



A DFT study on pyridine-derived *N*-heterocyclic carbenes

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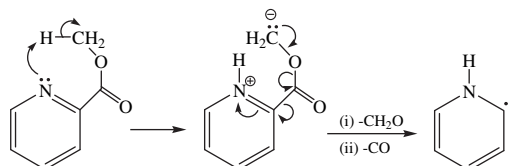
ABSTRACT

To appreciate the chemistry of *N*-heterocyclic carbenes (NHCs), eight carbenic tautomers of pyridine (azacyclohexadienylidenes) are studied at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G* and B3LYP/6-311++G**//B3LYP/6-31+G* levels of theory. Various thermodynamic parameters are calculated for these minima, along with a kinetic focus on carbene–pyridine tautomerization. Appropriate isodesmic reactions show stabilization energies of 2-azacyclohexa-3,5-dienylidene (**1**) and 4-azacyclohexa-2,5-dienylidene (**6**) as 119.4 and 104.1 kcal/mol, rather close to that of the synthesized 1,3-dimethylimidazol-2-ylidene (129.2 kcal/mol). Three different mechanisms are suggested for the tautomerizations including: [1,2]-H shift, [1,4]-H shift, and three sequential [1,2]-H shifts. The calculated energy barrier for [1,2]-H shift of **1** is 44.6 kcal/mol, while the first [1,2]-H shift for the proposed sequential mechanism of **6** requires 65.1 kcal/mol. Three preliminary minimum templates are introduced, which may possess the potential of synthetic consideration: 2,6-di(X)-3,5-dichloro-4-azacyclohexa-2,5-dienylidene for X=Mes, *t*-Bu, and Ad.

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1. Introduction

The exciting report on the synthesis of 1,3-di-1-adamantylimidazol-2-ylidene by Arduengo in 1991 was a brilliant point in the history of *N*-heterocyclic carbenes (NHC).¹ Synthesis of this molecule and the wide variety of its analogues date back to the desire of Wanzlick in 1960s on acquiring a carbenic center stabilized by two adjacent electron-donating nitrogen atoms.² Interestingly, 20 years prior to Wanzlick's work, Hammick had postulated the existence of pyridine-2-ylidene (**1**) to explain the accelerated decarboxylation rate of 2-picolinic acid (Scheme 1).³ This was later recognized as an NHC benefiting from stabilization of only one mesomeric nitrogen.⁴ But its chemistry was ignored until 1996 when Schwarz proved its stability on the microsecond time scale via mass spectrometry.⁵ His concurrent computational studies on this minimum species



Scheme 1.

predicted it to lie 40–50 kcal/mol above the stable pyridine (**9**). From a kinetic point of view, Schwarz estimated an energy barrier of 38.4 kcal/mol for tautomerization of **1** to **9** at B3LYP/6-31G**.

Three classes of pyridine-derived NHCs are identified: normal non-remote, abnormal remote, and normal remote. The distinction between these three classes is the relationship between heteroatom and carbenic center, which is *ortho*, *meta*, and *para*, respectively.⁶ Considering this fact, seven isomers of **1** can be imagined all of which fall in one of the above classes (Scheme 2). This arises a key question: can any of the other carbenic tautomers of pyridine compete with **1** in either thermodynamic or kinetic stability?

Accordingly, in this computational study, the thermodynamic stabilities of eight carbenic tautomers of pyridine are investigated using several parameters while applying appropriate isodesmic reactions. Our thermodynamic discussion is supported by the kinetic examination of possible tautomerizations of these carbenes to pyridine, through suitable mechanisms. Eventually, their potential application in coordination chemistry is probed via the measurement of their nucleophilicity and electrophilicity by means of appropriate indices.

2. Computational methods

Full geometry optimizations are accomplished without any symmetry constraints by means of hybrid functional B3LYP^{7–9} and the 6-31+G* basis set, employing the Gaussian 98 code.¹⁰ The applied basis set is comprised of Pople's well known 6-31G* basis

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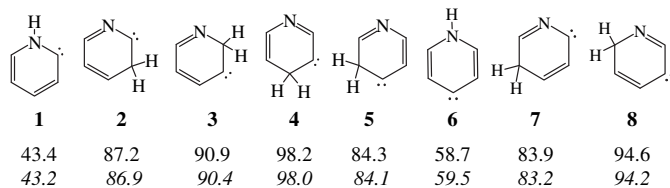
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set^{11,12} and an extra plus due to the importance of diffuse functions.^{13,14} To obtain more accurate energetic data, single point calculations are performed at the B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*¹⁵ and B3LYP/6-311++G**//B3LYP/6-31+G*¹⁶ levels of theory. Interestingly, the results obtained from high level B3LYP/AUG-cc-pVTZ are very similar to those of B3LYP/6-311++G**, an evidence on the reliability of the latter. We use the results of B3LYP/AUG-cc-pVTZ within the text unless the method is mentioned. The transition states (TSs) linking the initial and final structures are found using the reactants–products quasi-synchronous transit (QST2) algorithm.¹⁰ The frequency calculations are applied to characterize the structures as minima or transition states.¹⁷ Nucleus independent chemical shift (NICS) calculations¹⁸ are performed using the gauge independent atomic orbital (GIAO) method at B3LYP/6-311++G**//B3LYP/6-31+G* level.

The nucleophilicity index, *N*, which was recently introduced by Domingo et al.,¹⁹ is calculated as $N = E_{\text{HOMO}}(\text{Nu}) - E_{\text{HOMO}}(\text{TCE})$, where tetracyanoethylene (TCE) is chosen as the reference. The global electrophilicity, ω ,²⁰ is also calculated following the expression, $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu \approx (E_{\text{HOMO}} + E_{\text{LUMO}})/2$) and η is the chemical hardness ($\eta = E_{\text{LUMO}} - E_{\text{HOMO}}$).²¹

3. Results and discussion

The current work covers both the thermodynamic and kinetic aspects of 2-azacyclohexa-3,5-dienylidene (**1**) along with its seven carbene isomers, **2–8** (Scheme 2). Except for **1** and **6**, with *C*_s and *C*_{2v} symmetries, respectively, the other six isomers are found to be nonplanar (*C*₁). The principal geometry parameters and all the xyz coordinates are given in Supplementary data section.



Scheme 2. Eight carbene tautomers of pyridine (**1–8**) and their relative energies (kcal/mol) at B3LYP/AUG-cc-pVTZ and B3LYP/6-311++G** (values in italic).

3.1. Thermodynamics

Apparently, planar aromatic pyridine (**9**) appears as the global minimum on the C₅H₅N potential energy surface, while **1** lies 43.4 kcal/mol above it (Scheme 2). This value is in accord with the 46.8 kcal/mol energy difference calculated by Schwarz et al. at B3LYP/6-31G**.⁵ Among **1–8**, the most thermodynamically stable carbene tautomer of pyridine is **1** followed by **6**, which lies 58.7 kcal/mol higher than **9**. The energies of the other six tautomers (relative to **9**) are stretched in a range of 83.9–98.2 kcal/mol, indicating **4** as the least stable.

The conjugation of the nitrogen lone pair with the vacant p orbital of the carbene centers in **1** and **6** increase their stabilities. Similar stabilizing effects of nitrogen on **1** and **6** can be qualified by means of NICS calculations. Interestingly, the NICS(1)_{zz}²² values of –24.47 and –24.17 ppm for **1** and **6**, respectively, are comparable to that of the aromatic **9** (–28.46 ppm) (See the table of NICS data in Supplementary data).

To reach at a rather complete overview on the thermodynamic stabilities, the singlet–triplet ($\Delta E_{\text{s-t}}$) and HOMO–LUMO energy gaps ($\Delta E_{\text{HOMO-LUMO}}$) as well as the heats of hydrogenation (ΔE_{H} , Eq. 1) for **1–8** are compared to each other and to the Ardueng's (**A**)²³ and Bertrand's (**B**)²⁴ synthesized carbenes (Table 1).



Table 1

Calculated thermodynamic data (kcal/mol) for the eight carbene tautomers of pyridine (**1–8**) along with those of Arduengo (**A**)²³ and Bertrand (**B**)²⁴ N-heterocyclic carbenes at B3LYP/AUG-cc-pVTZ and B3LYP/6-311++G** (values in italic) levels

Structure	$\Delta E_{\text{s-t}}$	ΔE_{H}	$\Delta E_{\text{HOMO-LUMO}}$
1	38.4, 39.1	–41.2, –40.9	87.9, 88.0
2	–9.0, –8.9	–84.9, –84.7	72.7, 72.6
3	–5.7, –5.5	–88.1, –88.2	60.7, 60.7
4	–10.9, –11.1	–94.4, –95.9	54.2, 54.1
5	1.2, 1.2	–80.4, –82.0	69.6, 69.7
6	22.4, 22.0	–59.2, –59.7	70.6, 70.7
7	–0.4, 0.1	–81.3, –80.5	75.6, 75.3
8	–6.2, –6.2	–91.7, –91.5	57.9, 57.6
A	84.5, 84.0	–19.8, –20.2	128.5, 131.0
B	65.6, 65.4	–38.4, –37.3	112.9, 111.5

The stability of the singlet state is indicated by the positive high value of $\Delta E_{\text{s-t}}$ and the low absolute value of ΔE_{H} . Interestingly, tautomers **2**, **3**, **4**, **7**, and **8** exhibit negative $\Delta E_{\text{s-t}}$, meaning the higher stability of the triplet states. While the positive $\Delta E_{\text{s-t}}$ of **5** is rather insignificant (1.2 kcal/mol), those of **1** and **6** strongly prefer singlet states ($\Delta E_{\text{s-t}}$ = 38.4 and 22.4 kcal/mol, respectively). In other words, only one non-remote and two normal remote species are singlet ground states while the other two non-remote and all the abnormal remote ones prefer triplet state. These findings are confirmed by the lower absolute ΔE_{H} values for **1** and **6** (–41.2 and –59.2 kcal/mol, respectively) compared to the rest (ranging from –80.4 to –94.4 kcal/mol) (Table 1). Comparison of these data with those of the stable synthesized carbenes stimulated us to focus on **1** and **6**. Evidently, a molecule may be called stable if its computed smallest vibrational frequency is at least 100 cm^{–1} and shows a large HOMO–LUMO separation.²⁵ Fortunately, the smallest frequencies of **1** and **6** fulfill the first demand with the values of about 334 and 317 cm^{–1}, respectively. Also their $\Delta E_{\text{HOMO-LUMO}}$ s of 87.9 and 70.6 kcal/mol seem large enough to be worth further investigation.

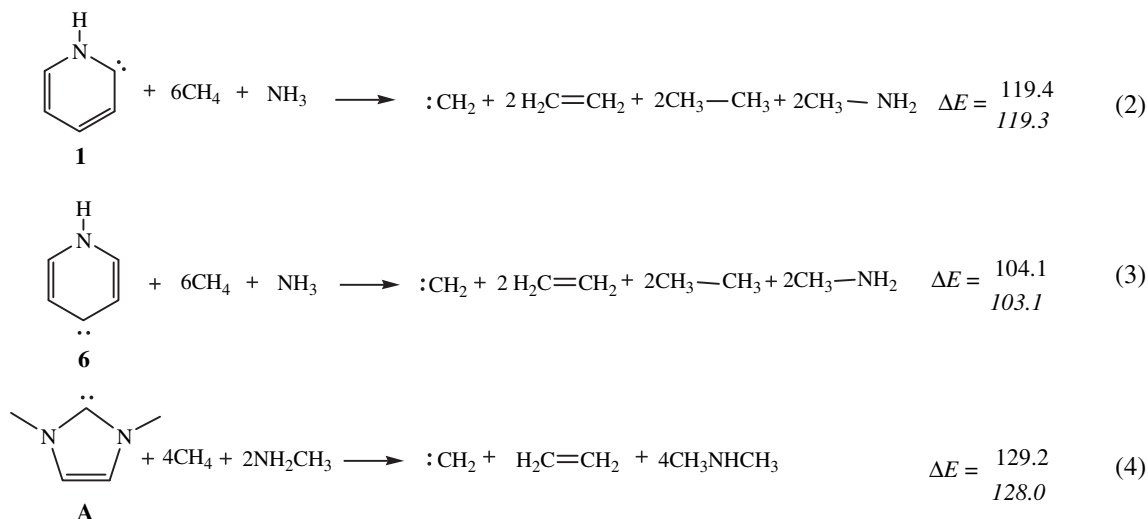
Applying appropriate isodesmic reactions, we can simultaneously estimate the stabilizing effects of nitrogen, double bonds, and cyclization (Scheme 3).

Isodesmic Reactions 2 and 3 indicate the stabilizing effects of these factors when accumulated in forms **1** and **6** compared to the state where all are apart from each other. The calculated ΔE value of 119.4 kcal/mol for Reaction 2 is only 9.8 kcal/mol less than that for Reaction 4, applied on **A**, which benefits from two adjacent nitrogen atoms. Interestingly, the positive ΔE value for Reaction 3 is also significant and is acceptably near to that of Reaction 2. Similarly, based on Eq. 2, the stabilizing energies of **1** and **6** can be compared to **A**, using the parent methylene as a reference.

Subsequently, the obtained ΔE values of 88.6 and 70.6 kcal/mol for **1** and **6** are expectedly less than 110.0 kcal/mol for **A**.

3.2. Kinetics

As stated by Hoffmann et al., to talk about the stability of a reactive species, it should be resistant to isomerization, which necessitates identifying and computing activation energies for such processes.²⁵ Hence, tautomerization to the global minimum pyridine is worthy of investigation for our eight carbenes (**1–8**).



Scheme 3. Isodesmic reactions used to estimate various stabilizing effects (ΔE , kcal/mol) for singlet carbenes, **1**, **6**, and **A**, at B3LYP/AUG-cc-pVTZ and B3LYP/6-311++G** (values in italic).

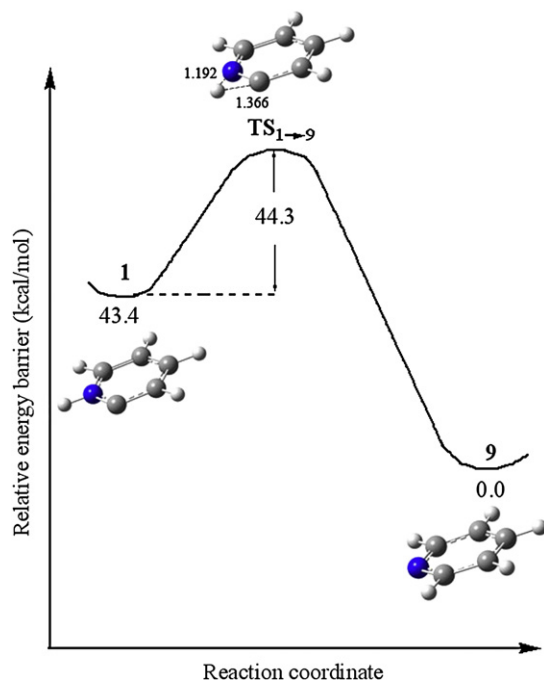
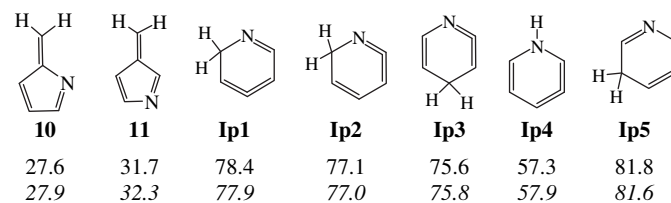


Figure 1. B3LYP/AUG-cc-pVTZ schematic energy diagram of tautomerization for **1** to **9** through [1,2]-H shift.

Assigning reasonable energy barriers for the rearrangements requires consideration of appropriate mechanisms. Consequently, three different mechanisms are suggested for the carbene-pyridine tautomerizations including: [1,2]-H shift for **1–5**, as well as [1,4]-H shift via a boat transition state, and/or three sequential [1,2]-H shifts for **6–8**.²⁶ Tautomerizations of **2–5** to **9** may be restricted by a competitive [1,2]-alkyl shift, which is considered as another possible isomerization path for these species. The highest energy barrier for [1,2]-H shift tautomerizations of **1–5** to **9** is encountered for **1** ($\Delta E^\ddagger=44.3$ kcal/mol) (Fig. 1).

Barriers of tautomerizations for **2–5** (0.3–13.6 kcal/mol) are much less than that of **1** (Table 2). The competitive [1,2]-alkyl shift of **2** results in the formation of **10**, a five-membered *N*-heterocyclic ring, with the relative energy of 27.6 kcal/mol (Scheme 4). In spite of being higher than pyridine in energy, **10** is a kinetic product owing to its lower ΔE^\ddagger (10.1 vs 13.6 kcal/mol). Such an alkyl shift is also possible for **3**, which gives **10**, as well as **4** and **5**, both of which



Scheme 4. Relative energies (kcal/mol) of secondary structures formed upon rearrangements of *N*-heterocyclic carbenes at B3LYP/AUG-cc-pVTZ and B3LYP/6-311++G** (values in italic) levels, where **10** comes from [1,2]-alkyl shifts of **2** and **3**, while **11** results from **4** and **5**; and **Ip1–Ip5** are intermediates encountered in the sequential mechanisms proposed for **6–8**.

Table 2

Energy barriers (ΔE^\ddagger , in kcal/mol) for rearrangements of **1–8** at B3LYP/AUG-cc-pVTZ and B3LYP/6-311++G** (values in italic)

Structure	[1,2]-H shift	[1,2]-alkyl shift	Structure	[1,4]-H shift	Sequential mechanism		
					First step	Second step	Third step
1	44.3, 44.7	—	6	78.9, 78.9	65.1, 64.4	30.3, 31.2	11.2, 11.0
2	13.6, 14.7	10.1, 10.8	7	35.1, 32.3	37.9, ^a 38.8 ^a 42.3, ^b 43.8 ^b	44.6, ^a 45.1 ^a 43.7, ^b 43.7 ^b	44.3, ^a 44.7 ^a 13.6, ^b 14.7 ^b
3	4.8, 4.4	16.1, 16.5	8	35.7, 35.5	27.4, ^a 28.2 ^a 21.2, ^b 21.8 ^b	60.2, ^a 9.7 ^a 31.3, ^b 31.8 ^b	4.8, ^a 4.4 ^a 0.3, ^b 0.7 ^b
4	0.3, 0.7	9.7, 9.7					
5	11.2, 11.0	11.0, 11.2					

^a For the first sequential pathway of **7** and **8**.²⁸

^b For the second sequential pathway of **7** and **8**.²⁸

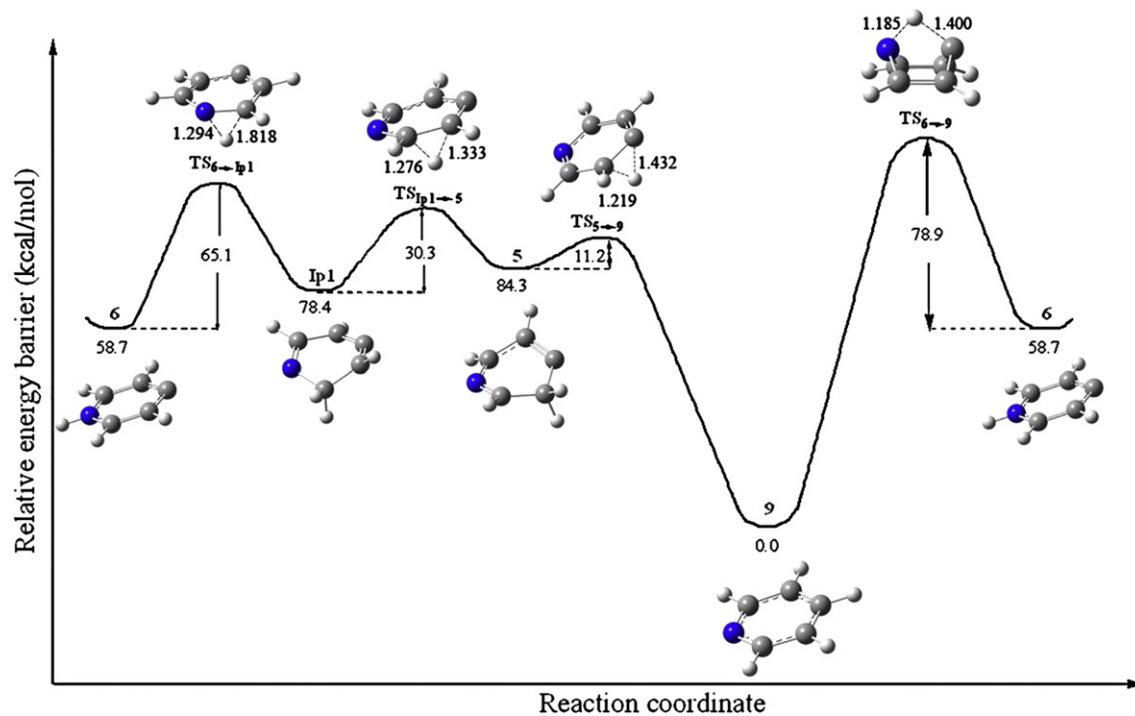
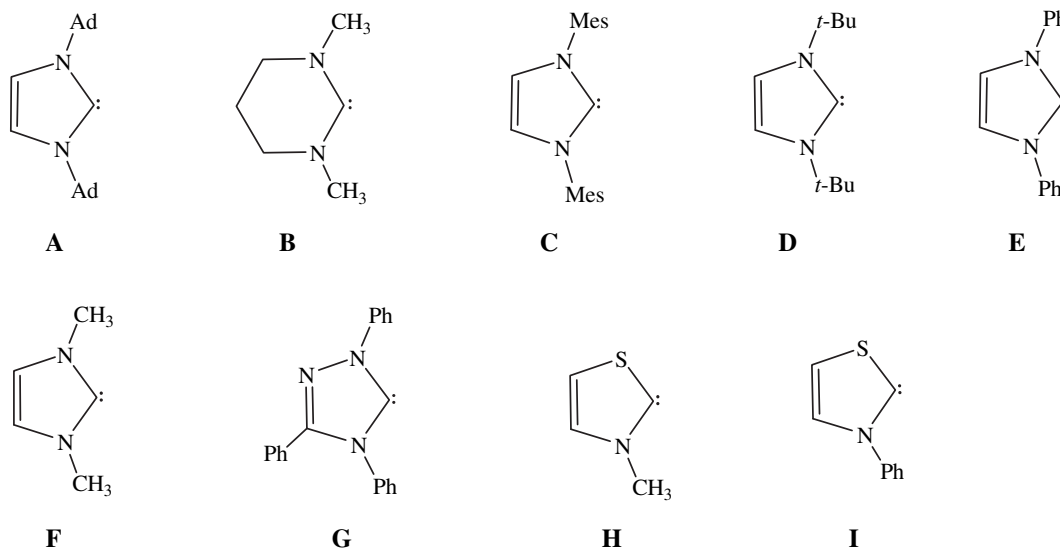


Figure 2. B3LYP/AUG-cc-pVTZ schematic energy diagram for [1,4]-H shift (right), and the favored sequential mechanism (left) for the conversion of **6** to **9**.

Table 3
The frontier molecular orbital energies (HOMO and LUMO), global electrophilicity (ω), and nucleophilicity (N) for our scrutinized *N*-heterocyclic carbenes (**1** and **6**) compared to the common NHCs (A–I)



Structures	HOMO (au)	LUMO (au)	N (eV)	ω (eV)
1	-0.19746	-0.05727	4.09	1.57
6	-0.16904	-0.05629	4.86	1.53
A	-0.20751	-0.01858	3.81	0.92
B	-0.19259	-0.01485	4.22	0.82
C	-0.21753	-0.01858	3.54	0.95
D	-0.20902	-0.01098	3.77	0.83
E	-0.22738	-0.03619	3.27	1.24
F	-0.21693	-0.00817	3.56	0.83
G	-0.23036	-0.05407	3.19	1.56
H	-0.23188	-0.02357	3.15	1.07
I	-0.23474	-0.04272	3.07	1.36

isomerize to **11**. However, in the cases of **3** and **4** the alkyl shift requires more energy than the [1,2]-H shift (Table 2).

On the other hand, in the case of **6**, **7**, and **8**, [1,4]-H shift appears as the first possible mechanism for their tautomerizations to **9**. Due to a boat transition state (TS), which is necessary for this route, the highest energy barrier is associated with the planar **6** ($\Delta E^\ddagger=78.9$ kcal/mol) (Table 2). In contrast, the nonplanar structures **7** and **8** exhibit much smaller ΔE^\ddagger s of 35.1 and 35.7 kcal/mol, respectively. Further examination of these tautomers hints to a sequential mechanism comprised of three [1,2]-H shifts (Fig. 2).²⁶

This process is apparently preferred for **6** as the ΔE^\ddagger of its first step is 13.8 kcal/mol less than that of a boat TS demanded by the [1,4]-H shift. Proposing this mechanism necessitates introducing a new tautomer of pyridine, isopyridine (**Ip1**), which contains an allenic moiety and lies 78.4 kcal/mol higher in energy than **9** (Fig. 2 and Scheme 4). In the second step, **Ip1** rearranges to **5**, after passing a ΔE^\ddagger of 30.3 kcal/mol, which in turn rearranges to **9** ($\Delta E^\ddagger=11.2$ kcal/mol). Thus, we propose a less energy requiring sequential mechanism for tautomerization of **6** to **9**, in contrast to the [1,4]-H shift, which was referred by Kunz.²⁷ Interestingly, the three TSs of the sequential mechanism involved in conversion of **6** to **9** are found to be aromatic with acceptable negative NICS(1)_{ZZ} values of -21.97, -25.03, and -20.20 ppm, justifying the preference of the sequential mechanism over the [1,4]-H shift (with a non-planar TS).

Considering each of **7** and **8**, a sequential mechanism can take place through two different pathways as demanded by their lack of symmetry.²⁸ Therefore, four isomers of isopyridine appear as possible intermediates: **Ip2** and **Ip3** from **7**, while **Ip4** and **Ip5** may result from **8** (Scheme 4). Eventually, tautomerization of **7** to **9** proceeds more favorably through a [1,4]-H shift, with 2.8 kcal/mol preference. In the case of **8** to **9** the sequential mechanism through the second pathway, including **Ip5** as an intermediate, is preferred (Table 1).²⁸

3.3. Nucleophilicity

The excellent σ -donating properties of NHCs make them ligands of choice for transition metals, thus leading to the preparation of organometallic catalysts of enormous utility in organic synthesis.^{29,30} As a pyridine-derived normal non-remote NHC, **1** was also considered in coordination chemistry as a carbene ligand^{27,31–33} with better σ -donor and π -acceptor characteristics³¹ relative to imidazolium derived carbenes.^{34–37} Moreover, there is an increasing number of experimental investigations on **6** as a remote NHC ligand in order to establish new metal complexes.⁶ Hence, to probe the coordinating characteristics, the nucleophilicity (N) and the global electrophilicity (ω) indices were calculated for **1** and **6**, as the most thermodynamically and kinetically stable species, along with a wide variety of NHCs that have been either successfully synthesized or even used as reactants or catalysts in organic reactions (Table 3).

A generally astonishing result is the higher nucleophilicities of the six-membered NHCs compared to the renowned five-membered ones. Where the highest N of the six-membered NHCs is encountered for **6** with the value of 4.86 eV, the highest value for five-membered ones is 3.81 eV in the case of **A**. This phenomenon could be related to the smaller divalent angle of the five-membered rings (about 10°), which enhances the p character of the bonding sp^2 orbitals and the s character of its nonbonding σ orbital. The more s character of σ orbital induces its shortening and the overall result is the decrease in nucleophilicity. Among our six-membered NHCs, **1** and Bertrand's NHC (**B**) demonstrate less nucleophilicity than **6** due to the inductive electron-attracting effect of the adjacent nitrogen(s).

The highest nucleophilicity of **6** as well as its thermodynamic and kinetic stability makes it worthy of synthetic considerations. Therefore, three preliminary minima templates, possessing the stable nucleophilic **6** as the main core are introduced: 2,6-di(X)-3,5-dichloro-4-azacyclohexa-2,5-dienylidene (X=Mes, *t*-Bu, and Ad) (Fig. 3).

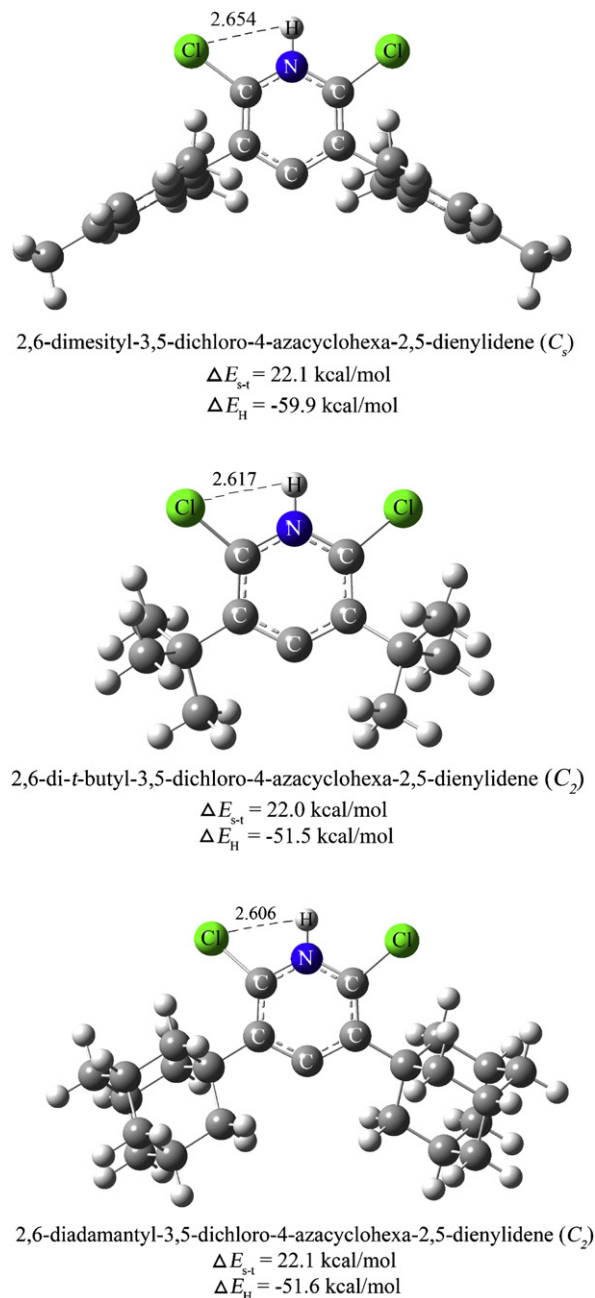


Figure 3. Our suggested optimized templates (at B3LYP/6-31+G⁺) for the synthetic considerations of NHCs.

These templates bear bulky substitutions on carbons 2 and 6 to minimize the possibility of dimerization. Additionally, two chlorine substituents are introduced on carbons 3 and 5 to reduce reactivity³⁸ and to benefit from the stabilizing effects of hydrogen bonding. Interestingly, the optimized distances between the Cl and H atoms in all three templates are shorter than the sum of the van der Waals radii of Cl and H (3.01 Å) confirming intramolecular hydrogen bonding, which may restrict the hydrogen shifts.

We hope these preliminary templates fall beyond the computational discussion and draw synthetic considerations toward the new carbenic structures.

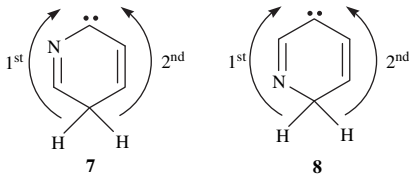
4. Conclusion

Employing B3LYP/AUG-cc-pVTZ and B3LYP/6-311++G** calculations, eight carbenic tautomers of pyridine (**1–8**) were scrutinized. All thermodynamic parameters including relative energies, ΔE_{S-T} , $\Delta E_{HOMO-LUMO}$, and ΔE_{HS} support the stability of the singlet states of **1** and **6**. Based on the established isodesmic reactions, the stabilization energies of **1** and **6** ($\Delta E=119.4$ and 104.1 kcal/mol, respectively) appear to be close to that of the stable synthesized 1,3-dimethylimidazol-2-ylidene ($\Delta E=129.2$ kcal/mol). Due to the importance of the kinetic stability, the tautomerizations of our eight carbenes to pyridine (the global minimum) were investigated. Three different mechanisms were suggested for the tautomerizations: [1,2]-H shift for **1–5**, as well as [1,4]-H shift and/or three sequential [1,2]-H shifts for **6–8**. The competitive [1,2]-alkyl shift was also investigated for **2–5** and shown that is preferred over tautomerization to pyridine in the case of **2**. Our proposed sequential mechanism for **6** is more favorable than previously stated [1,4]-H shift by 13.8 kcal/mol. The calculated energy barrier for [1,2]-H shift of **1** is 44.6 kcal/mol, while the first [1,2]-H shift for the proposed sequential mechanism of **6** requires 65.1 kcal/mol, indicating their kinetic stabilities. The calculated nucleophilicity indices show more nucleophilicity of the six-membered NHCs compared to the five-membered Arduengo ones. Between **1** and **6**, the former possesses a higher nucleophilicity index: $N=4.86$ versus 4.06 eV. Finally, the stable **6** promoted three templates, 2,6-di(X)-3,5-dichloro-4-azacyclohexa-2,5-dienylidene for X=Mes, *t*-Bu, and Ad (a kind of NHC bearing a hydrogen atom on N), which are suggested as synthetic targets.

Supplementary data

Full reference for Gaussian 98, geometrical parameters, the shapes of the molecular orbitals and Cartesian coordinates for all calculated structures, as well as NICS calculations for the planar species. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2009.09.043.

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