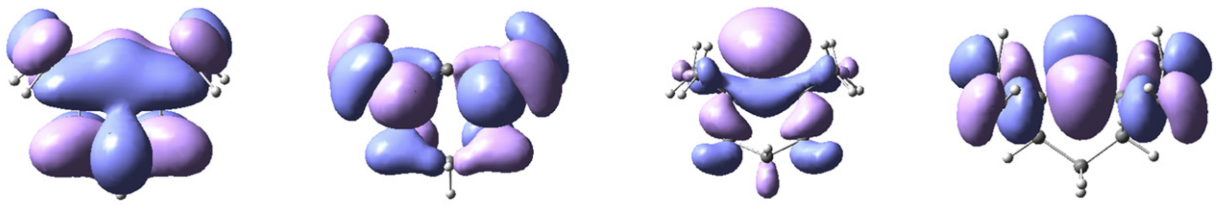
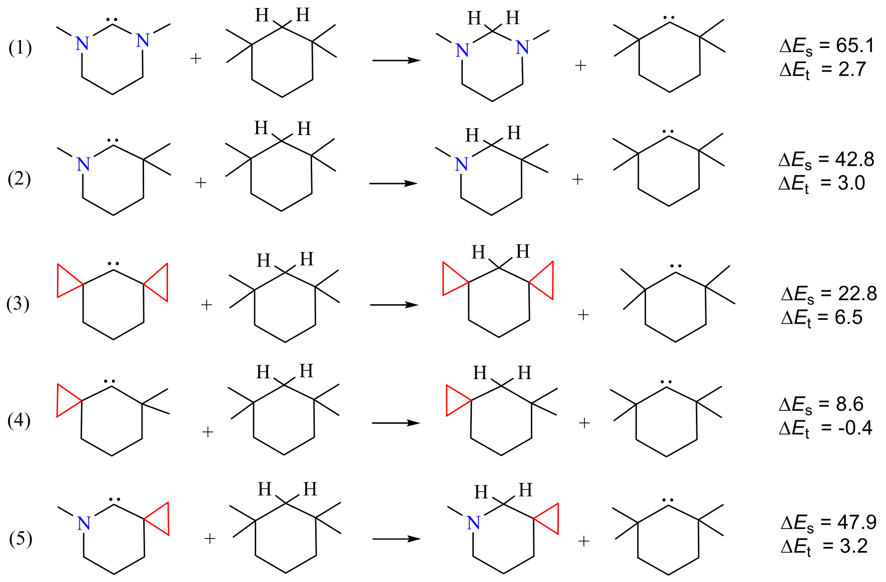

HOMO-2 HOMO-1 HOMO LUMO

Fig. 3. The molecular orbitals of **3a**(s).



Scheme 4. The energy values are in kcal/mol.

reliable criteria for analyzing the effects of monoheteroatom substitutions.

Is the stabilization effect of two amino groups equal to the algebraic summation of one? The isodesmic reaction 2 may provide an answer to this question. The reaction shows that the $n \rightarrow p$ interaction of one amino group stabilizes **1a**(s) by 42.8 kcal/mol, which is 10.2 kcal/mol more than half of the stabilizing effect of two amino groups. It seems that the first $n \rightarrow p$ interaction occupies the 2p orbital of the carbene center to the extent that it does not permit the maximum $n \rightarrow p$ interaction of the second amino group. The other result from this reaction is the slightly higher stabilization of one amino group on the triplet state (ΔE_t=3.0 kcal/mol).

On the other hand, based on the isodesmic reaction 3, two cyclopropyl groups demonstrate stabilizing energy of 22.8 kcal/mol in **3a**(s), which is significant for two alkyl groups. It seems that the presence of the second cyclopropyl enhances the stabilizing effect of the first one as in the case of $W \rightarrow p$ interaction. This phenomenon is repeated for **3a**(t), which is not affected with one cyclopropyl but is stabilized by 6.5 kcal/mol with two cyclopropyls. The simultaneous presence of one amino and one cyclopropyl exerts 47.9 kcal/mol stabilization to **2b**(s) (isodesmic reaction 5). Because the summation of ΔE_S values of isodesmic reactions 2 and 4 equals 51.4 kcal/mol, it can be said that the presence of the amino group reduces the stabilizing effect of the cyclopropyl group by about 3.5 kcal/mol.

Based on these isodesmic reactions, we conclude that in the stabilization of a carbene center of a six-membered ring, two strong π-donor amino groups weaken each other but two weak π-donor cyclopropyls fortify each other. On the other hand, the simultaneous presence of both amino and cyclopropyl groups leads to a decrease of the stabilizing effect of cyclopropyl.

3.2. Kinetics

3.2.1. Dimerization. Dimerization has been considered as one of the fundamental aspects of carbene behavior. In the classic dimerization mechanism for singlet carbenes, the filled σ orbital of each carbene is anticipated to interact with the empty p orbital on the other.[31] Recently, Alder et al. have shown that most diaminocarbenes dimerize through proton-catalyzed or possibly metal-ion-catalyzed routes.[12] Hence, they have concluded that in the absence of appropriate catalyst several diaminocarbenes including **1a** do not dimerize within a reasonable time frame at ambient temperature in THF. This is in accord with the CGMT model where doubly bonded dimers are expected to be formed only when the sum of the ΔE_{s-t} values of two interacting carbenes ($\sum \Delta E_{s-t}$) is smaller than the corresponding double bond energy (expressed based on ΔE_{dim} values).[32] The $\sum \Delta E_{s-t}$ values for diaminocarbenes **1a** and **1b** are multiple times of the double bond energies (121.8 vs 13.6 and 126.6 vs 16.0 kcal/mol, respectively), which strongly reduces the probability of dimerization (Table 2).

In comparison, the double bonds of the dimers of aminocyclopropyl carbenes are stronger than those of diaminocarbenes due to the higher exothermicity of their dimerizations. The strongest double bond of aminocyclopropyl carbenes belongs to the dimer of **2c** (with ΔE_{dim}=−50.5 kcal/mol) (Table 2). However, the calculated $\sum \Delta E_{s-t}$ for **2c** is 80.4 kcal/mol, which appears to be 29.9 kcal/mol larger than the corresponding double bond energy, which indicates that this carbene does not dimerize. In contrast, the $\sum \Delta E_{s-t}$ values of **3a** and **3b** (29.6 and 35.8 kcal/mol, respectively) are smaller than the corresponding double bond energies (about 87.9 kcal/mol), therefore these carbenes could theoretically dimerize.

3.2.2. Kinetic stability through 1,2-C shifts. Cyclopropyl carbene is one of the few carbenes, which prefer a 1,2-*C* shift over a 1,2-*H* shift.[7,8] Hence, from a kinetic viewpoint, the most probable rearrangement affect the stability of the singlet *syn* cyclopropylcarbenes is the ring expansion to the corresponding cyclobutenes. The energy barrier ($\Delta E^{\ddagger}$) of such a rearrangement for cyclopropylcarbene, based on our calculations, is calculated to be 4.1 kcal/mol, which is lower than 5.0 kcal/mol reported by Shevline and McKee at HF/6-31G level of theory.[8] Interestingly, in the presence of the amino group in **2a** this barrier is increased to the value of 27.2 kcal/mol (Table 2). This is due to the $n\rightarrow p$ interaction, which partially occupies the empty carbene 2*p* orbital and prevents the attack of C–C σ bond. As mentioned earlier, unsaturation decreases the $n\rightarrow p$ interaction and hence is anticipated to decrease the energy barrier for 1,2-*C* shift. However, **2b** and **2c** still show $\Delta E^{\ddagger}$s of 22.8 and 18.7 kcal/mol, respectively (Table 2).

On the other hand, substitution of the second cyclopropyl increases $\Delta E^{\ddagger}$ value from 4.1 kcal/mol for cyclopropylcarbene to 9.7 kcal/mol for **3a** due to the concurrent $W\rightarrow p$ interaction. The calculated barriers for ring opening of two cyclopropyl groups appear different in **3b** due to the unsaturation. Here, we are again encountering with an increase of $\Delta E^{\ddagger}$ value to 6.8 kcal/mol (for the cyclopropyl by the *exo* double bond) and 9.4 kcal/mol (for the cyclopropyl by the *endo* double bond).

3.2.3. Reactivity in terms of nucleophilicity, electrophilicity, and proton affinity. The excellent σ-donating property of NHCs makes them suitable ligands for transition metals in organometallic synthesis.[33] The same effect of amino alkylcarbenes[9] encourages the investigation of the nucleophilicity and the electrophilicity of these carbenes (**1a**, **2a**, **3a**, **1b**, **2b**, **3b**, and **2c**). On the other hand, the basicity of NHCs and the acidity of the corresponding imidazolium salts have been studied by several groups.[34–37] The gas-phase proton affinity of carbenes (PA, the negative of the enthalpies of their protonation reactions) is an accepted criterion to discuss the basicity of carbenes.[38] Hence, both the nucleophilicity (N) and the global electrophilicity (ω) indices as well as the PAs for the singlet ground state divalent species are calculated at B3LYP/6-311++G**//B3LYP/6-31+G* level to reach a better understanding of their reactivities (Table 3). To find a practical comparison, the same data for some synthesized NHCs are also presented.

From saturated diaminocarbenes to dicyclopropylcarbenes a slight increase in the nucleophilicities is observed with the highest nucleophilicity for **3a** (N=4.41 au). This can be attributed to the lower electronegativity of the cyclopropyl groups compared to amino groups. On the other hand, unsaturation decreases the nucleophilicity of all carbenes and among them, the highest nucleophilicity value is observed for dicyclopropyl carbene **3b** (4.12 au). While **1a** and **2a** show similar electrophilicities of about 0.81 au, this increases to 1.43 au for **3a**. Due to the increase of electrophilicity through unsaturation, **3b** is the most electrophilic species (with ω=1.63 au). Subsequently, it is found that changing from diamino to dicyclopro pylcarbenes there is no considerable difference in basicity.

Table 3

The nucleophilicity (N) and the global electrophilicity (ω) indices and proton affinity (PA) for the singlet states of all the scrutinized carbenes compared to the synthesized NHCs **A**–**E**

Structure	HOMO (au)	LUMO (au)	$\Delta E_{\text{HOMO-LUMO}}$	N (eV)	ω (eV)	PA
1a	−0.19326	−0.01498	111.9	4.20	0.83	278.58
1b	−0.20114	−0.03294	105.5	3.99	1.11	267.04
2a	−0.18635	−0.01434	107.9	4.39	0.80	279.33
2b	−0.20141	−0.04571	97.7	3.98	1.33	273.15
2c	−0.20218	−0.05515	92.3	3.96	1.53	273.82
3a	−0.18541	−0.05161	84.0	4.41	1.43	280.06
3b	−0.19631	−0.05962	85.8	4.12	1.63	276.28
A	−0.21693	−0.00817	131.00	3.56	0.83	267.98
B	−0.20902	−0.01098	124.27	3.77	0.83	276.33
C	−0.22738	−0.03619	119.97	3.27	1.24	270.59
D	−0.23188	−0.02357	130.71	3.15	1.07	256.74
E	−0.23474	−0.04272	120.49	3.07	1.36	259.99

Generally, compared to NHCs **A**–**E**, our studied carbenes show higher nucleophilicities and electrophilicities. This phenomenon could be related to the smaller divalent angle of the five-membered rings compared to the six-membered ones (about 10°), which enhances the *p* character of the bonding sp^2 orbitals but the *s* character of the nonbonding σ orbital. The calculated PAs for our carbenes resemble to those of common NHCs **A**–**E** (Table 3).

4. Conclusion

$\Delta E_{\text{s-t}}$ values of 60.9, 43.3, and 14.8 kcal/mol are calculated for amino and cyclopropyl substituted six-membered ring carbenes **1a**, **2a**, and **3a**, respectively, at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G* levels of theory. Appropriate isodesmic reactions show that the $\Delta E_{\text{s-t}}$ values are results of the stabilization of both singlet and triplet state carbenes due to the substituents. Two strong π-donor amino groups have stabilizing effect of 65.1 kcal/mol on **1a**(s) while the effect of one amino group is 42.8 kcal/mol. On the other hand, two weak π-donor cyclopropyls stabilize **3a**(s) by 22.8 kcal/mol while the effect of one cyclopropyl is 8.6 kcal/mol. The amino group considerably increases the energy barrier for 1,2-*C* shift leading to opening of the cyclopropyl. The energy barrier for this shift is 27.2 kcal/mol in **2a** and 9.7 kcal/mol in **3a**. Based on the CGMT model, it is shown that the saturated and unsaturated diamino- and aminocyclopropyl carbenes are unlikely to undergo dimerization. Six-membered ring saturated **1a**, **2a**, and **3a** are more nucleophilic than common five-membered ring NHCs with N values of about 4.33 au. Our carbenes seem to be as basic as the common NHCs considering their similar PAs.

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Supplementary data

Full references for Guassian 98, number of imaginary frequencies, total energies, Cartesian coordinates, $<S^2>$ parameter for the open shell structures and frontier molecular orbitals for all the studied carbenes. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2010.11.056. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. For pertinent books on carbene chemistry, see: (a) Kirmse, W. *Carbene Chemistry*; Academic: New York, NY, 1971; (b) Regitz, M. *Carbene (Carbenoid) in Mothoden der Organischen Chemie (Houben-Weyl)*; George Thieme: Stuttgart, 1989; Vol. E19b; (c) Jones, M.; Moss, R. A. *Carbenes*; Wiley Interscience: New York, NY, 1973 and 1975; Vols. 1 and 2; (d) Brinker, U. H. *Advanced in Carbene Chemistry*; JAI: Greenwich, 1994; Vol. 1; JAI: Stamford, 1998; Vol. 2; Elsevier: Amsterdam, 2001; Vol. 3; (e) Moss, R. A.; Platz, M. S.; Jones, M., Jr. *Reactive Intermediate Chemistry*; Wiley Interscience: Hoboken, 2004.
2. Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91.
3. Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
4. For stabilizing effects of π-donor heteroatoms on the singlet carbenes, see, for example,: (a) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A. *Tetrahedron Lett.* **1985**, *41*, 1587–1600; (b) Le, H. T.; Nguyen, T. L.; Lahem, D.; Flammang, R.; Nguyen, M. T. *Phys. Chem. Chem. Phys.* **1999**, *1*, 755–760; (c) Matus, M. H.; Nguyen, M. T.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 8864–8891; (d) Mendez, F.; Garcia-Garibay, M. A. *J. Org. Chem.* **1999**, *64*, 7061–7066; (e) Canac, Y.; Conejero, S.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2005**, *127*, 7312–7313; (f) Heinemann, C.; Thiel, W. *Chem. Phys. Lett.* **1994**, *217*, 11–16; (g) Alder, R. W.; Blake, M. E. *Chem. Commun.*

1997, 1513–1514; (h) Moss, R. A.; Wlostowski, M.; Shen, S.; Krough-Jespersen, K.; Matro, A. *J. Am. Chem. Soc.* **1988**, *110*, 4443–4444; (i) Du, X. M.; Fan, H.; Goodman, J. L.; Kessermayer, M. A.; Krough-Jespersen, K.; LaVilla, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 1920–1926.

5. Ammann, J. R.; Subramanian, R.; Sheridan, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 7592–7594.
6. Schoeller, W. W. *J. Org. Chem.* **1980**, *45*, 2161–2165.
7. Moss, R. A.; Fantina, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 6788–6790.
8. Shevlin, P. B.; McKee, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 519–524.
9. (a) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705–5709; (b) Lavallo, V.; Canac, Y.; DeHope, A.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 7236–7239; (c) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439–441; (d) Jazzar, R.; Dewhurst, R. D.; Bourg, J. B.; Donnadieu, B.; Canac, Y.; Bertrand, G. *Angew. Chem., Int. Ed.* **2007**, *49*, 2899–2902; (e) Frey, G. D.; Dewhurst, R. D.; Kousar, S.; Donnadieu, B.; Bertrand, G. *J. Organomet. Chem.* **2008**, *693*, 1674–1682; (f) Zeng, X.; Frey, G. D.; Kinjo, R.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2009**, *131*, 8690–8696.
10. Kassaee, M. Z.; Momeni, M. R.; Shakib, F. A.; Ghambarian, M.; Musavi, S. M. *Struct. Chem.* **2010**, *21*, 593–598.
11. Kassaee, M. Z.; Ghambarian, M.; Musavi, S. M.; Shakib, F. A.; Momeni, M. R. *J. Phys. Org. Chem.* **2009**, *22*, 919–924.
12. Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896–5911.
13. Otto, M.; Conejero, S.; Canac, Y.; Romanenko, V. D.; Rudzevitch, V.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1016–1017.
14. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
15. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
16. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
17. Frisch, M. J., et al. *Gaussian 98*; Gaussian: Pittsburgh, PA, 1998; See the supplementary data for the full reference.
18. Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209–214.
19. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665.
20. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comput. Chem.* **1983**, *4*, 294–301.
21. Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
22. Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6808.
23. Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, NY, 1986.
24. Glendening, E.D.; Reed, A.E.; Carpenter, J.E.; Weinhold, F. NBO Version 3.1.
25. Domingo, L. R.; Chamorro, E.; Pérez, P. *J. Org. Chem.* **2008**, *73*, 4615–4624.
26. Parr, R. G.; Szentpaly, L.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922–1924.
27. (a) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516; (b) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University: New York, NY, 1989.
28. Alder, R. W.; Blake, M. E.; Oliva, J. M. *J. Phys.Chem. A* **1999**, *103*, 11200–11211.
29. Alder, R. W.; Blake, M. E.; Bortolotti, C.; Bufali, S.; Butts, C. P.; Linehan, E.; Oliva, J. M.; Orpen, A. G.; Quayle, M. J. *Chem. Commun.* **1999**, 241–242.
30. Nemirowski, A.; Schreiner, P. R. *J. Org. Chem.* **2007**, *72*, 9533–9540.
31. Hoffmann, R.; Gleiter, R.; Mallory, F. B. *J. Am. Chem. Soc.* **1970**, *92*, 1460–1466.
32. This model was suggested independently by Carter and Goddard and by Trinquier and Malrieu: (a) Carter, A. E.; Goddard, W. A., III. *J. Phys. Chem.* **1986**, *90*, 998–1001; (b) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303–5315; (c) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916–5921; (d) Liong, C.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 1039–1041.
33. (a) Herrmann, W. A. *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309; (b) Herrmann, W. A.; Köcher, C. *Angew. Chem.* **1997**, *109*, 2257–2282; *Angew. Chem., Int. Ed.* **1997**, *36*, 2162–2187; (c) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem.* **1998**, *110*, 2631–2634; *Angew. Chem., Int. Ed.* **1998**, *37*, 2490–2493; (d) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194–16195.
34. (a) Alder, R. W.; Allen, P. R.; Williams, S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1267–1268; (b) Kim, Y.-J.; Streitwieser, A. *J. Am. Chem. Soc.* **2002**, *124*, 5757–5761; (c) Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K. *J. Am. Chem. Soc.* **2004**, *126*, 4366–4374.
35. Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem. A* **2006**, *110*, 1968–1974.
36. Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem.* **1991**, *95*, 4180–4182.
37. Chen, H.; Justes, D. R.; Cooks, R. G. *Org. Lett.* **2005**, *7*, 3949–3952.
38. (a) Maxwell, J. L.; Brown, K. C.; Bartley, D. W.; Kodadek, T. *Science* **1992**, *256*, 1544–1547; (b) Martin-Matute, B.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757–5766.