# Nucleophilicity of normal and abnormal N-heterocyclic carbenes at DFT: Steric effects on tetrazole-5-ylidenes

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# Nucleophilicity of normal and abnormal N-heterocyclic carbenes at DFT: Steric effects on tetrazole-5-ylidenes

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Nucleophilicity ($N$) is a crucial factor for coordination of N-heterocyclic carbenes (NHCs) to transition metal complexes. In this work a comparison is made between $N$ of a series of 1,4-disubstituted, “normal”, tetrazol-5-ylidens ($\mathbf{1_R}$), and their corresponding 1,3-disubstituted, “mesoionic, or abnormal”, isomers ($\mathbf{2_R}$), at the M06/6-311++G** level of theory; where R = H, methyl, ethyl, *i*-propyl, and *t*-butyl. Every abnormal $\mathbf{2_R}$ appears more nucleophilic than its related normal $\mathbf{1_R}$ isomer. Similarly, every $\mathbf{2_R}$ (except $\mathbf{2_{methyl}}$) emerges more aromatic than its corresponding normal $\mathbf{1_R}$ isomer. In addition, $N$ increases as the size of the substituent increases. The global electrophilicity ($\omega$) trend takes on an exactly opposite direction. Stabilities of $\mathbf{1_R}$ and $\mathbf{2_R}$ carbenic species are presumed to be related to their singlet-triplet energy gaps ($\Delta E_{\text{S-T}}$, kcal/mol). Every normal $\mathbf{1_R}$ appears more stable than its corresponding abnormal $\mathbf{2_R}$ isomer. The most stable is $\mathbf{1_{ethyl}}$ in the normal and $\mathbf{2_{ethyl}}$ in the abnormal series. The least stable are $\mathbf{1_{methyl}}$ and $\mathbf{2_{methyl}}$ structures, respectively. Lower stability of the latter two species is attributed to their relatively lower NICS, higher proton affinity (PA), higher aptitude for dimerization, wider carbenic bond angles (N—$\hat{\text{C}}_{\text{carbene}}$—N), and longer $\text{C}_{\text{carbene}}$—N bond lengths. Interestingly, the charge on carbenic carbon is the highest for $\mathbf{1}_{\boldsymbol{t}\textbf{-butyl}}$ and lowest for $\mathbf{2}_{\boldsymbol{t}\textbf{-butyl}}$. Every normal $\mathbf{1_R}$ shows a wider band gap than its corresponding abnormal $\mathbf{2_R}$, for showing a larger $\Delta E_{\text{HOMO-LUMO}}$. Finally, due to the steric effects, $\mathbf{1}_{\boldsymbol{t}\textbf{-butyl}}$ does not dimerize, while all other normal $\mathbf{1_R}$ carbenes, as well as abnormal $\mathbf{2_{methyl}}$ give doubly bonded dimers (head-to-head).

## 1 Introduction

In 1885, Buchner and Curtius discovered carbenes as reactivate intermediates that seemed impossible to be isolated.[1] Yet in 1988, Bertrand successfully synthesized NHCs in the form of five membered carbene rings that contained α-nitrogen atoms.[2,3] NHCs have been utilized as organocatalysts and ligands for transition metals in many fields of applied chemistry.[4–8] The size and substitution pattern of the nitrogen heterocycle can have a large effect on the properties of the carbene.[9,10] The ground-state electronic structure of NHCs provides a framework for understanding their reactivity. The lone pair situated in the plane of the heterocyclic ring makes them nucleophilic.[11] The nitrogen-substituents or other groups situated adjacent to $\text{C}_{\text{carbene}}$ have the largest influence on the steric environment at the carbene center.[12] Majority of applications of N-heterocyclic carbenes involve their coordination to transition metals. NHCs are excellent σ-donors and readily bind to transition metals. This feature has led to the most important application of them as auxiliary ligands in homogeneous transition-metal catalysis. NHC-Metal complexes also find many different applications as organometallic materials and as metallo-pharmaceuticals.[11] Major applications of NHCs are: coordination to p-block elements, activating small molecules, and acting as organocatalysts.[13,14] Majority of these processes are initiated by nucleophilic attack of the carbene on carbonyl groups present in organic substrates.[15,16]

The influence of delocalization of p-electrons and the number of nitrogen atoms in the five membered ring is investigated with imidazole-2-ylidene, imidazoline-2-ylidene, 1,2,4-triazole-5-ylidene and tetrazole-5-ylidene.[17] With increasing number of nitrogen atoms in the heterocycle, the nucleophilicity of the carbene decreases. Not only are the number of nitrogen atoms, but also their position is important. Nucleophilicity of the carbene carbon atom is increased due to lower electronegativity and hence less inductive electron withdrawal from the adjacent carbon atom. Its electrophilicity is also increased due to the lack of p-donation.[18,19] F. E. Kühn and co-workers have reported the synthesis and comparison of transition metal complexes of abnormal and normal tetrazolylidenes.[20] Variation between normal and abnormal substitution pattern brings an effect on $\sigma$–donor abilities of the ligands. It is found that ligands with the normal 1,4-substitution show only limited stability compared to their abnormal congeners.[20]

In this manuscript we try to respond to the important question of: “How $N$ is influenced by steric effects in NHCs? Hence we scrutinized normal 1,4-disubstituted tetrazol-5-ylidens ($\mathbf{1_R}$), and abnormal 1,3-disubstituted tetrazol-5-ylidens ($\mathbf{2_R}$); for R = H, methyl, ethyl, *i*-propyl, or *t*-butyl (Fig. 1).

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## 2 Computational Methods

Geometry optimizations of all compounds are carried out with the Gaussian 09 program at the M06 level, and the 6-311++G** basis set.[21] Dynamics are studied at different levels of accuracy with the DFT outcome expected to provide the more accurate structural and energetic results. In addition, for more accurate energetic data, single point calculations are performed at the same M06/6-311++G** level of theory.[22, 23] The nature of all optimized structures was determined by calculating the harmonic vibrational frequencies (minima with no imaginary frequency and transition states with only one imaginary frequency). The frequency calculations also provided thermodynamic quantities such as the zero-point vibrational energy, thermal correction, enthalpies, Gibbs free energies, and entropies at 298.15 K and 1.0 atm. Intrinsic reaction coordinate (IRC) paths were traced to confirm that each transition state was directly connected with two associated minima on the potential energy profile.

Nucleophilicity index, $N$ [24] is calculated as $N = E_{\text{HOMO(Nu)}} - E_{\text{HOMO(TCNE)}}$, where HOMO (Nu) and HOMO (TCNE) are the highest occupied molecular orbitals of NHCs and the reference tetracyanoethylene, respectively. The global electrophilicity ($\omega$) [25] is also calculated using the expression, $\omega = (\mu^2/2\eta)$, where $\mu$ is the chemical potential ($\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2$) and $\eta$ is the chemical hardness ($\eta = E_{\text{HOMO}} - E_{\text{LUMO}}$).[26]

## 3 Results and discussion

We have compared and contrasted normal 1,4-disubstituted tetrazol-5-ylidens (**1$_R$**), with abnormal 1,3-disubstituted tetrazol-5-ylidens (**2$_R$**), at M06/6-311++G** level of theory, where R is H, methyl, ethyl, *i*-propyl, or *t*-butyl (Fig. 1, 2). Specifically, to probe steric effects on nucleophilicity of **1$_R$** and **2$_R$**, we have examined thermodynamic parameters of our carbenes including: singlet-triplet energy gaps ($\Delta E_{\text{S-T}} = E_T - E_S$), proton affinity ($\Delta E_{\text{PA}}$), dimerization ($\Delta E_{\text{dim}}$), nucleophilicity ($N$), electrophilicity ($\omega$), and band gap ($\Delta E_{\text{HOMO-LUMO}}$) (Fig. 2).

We used acetaldehyde as a target molecule to test whether the real nucleophilic reaction is influenced by the size of substituents. The addition reactions of **1$_R$** and **2$_R$** with acetaldehyde in the gas phase are characterized by an asymmetrical double-well potential energy surface (PES); the reactants (**1$_R$**-**2$_R$** and acetaldehyde) initially forming a stable ion-molecule complex (**RC**), then overcoming the central barrier ($\Delta G^{\ddagger}$), proceeding through a transition state (**TS**) to the product (see Scheme 1).

### 3.1 Substituent effects on nucleophilicity of normal 1$_R$ and abnormal 2$_R$ carbenes

The nucleophilicity index, $N$, which was introduced by Domingo *et al.*[24] is a crucial factor for coordination of NHCs to transition metal complexes. The results of our calculations indicate that every abnormal **2$_R$** is more nucleophilic than its corresponding normal **1$_R$** isomer. For instance, abnormal **2$_{t\text{-butyl}}$** ($N$ = 3.72 eV) exerts more nucleophilicity than its corresponding normal **1$_{t\text{-butyl}}$** isomer ($N$ = 2.89 eV) (Table 1). Beyond this phenomenon lays many observations. Firstly, every asymmetric **2$_R$** carbene is kinetically more accessible than its corresponding symmetric **1$_R$** isomer, since the latter is sterically more hindered. Secondly, carbene angle for every **2$_R$** is larger than its corresponding **1$_R$**. For instance, carbene angle for **2$_{\text{methyl}}$** is almost 6 degrees wider than **1$_{\text{methyl}}$** (Table 2). Thirdly, the band gap of every **2$_R$** appears narrower than its corresponding **1$_R$**. For instance, $\Delta E_{\text{HOMO-LUMO}}$ of **2$_{\text{methyl}}$** is 38 kcal/mol narrower than that of **1$_{\text{methyl}}$** (Table 1).

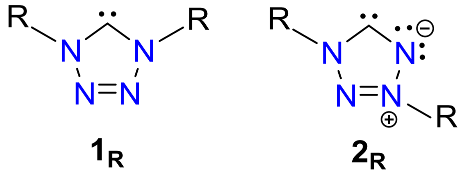


**Fig. 1** Scrutinized carbenes including normal 1,4-disubstituted tetrazol-5-ylidens (**1$_R$**), and abnormal 1,3-disubstituted tetrazol-5-ylidens (**2$_R$**); for R= H, methyl, ethyl, *i*-propyl, or *t*-butyl

Fourthly, every **2$_R$** appears less stable than its corresponding **1$_R$** for exhibiting a smaller $\Delta E_{\text{S-T}}$. For instance, **2$_{\text{ethyl}}$** appears almost 34 kcal/mol less stable than **1$_{\text{ethyl}}$** (Table 3). Fifthly, $C_{\text{carbene}}$—N bond lengths in every **2$_R$** remains equal or more than that in its corresponding **1$_R$**. For instance, $C_{\text{carbene}}$—N in **2$_H$** is 0.04 Å longer than that in **1$_H$** (Table 2). Sixthly, the singlet state of every **2$_R$** carbene appears at a higher level of energy than that in its corresponding **1$_R$**. For instance, **2$_H$** appears at almost 20 kcal/mol higher than that of **1$_H$** (Table 3). Seventhly, the triplet state of every **2$_R$** carbene appears at a lower level of energy than the corresponding **1$_R$**. For instance, **2$_{\text{ethyl}}$** appears at almost 17 kcal/mol lower in energy than that of **1$_{\text{ethyl}}$** (Table 3).

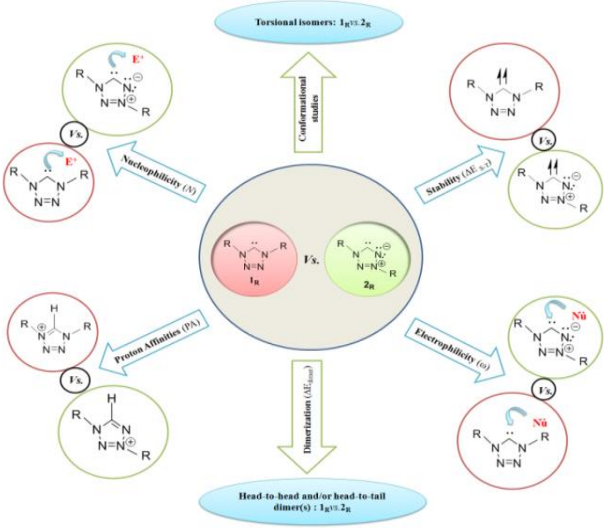
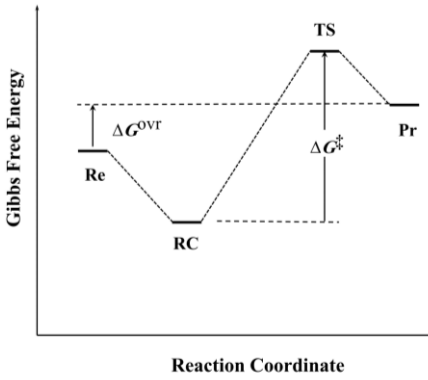


**Fig. 2** A flow chart for scrutiny of normal *vs.* abnormal tetrazole-5-ylidenes.



**Scheme 1** Schematic potential energy profile for the nucleophilic attacks of **1$_R$** and **2$_R$** to acetaldehyde

**Table 1** The highest occupied molecular orbital energies ($E_{HOMO}$/eV) and the lowest unoccupied molecular orbital energies ($E_{LUMO}$/eV), along with HOMO-LUMO energy differences ($\Delta E_{HOMO\text{-}LUMO}$, kcal/mol), nucleophilicity (*N*), and global electrophilicity (*ω*) for singlet states of scrutinized NHCs, at M06/6-311++G**

| NHCs | $E_{HOMO}$ | $E_{LUMO}$ | $\Delta E_{HOMO\text{-}LUMO}$ | *N* | *ω* |
|---|---|---|---|---|---|
| $\mathbf{1}_{H}$ | -7.63 | -1.19 | 148.53 | 2.19 | -0.042 |
| $\mathbf{1}_{methyl}$ | -7.33 | -1.20 | 141.41 | 2.48 | -0.038 |
| $\mathbf{1}_{ethyl}$ | -7.19 | -1.06 | 141.50 | 2.62 | -0.035 |
| $\mathbf{1}_{i\text{-}propyl}$ | -7.09 | -1.09 | 138.19 | 2.70 | -0.034 |
| $\mathbf{1}_{t\text{-}butyl}$ | -6.92 | -1.12 | 133.92 | 2.89 | -0.032 |
| $\mathbf{2}_{H}$ | -6.77 | -1.74 | 116.16 | 3.04 | -0.031 |
| $\mathbf{2}_{methyl}$ | -6.55 | -2.06 | 103.37 | 3.27 | -0.028 |
| $\mathbf{2}_{ethyl}$ | -6.31 | -1.34 | 114.60 | 3.50 | -0.025 |
| $\mathbf{2}_{i\text{-}propyl}$ | -6.22 | -1.26 | 114.48 | 3.59 | -0.023 |
| $\mathbf{2}_{t\text{-}butyl}$ | -6.10 | -1.27 | 111.49 | 3.72 | -0.022 |

**Table 2** Geometrical parameters including, carbenic bond lengths (Å), carbenic bond angles (deg), and dihedral angle ($C_{carbene}$—$N_1$—$N_2$—$N_3$, D) in degrees, at M06/6-311++G** level of theory

| NHCs | N—$C_{carbene}$ | $C_{carbene}$—N | N—$\hat{C}_{carbene}$—N | D |
|---|---|---|---|---|
| $\mathbf{1}_{H}$ | 1.34 | 1.34 | 97.89 | 0.0 |
| $\mathbf{1}_{methyl}$ | 1.41 | 1.41 | 99.87 | 9.2 |
| $\mathbf{1}_{ethyl}$ | 1.35 | 1.35 | 99.07 | 0.5 |
| $\mathbf{1}_{i\text{-}propyl}$ | 1.35 | 1.35 | 99.22 | 0.8 |
| $\mathbf{1}_{t\text{-}butyl}$ | 1.35 | 1.35 | 99.63 | 0.2 |
| $\mathbf{2}_{H}$ | 1.38 | 1.35 | 101.81 | 0.0 |
| $\mathbf{2}_{methyl}$ | 1.42 | 1.42 | 105.51 | 12.4 |
| $\mathbf{2}_{ethyl}$ | 1.38 | 1.35 | 102.35 | 0.4 |
| $\mathbf{2}_{i\text{-}propyl}$ | 1.38 | 1.35 | 102.52 | 0.4 |
| $\mathbf{2}_{t\text{-}butyl}$ | 1.38 | 1.35 | 102.58 | 0.8 |

**Table 3** Symmetry of normal and abnormal NHCs, singlet-triplet energy gaps ($\Delta E_{S\text{-}T}$, kcal/mol), along with dipole moments (*D*) and the smallest calculated vibrational frequencies ($\upsilon_{min}$, $cm^{-1}$) for two series of carbenes ($\mathbf{1}_R$ and $\mathbf{2}_R$), at M06/6-311++G** level of theory

| Carbenes | Symmetry | $\Delta E_{S\text{-}T}$ | $D^c$ | $\upsilon_{min}^{\ c}$ |
|---|---|---|---|---|
| $\mathbf{1}_{H}$ | $C_{2V}$ | 87.93 | 0.58 | 613.39 |
| $\mathbf{1}_{methyl}$ | $C_2$ | 73.16 | 0.96 | 93.56 |
| $\mathbf{1}_{ethyl}$ | $C_s$ | 90.25 | 0.98 | 45.05 |
| $\mathbf{1}_{i\text{-}propyl}$ | $C_1$ | 87.47 | 0.94 | 19.68 |
| $\mathbf{1}_{t\text{-}butyl}$ | $C_2$ | 85.61 | 0.87 | 29.26 |
| $\mathbf{2}_{H}$ | $C_s$ | 54.18 | 4.18 | 657.29 |
| $\mathbf{2}_{methyl}$ | $C_1$ | 39.92 | 4.49 | 140.16 |
| $\mathbf{2}_{ethyl}$ | $C_1$ | 56.44 | 4.50 | 4.59 |
| $\mathbf{2}_{i\text{-}propyl}$ | $C_1$ | 56.03 | 4.51 | 17.24 |
| $\mathbf{2}_{t\text{-}butyl}$ | $C_1$ | 54.05 | 4.39 | 20.48 |

The results of our calculations also indicate that *N* increases as the size of the substituent increases, with $\mathbf{2}_{t\text{-}butyl}$ and $\mathbf{1}_{H}$ as the most and the least nucleophilic species, respectively. So the inclusive calculated trend of *N* is: $\mathbf{1}_{H} < \mathbf{1}_{methyl} < \mathbf{1}_{ethyl} < \mathbf{1}_{i\text{-}propyl} < \mathbf{1}_{t\text{-}butyl} < \mathbf{2}_{H} < \mathbf{2}_{methyl} < \mathbf{2}_{ethyl} < \mathbf{2}_{i\text{-}propyl} < \mathbf{2}_{t\text{-}butyl}$ (Table 1). Similarly, beyond this phenomenon lays several views. For instance,

- The orders of our calculated *N* values appear consistent with the trend of the σ-donor abilities of the employed substituents: *t*-butyl > *i*-propyl > ethyl > methyl > H. The more negative is the Hammett substituent constant, the higher is *N*. For instance, $\mathbf{2}_{t\text{-}butyl}$ and $\mathbf{1}_{H}$ with $\sigma_p$ values of -0.20 and 0.00 displays *N* values of 3.72 and 2.19, respectively (Table 1 and Table 1 in Supplementary Information).
- For each species *N* is directly proportional to the energy of its highest occupied molecular orbital ($E_{HOMO}$).[27] Nucleophilicity for our ten scrutinized carbenes, firstly appears as a function of substituent size (Fig. 3). Secondly, the trend of *N* values (*t*-butyl > *i*-propyl > ethyl > methyl > H) emerges consistent with the size of substituents for both normal $\mathbf{1}_R$ and abnormal $\mathbf{2}_R$ carbenes. Thirdly, each $\mathbf{2}_R$ has a higher *N* than its corresponding $\mathbf{1}_R$ (Table 1). Fourthly, $\mathbf{2}_R$ carbenes series are more nucleophilic than the $\mathbf{1}_R$ series (Fig. 3). Fifthly, the highest and lowest *N* are exhibited by $\mathbf{2}_{t\text{-}butyl}$ and $\mathbf{1}_{H}$, with *N* of 3.72 and 2.19 eV, respectively (Table 1).
- Evidently, among simple alkyl carbocations the order of stability is tertiary > secondary > primary; with the latter being more stable than $H^+$.[28] Hence, contributions of canonical forms in set III and V to the hybrid structure $\mathbf{1}_R$ increase in the order of *t*-butyl > *i*-propyl > ethyl > methyl > H (Scheme 2). Such an incident results in a higher *N* with the above order, due to the higher electron density and negative charge on the carbenic carbon. For the same reasons, contributions of canonical forms III' and IV' to the hybrid structure $\mathbf{2}_R$ increase in the order of *t*-butyl > *i*-propyl > ethyl > methyl > H (Scheme 3).

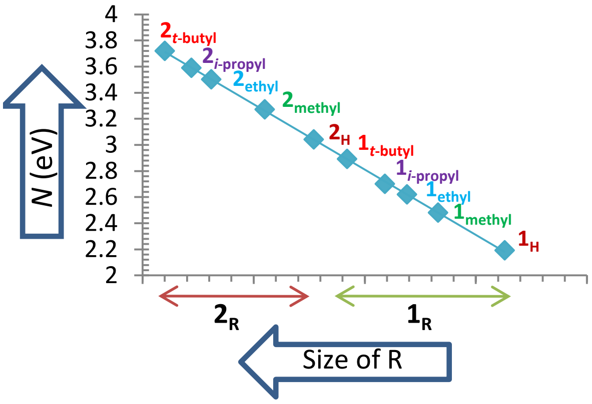
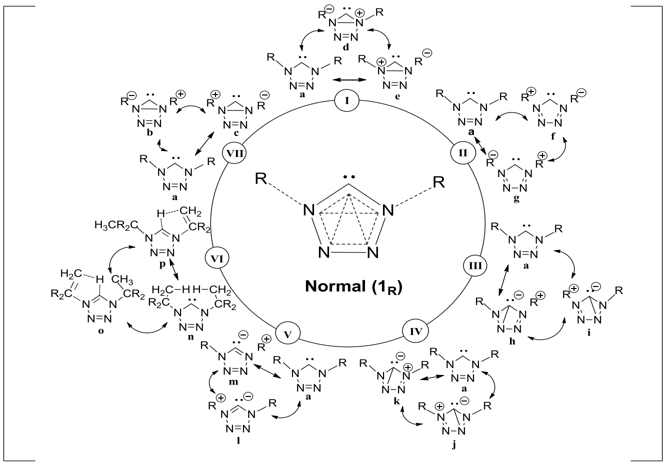


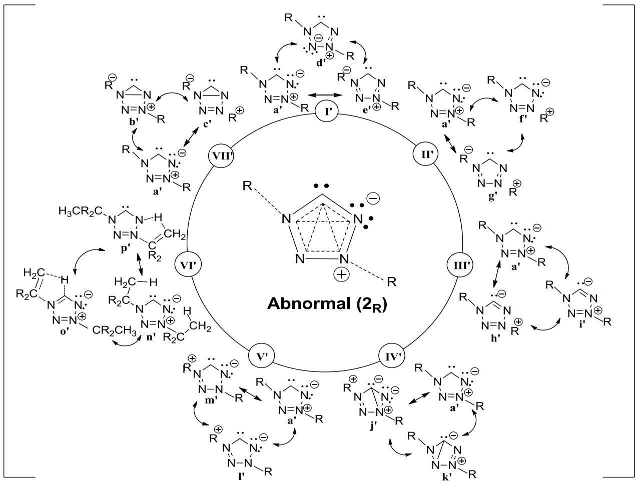
**Fig. 3** Nucleophilicity (*N*) as a function of substituent size.

The structure of $\mathbf{1}_R$ is a hybrid of seven sets of resonance types involving different bond.



**Scheme 2** Electron delocalizations through seven sets of possible canonical forms (I-VII) for our normal **1**$_{\mathrm{R}}$ carbenes

The structure of **2**$_{\mathrm{R}}$ is a hybrid of seven sets of resonance types involving different bond.



**Scheme 3** Electron delocalizations through seven sets of possible canonical forms (I'-VII") for our abnormal **2**$_{\mathrm{R}}$ carbenes

Our calculated global electrophilicity (*ω* / eV) [25, 26] takes on a trend with an exactly opposite direction from *N* (Table 1). Every abnormal **2**$_{\mathrm{R}}$ is less electrophilic than its corresponding normal **1**$_{\mathrm{R}}$ isomer. For instance, abnormal **2**$_{t\text{-butyl}}$ ($\omega$ = -0.022 eV) emerges more electrophilic than its corresponding normal **1**$_{t\text{-butyl}}$ isomer ($\omega$ = -0.032 eV) (Table 1).

N-Heterocyclic carbenes (NHCs) propensity to coordinate to carbon-electrophiles has led to a major class of applications, in which NHCs act as organocatalysts.[1,16] The majority of these processes are initiated by nucleophilic attack of the carbene onto carbonyl groups present in organic substrates. Therefore, in this work we have used acetaldehyde as a target molecule for probing real nucleophilic reactions as functions of the size of substituents, at M06/6-311++G** level of theory (Fig. 4). Every abnormal **2**$_{\mathrm{R}}$ appears more nucleophilic than its corresponding normal **1**$_{\mathrm{R}}$ isomer, since every **2**$_{\mathrm{R}}$ turns out more reactive than its corresponding **1**$_{\mathrm{R}}$ for exhibiting a smaller Δ*G*$^{\ddagger}$ (Table 4). So in arrangement with the nucleophilicity indexes (Table 1), every asymmetric **2**$_{\mathrm{R}}$ carbene is kinetically more accessible than its corresponding symmetric **1**$_{\mathrm{R}}$ isomer.

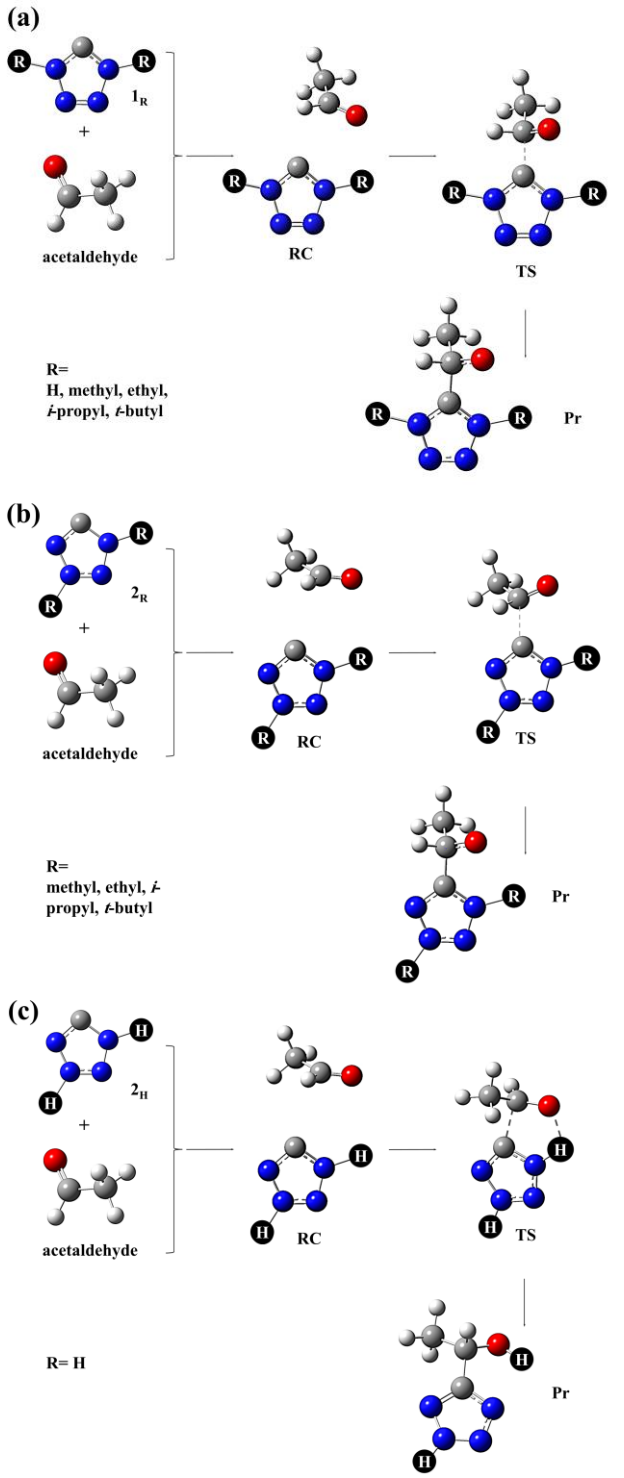


**Fig. 4** Reaction pathway of the nucleophilic attacks of (a) **1**$_{\mathrm{R}}$ (b) **2**$_{\mathrm{R}}$ (c) **2**$_{\mathrm{H}}$ onto carbonyl group in acetaldehyde

In normal series, Δ*G*$^{\ddagger}$ increases as the nucleophile is varied from **1**$_{\mathrm{methyl}}$, **1**$_{i\text{-propyl}}$, **1**$_{\mathrm{ethyl}}$, **1**$_{\mathrm{H}}$ to **1**$_{t\text{-butyl}}$. However, in abnormal series, this trend holds except for **2**$_{\mathrm{H}}$ witch seems to be more reactive than **2**$_{\mathrm{ethyl}}$. In comparison to the nucleophilicity indexes that only cover substituents σ-donor abilities, here the results simultaneously include the latter plus steric effects.

**Table 4** Central barrier free energies ($\Delta G^{\ddagger}$, kcal mol$^{-1}$), overall reaction free energies ($\Delta G^{\mathrm{ovr}}$, kcal mol$^{-1}$) for the nucleophilic reactions of carbenes onto carbonyl group in acetaldehyde, at M06/6-311++G** level of theory

| Carbenes | ΔG$^{\#}$(kcal/mol) | ΔG$^{over}$(kcal/mol) |
|---|---|---|
| $\mathbf{1}_{\mathrm{H}}$ | 16.54 | 18.54 |
| $\mathbf{1}_{\mathrm{methyl}}$ | 11.71 | 3.46 |
| $\mathbf{1}_{\mathrm{ethyl}}$ | 14.48 | 21.31 |
| $\mathbf{1}_{i\text{-propyl}}$ | 13.39 | 19.18 |
| $\mathbf{1}_{t\text{-butyl}}$ | 19.99 | 25.21 |
| $\mathbf{2}_{\mathrm{H}}$ | 8.86 | -41.98 |
| $\mathbf{2}_{\mathrm{methyl}}$ | 7.61 | -6.24 |
| $\mathbf{2}_{\mathrm{ethyl}}$ | 9.32 | 10.68 |
| $\mathbf{2}_{i\text{-propyl}}$ | 8.10 | 9.04 |
| $\mathbf{2}_{t\text{-butyl}}$ | 9.93 | 12.11 |

The trends of reactivity indicate that $\mathbf{1}_{\mathrm{methyl}}$ and $\mathbf{2}_{\mathrm{methyl}}$ are more reactive than other species in their corresponding $\mathbf{1}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{R}}$ series, respectively. The trend of reactivity for $\mathbf{1}_{i\text{-propyl}}$ ($\mathbf{2}_{i\text{-propyl}}$), $\mathbf{1}_{\mathrm{ethyl}}$ ($\mathbf{2}_{\mathrm{ethyl}}$), and $\mathbf{1}_{t\text{-butyl}}$ ($\mathbf{2}_{t\text{-butyl}}$) indicates that the former is more reactive than the other two. Since it is a better σ-donor than $\mathbf{1}_{\mathrm{ethyl}}$ ($\mathbf{2}_{\mathrm{ethyl}}$) on one hand, and has less steric effects than $\mathbf{1}_{t\text{-butyl}}$ ($\mathbf{2}_{t\text{-butyl}}$) on the other hand.

For addition reaction of $\mathbf{2}_{\mathrm{H}}$, the ring hydrogen on N1 may transfer on the oxygen atom of acetaldehyde through a concerted pathway, giving a resonance stabilized product ($\Delta G^{\mathrm{ovr}} = -41.98$ kcal/mol) (Fig. 4c). However, such process does not seem to occur readily for other species, not even for the its close isomer ($\mathbf{1}_{\mathrm{H}}$), because their products do not appear to be that stable, for the involvement of less important charge separated canonical forms (Fig. 5). Likewise, as mentioned above $\mathbf{2}_{\mathrm{H}}$ appears more reactive than $\mathbf{2}_{\mathrm{ethyl}}$ because of the possibility of a concerted H-transfer reaction for the former.

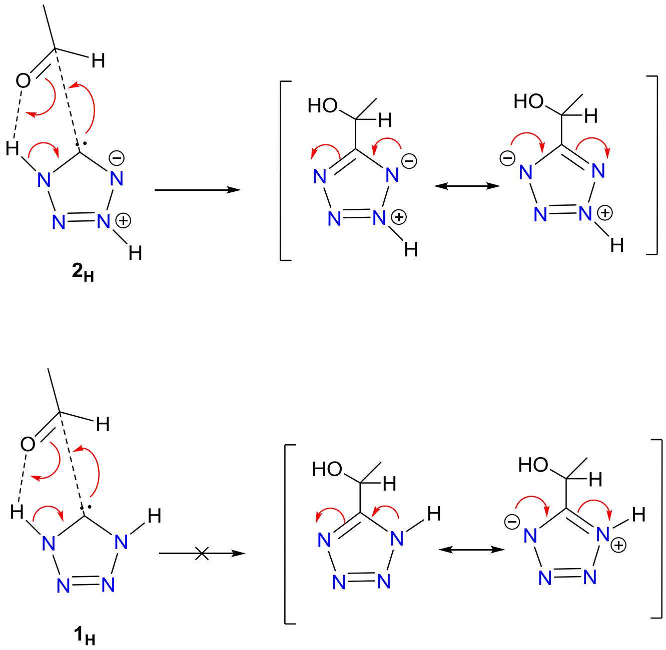


**Fig. 5** A possible mechanism for the nucleophilic attacks of $\mathbf{1}_{\mathrm{H}}$ and $\mathbf{2}_{\mathrm{H}}$ onto carbonyl group in acetaldehyde

### 3.2 Dihedral angles ($C_{\mathrm{carbene}}$—$N_1$—$N_2$—$N_3$, D) or degrees of puckering for $\mathbf{1}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{R}}$ species

All scrutinized species ($\mathbf{1}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{R}}$) including *E* isomer of $\mathbf{1}_{\mathrm{methyl}}$ appear as minima on their potential energy surfaces. In contrast, the *Z* isomer of $\mathbf{1}_{\mathrm{methyl}}$ shows two negative force constant, suggesting evolvement of a saddle point structure (Scheme 2 in Supplementary Information).

Among the ten species scrutinized ($\mathbf{1}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{R}}$), $\mathbf{1}_{\mathrm{methyl}}$ and $\mathbf{2}_{\mathrm{methyl}}$ stand out for their highest degrees of puckering of 9.2 and 12.4 degrees, respectively (Table 2). In contrast, the most planar species turn out to be $\mathbf{1}_{\mathrm{H}}$ and $\mathbf{2}_{\mathrm{H}}$.

Perhaps the most conspicuous difference between methyl substituted species ($\mathbf{1}_{\mathrm{methyl}}$ and $\mathbf{2}_{\mathrm{methyl}}$) and the rest is their nonplanarity for showing puckered type of structures.

### 3.3 Nucleophilicity *vs.* carbenic bond angle (N—$\hat{C}_{\mathrm{carbene}}$—N)

A smaller divalent angle imposes more p character to the covalent sp$^2$ bonding orbitals which is compensated with more s character of the non-bonding σ orbital of the carbene. This causes the lowering of the energy state of the σ orbital and enlargement σ–p$_\pi$ gap leading to the favorable singlet and rather unstable triplet states.[29] Hence, the more s character of σ orbital induces its shortening and the overall result is the decrease in nucleophilicity.[30,31] Interestingly, except for nonplanar $\mathbf{1}_{\mathrm{methyl}}$, the trend of (N—$\hat{C}_{\mathrm{carbene}}$—N) angle for planar species is $\mathbf{1}_{t\text{-butyl}} > \mathbf{1}_{i\text{-propyl}} > \mathbf{1}_{\mathrm{ethyl}} > \mathbf{1}_{\mathrm{H}}$ (Table 2). This trend appears consistent with that of nucleophilicity (Table 1). Similarly, the highest carbenic angle in abnormal $\mathbf{2}_{\mathrm{R}}$ carbenes is for nonplanar $\mathbf{2}_{\mathrm{methyl}}$ (Table 2). Except for the latter, the trend of (N—$\hat{C}_{\mathrm{carbene}}$—N) angle for planar abnormal species is $\mathbf{2}_{t\text{-butyl}} > \mathbf{2}_{i\text{-propyl}} > \mathbf{2}_{\mathrm{ethyl}} > \mathbf{2}_{\mathrm{H}}$ (Table 2). This trend also appears consistent with that of their nucleophilicity values (Table 1).

According to our calculation the angle (N—$\hat{C}_{\mathrm{carbene}}$—N) is increased from normal to abnormal carbenes (Table 2). Likewise, nucleophilicity is also increased from normal to abnormal carbenes (Fig. 3, Table 1).

### 3.4 Nucleophilicity *vs.* $\Delta E_{\mathrm{S\text{-}T}}$ of normal $1_{\mathrm{R}}$ and abnormal $2_{\mathrm{R}}$ carbenes

Stability of carbenic species are presumed to be related to their singlet-triplet energy gaps ($\Delta E_{\mathrm{S\text{-}T}}$, kcal/mol). We have calculated $\Delta E_{\mathrm{S\text{-}T}}$ of $\mathbf{1}_{\mathrm{R}}$ and $\mathbf{2}_{\mathrm{R}}$ at M06/6-311++G** level of theory (Table 3). Every normal $\mathbf{1}_{\mathrm{R}}$ appears more stable but less nucleophilic than its corresponding abnormal $\mathbf{2}_{\mathrm{R}}$ isomer (Table 1). Hence, nucleophilicity of an isomeric carbene appears to be indirectly proportional to $\Delta E_{\mathrm{S\text{-}T}}$. Another words, the less stable is a carbene, the more nucleophilic it may be. Among normal carbenes, $\mathbf{1}_{\mathrm{ethyl}}$ appears as the most stable ($\Delta E_{\mathrm{S\text{-}T}}$ = 90.25 kcal/mol), while the least stable is $\mathbf{1}_{\mathrm{methyl}}$ with $\Delta E_{\mathrm{S\text{-}T}}$ = 73.16 kcal/mol (Table 3). Similarly in abnormal carbenes the highest $\Delta E_{\mathrm{S–T}}$ is found for $\mathbf{2}_{\mathrm{ethyl}}$ with $\Delta E_{\mathrm{S\text{-}T}}$ = 56.44 kcal/mol, while the lowest is found for $\mathbf{2}_{\mathrm{methyl}}$ with 39.92 kcal/mol (Table 3). The trend of $\Delta E_{\mathrm{S–T}}$/kcal/mol for our scrutinized normal carbenes is: $\mathbf{1}_{\mathrm{ethyl}}$ (90.25) > $\mathbf{1}_{\mathrm{H}}$ (87.93) > $\mathbf{1}_{i\text{-propyl}}$ (87.47) > $\mathbf{1}_{t\text{-butyl}}$ (85.61) > $\mathbf{1}_{\mathrm{methyl}}$ (73.16), and for abnormal carbenes is: $\mathbf{2}_{\mathrm{ethyl}}$ (56.44) > $\mathbf{2}_{i\text{-propyl}}$ (56.03) > $\mathbf{2}_{\mathrm{H}}$ (54.18) > $\mathbf{2}_{t\text{-butyl}}$ (54.05) > $\mathbf{2}_{\mathrm{methyl}}$ (39.92) (Table 3). Delocalization of the lone pair into the empty 2p$_z$ orbital leads to stabilization of the molecule. On the other hand, decrease of the electron deficiency of carbon leads to a decrease of the electrophilicity of the molecule. Intuitively, there should be an inverse relationship between the electrophilic and nucleophilic character of molecules, which is indeed found in the case of our carbenes. Stability ($\Delta E_{\mathrm{S\text{-}T}}$) for ten scrutinized carbenes, appears as a function of carbenic bond angles (N—$\hat{C}_{\mathrm{carbene}}$—N) with a correlation factor of $R^2 = 0.913$ (Fig. 6).

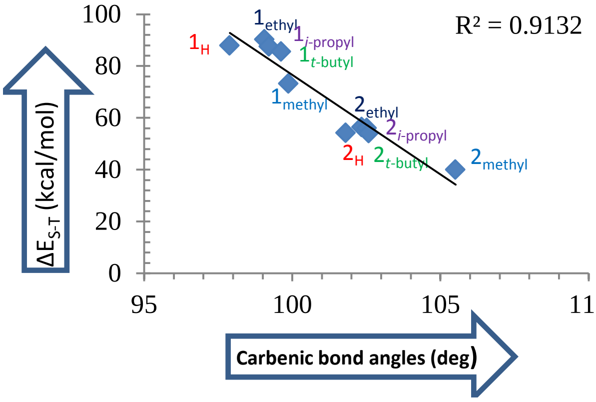


**Fig. 6** Stability ($\Delta E_{S\text{-}T}$) of normal and abnormal tetrazol-5-ylidenes as a function of their carbenic bond angles (N—$\hat{C}_{carbene}$—N) with a correlation factor of $R^2$ = 0.9132.

Among the abnormal ones, the most stable **$2_{ethyl}$** (and **$2_{i\text{-}propyl}$**) show the same but highest dipole moment of 4.51 D. In normal carbenes the highest dipole moment is only 0.98 D, exhibited by **$1_{ethyl}$** (Table 3).

Hoffmann, Schleyer, and Schaefer have emphasized that a molecule may be called "stable" if its computed smallest vibrational frequency ($\upsilon_{min}$) is at least 100 $cm^{-1}$.[32] In this calculation **$1_H$** (613.39 $cm^{-1}$), **$2_H$** (657.29 $cm^{-1}$) and **$2_{methyl}$** (140.16 $cm^{-1}$) have $\upsilon_{min}$ more than 100 $cm^{-1}$ (Table 3).

### 3.5 Nucleophilicity *vs.* carbenic bond lengths ($C_{carbene}$—N)

The following trend of $C_{carbene}$—N bond lengths is observed for our normal NHCs: **$1_{methyl}$** (1.41 Å) > **$1_{ethyl}$** (1.35 Å) ≈ **$1_{i\text{-}propyl}$** (1.35 Å) ≈ **$1_{t\text{-}butyl}$** (1.35 Å) > **$1_H$** (1.34 Å). Hyperconjugation may be held responsible for the shortest $C_{carbene}$—N bond lengths observed for **$1_H$** (Scheme 2, Set V and Scheme 3 in Supplementary Information). Similar bond lengths are observed for **$1_{ethyl}$**, **$1_{i\text{-}propyl}$**, and **$1_{t\text{-}butyl}$** which render relatively shorter $C_{carbene}$—N bond lengths than **$1_{methyl}$**. This is because of possible H-bonding type of interactions through reasonable 5-membered rings (Scheme 2, Set VI). The longest $C_{carbene}$—N in normal series is displayed by **$1_{methyl}$** for its disability of hyperconjugation on one hand, and its inability of H-bonding type on the other. Considering the number of hydrogens, anticipated ratio of 5-membered ring populations (discussed above) are 3, 6, and 9 for **$1_{ethyl}$**, **$1_{i\text{-}propyl}$**, and **$1_{t\text{-}butyl}$**, respectively. One may anticipate the trend of $C_{carbene}$—N bond lengths to be **$1_{t\text{-}butyl}$** > **$1_{i\text{-}propyl}$** > **$1_{ethyl}$**. Despite such anticipation the same bond lengths are observed (Scheme 1, Set VI). Interaction between carbene and the two symmetrical α and α′ substituents renders a cumulated or allenic type of double bond.

$C_{carbene}$—N bond lengths of our abnormal NHCs appear similar to those of normal NHCs: **$2_{methyl}$** (1.42 Å) > **$2_{ethyl}$** (1.38 Å) ≈ **$2_{i\text{-}propyl}$** (1.38 Å) ≈ **$2_{t\text{-}butyl}$** (1.38 Å) ≈ **$2_H$** (1.38 Å). Nevertheless, our calculations may not be sensitive enough to distinguish between **$2_{ethyl}$**, **$2_{i\text{-}propyl}$**, **$2_{t\text{-}butyl}$** and **$2_H$** $C_{carbene}$—N bond lengths. This may be due to lack of symmetry and interaction of only one α-substituent with the carbenic center. All the latter species have shorter $C_{carbene}$—N bond lengths than **$2_{methyl}$** for the possible H-bonding through reasonable 5-membered rings (Scheme 3, Set VI'). Again, the longest $C_{carbene}$—N for abnormal series is displayed by **$2_{methyl}$** for its inability of hyperconjugation and H-bonding, as well as its non-planarity due to the possible puckered forms (Scheme 3, Set II', VI' and Scheme 2 in Supplementary Information). Contributions of such canonical forms to the hybrid structure of **$1_{methyl}$** induces relatively highest dihedral angle $D_1$ = 9 (Table 2). According to the above bond length data, π-donations of the NHCs abnormal to carbene centers appear stronger than those of the NHCs normal.

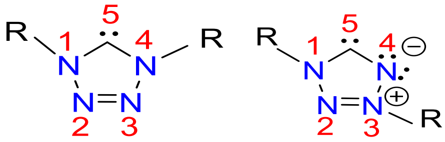
### 3.6 Effects of substituents on $C_{carbene}$—$N_2$ (or $C_{carbene}$—$N_3$)

In normal **$1_R$**, bond lengths between $C_{carbene}$—$N_2$ appear inversely proportional to the size of the substituents (R): **$1_H$** (2.289 Å) > **$1_{methyl}$** (2.282 Å) > **$1_{ethyl}$** (2.273 Å) > **$1_{i\text{-}propyl}$** (2.271 Å) > **$1_{t\text{-}butyl}$** (2.269 Å). Due to the symmetry, the same length is observed for $C_{carbene}$—$N_2$ and $C_{carbene}$—$N_3$ bonds (Scheme 2, Set III, IV, and VII). Beyond such a phenomenon lays possible resonance interactions (Scheme 2, Set III, IV, and VII).

### 3.7 Nucleophilicity *vs.* effects of substituents on atomic charge

Among the three canonical forms (Scheme 3, Set IV'), conceived for our abnormal NHCs (**$2_R$**), structure k' is anticipated to contribute the most, because of having octet for all of its 2nd row elements. The least stable canonical form is j' which suffers from excessive separation of charge (Scheme 3, Set IV'). Evidence for k' includes the low negative charge on $N_4$ and a higher negative charge on $C_{carbene}$ (Table 5).

**Table 5** NBO atomic charges on $C_{carbene}$ and $N_1$—$N_4$, at M06/6-311++G**



| Carbenes | $C_{carbene}$ (5) | $N_1$ | $N_2$ | $N_3$ | $N_4$ |
|---|---|---|---|---|---|
| **$1_H$** | -0.28 | 0.15 | -0.01 | -0.01 | 0.15 |
| **$1_{methyl}$** | -0.27 | 0.01 | -0.01 | -0.01 | 0.01 |
| **$1_{ethyl}$** | -0.19 | 0.13 | -0.06 | -0.06 | 0.13 |
| **$1_{i\text{-}propyl}$** | -0.33 | 0.36 | -0.19 | 0.14 | 0.06 |
| **$1_{t\text{-}butyl}$** | -0.37 | 0.28 | 0.02 | 0.02 | 0.28 |
| **$2_H$** | -0.36 | 0.14 | 0.11 | 0.23 | -0.12 |
| **$2_{methyl}$** | -0.30 | -0.07 | 0.02 | 0.12 | -0.09 |
| **$2_{ethyl}$** | -0.28 | -0.001 | 0.07 | 0.21 | -0.14 |
| **$2_{i\text{-}propyl}$** | -0.31 | 0.09 | 0.04 | 0.26 | -0.02 |
| **$2_{t\text{-}butyl}$** | -0.22 | 0.21 | 0.17 | 0.36 | -0.05 |

### 3.8 Nucleophilicity *vs.* proton affinity ($\Delta E_{PA}$):

For all singlet carbenes, the highest occupied Kohn–Sham orbital has σ symmetry with respect to the NHC plane and corresponds to the lone pair of the $C_{carbene}$ atom. Evidently, NHCs are strong bases.[19] Because ε (σ-HOMO) correlates not only to the first proton affinity, but more generally to the donor strength of the respective NHC, it is possible to rank the carbenes according to their donor strength based on the first proton affinities and the ε (σ-HOMO) values. By far the most weakly donating NHC is **$1_H$**, while **$1_{t\text{-}butyl}$** as well as other carbenes follow the order of increasing donor strength. Among normal carbenes, $\mathbf{1_{methyl}}$ shows the higher $\Delta E_{PA}$ = -49.47 kcal/mol because it has a small singlet-triplet energy gap (Table 6). Similarly in abnormal carbenes the highest $\Delta E_{PA}$ is found for $\mathbf{2_{methyl}}$ with $\Delta E_{PA}$ = -75.49 kcal/mol, while the lowest $\Delta E_{PA}$ is found for $\mathbf{1_H}$ with 56.21 kcal/mol in normal and for $\mathbf{2_{ethyl}}$ = -58.76 in abnormal tetrazol-5-ylidens (Table 6).

**Table 6** Proton affinities ($\Delta E_{PA}$, kcal/mol) in singlet carbenes ($\mathbf{1_R}$ and $\mathbf{2_R}$)

| NHCs | $\Delta E_{PA}$ |
|---|---|
| $\mathbf{1_H}$ | 56.21 |
| $\mathbf{1_{methyl}}$ | -49.47 |
| $\mathbf{1_{ethyl}}$ | -33.55 |
| $\mathbf{1_{\textit{i}-propyl}}$ | -34.76 |
| $\mathbf{1_{\textit{t}-butyl}}$ | -35.53 |
| $\mathbf{2_H}$ | -61.53 |
| $\mathbf{2_{methyl}}$ | -75.49 |
| $\mathbf{2_{ethyl}}$ | -58.76 |
| $\mathbf{2_{\textit{i}-propyl}}$ | -59.24 |
| $\mathbf{2_{\textit{t}-butyl}}$ | -59.47 |

### 3.9 Nucleophilicity *vs.* Dimerization:

Dimerization has been considered as one of the most important reactions of carbenes. In the classic dimerization mechanism of singlet carbenes, the filled σ orbital of each carbene was anticipated to interact with the empty p orbital of the other.[33] Alder *et al.* showed that most dimers are formed by proton-catalyzed or possibly metal ion-catalyzed routes.[34] Hence, they stated that in the absence of an appropriate catalyst, several carbenes including acyclic as well as saturated and unsaturated cyclics do not dimerize, within a reasonable frame of time, at ambient temperature (in THF). To reach an overview as completely as possible, we designed two sets of dimers: head-to-head and head-to-tail dimer(s) for our carbenes and calculated the energy differences of these two models of dimerization at M06/6-311++G** (Fig. 7). In the head-to-head form, $\mathbf{1_{\textit{t}-butyl}}$ does not dimerize, while all other normal $\mathbf{1_R}$ carbenes, plus abnormal $\mathbf{2_{methyl}}$ form doubly bonded (head-to-head) dimers (Table 7). In accord with the Carter, Goddard, Malrieu, and Trinquier model, doubly bonded dimers are expected to form if the sum of their $\Delta E_{s\text{–}t}$ values ($\sum\Delta E_{s\text{–}t}$) is smaller than the double bond energy of the dimer ($\Delta E_{dim}$).[35-38] Interestingly; the $\sum\Delta E_{s\text{–}t}$ values for our scrutinized carbenes are considerably greater than the related double bond energies (Table 7). This diminishes the possibility of their head-to-head dimerization. Finally, based on energy values, bulky *t*-butyl substituted emerges as the least probable candidate for dimerization at M06/6-311++G**. The cyclic bridged dimerization necessitates a formal negative charge on the carbene center and a formal positive charge on the nitrogen. For all our carbenes (except $\mathbf{1_{methyl}}$ and $\mathbf{2_{methyl}}$), cyclic bridged path is probable for being endothermic (see $\Delta E_{dim2}$ values in Table 7). Apeloig *et al.* reported that with increasing singlet-triplet energy separation, the energy of dimerization linearly decreases.[39] Unstable species for instance $\mathbf{1_{methyl}}$ and $\mathbf{2_{methyl}}$ have small singlet-triplet energy separations, they are expected to dimerize, and the dimers will be relatively stable. We showed above that the electrophilicity of carbenes continuously decreases with their decreasing stability from $\mathbf{1_R}$ to $\mathbf{2_R}$ and an increasing nucleophilicity from $\mathbf{2_R}$ to $\mathbf{1_R}$ (Table 7).

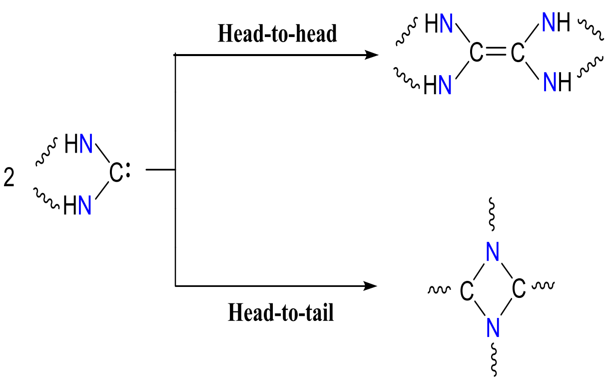


**Fig. 7** Possible dimerization forms of carbenes

**Table 7** M06/6-311++G** calculated dimerization energies leading to doubly bonded ($\Delta E_{dim1}$) and cyclic bridged ($\Delta E_{dim2}$) dimers for singlet ground states (kcal/mol) of $\mathbf{1_R}$ and $\mathbf{2_R}$ and sum of $\Delta E_{s\text{–}t}$ values ($\sum\Delta E_{s\text{–}t}$ / kcal/mol)

| NHCs | $\Delta E_{dimer1}$ (kcal/mol) | $\Delta E_{dimer2}$ (kcal/mol) | $\sum\Delta E_{s\text{–}t}$ |
|---|---|---|---|
| $\mathbf{1_H}$ | -4.69 | - | 175.86 |
| $\mathbf{1_{methyl}}$ | -31.33 | - | 146.32 |
| $\mathbf{1_{ethyl}}$ | -0.29 | - | 180.50 |
| $\mathbf{1_{\textit{i}-propyl}}$ | 13.15 | - | 174.94 |
| $\mathbf{2_H}$ | -15.58 | - | 108.36 |
| $\mathbf{2_{methyl}}$ | -46.94 | - | 79.84 |
| $\mathbf{2_{ethyl}}$ | -13.67 | - | 112.88 |
| $\mathbf{2_{\textit{i}-propyl}}$ | -14.78 | - | 112.06 |
| $\mathbf{2_{\textit{t}-butyl}}$ | -10.28 | - | 108.10 |
| $\mathbf{2_H}$ | - | 73.63 | 108.36 |
| $\mathbf{2_{ethyl}}$ | - | 73.71 | 112.88 |
| $\mathbf{2_{\textit{i}-propyl}}$ | - | -11.56 | 112.06 |
| $\mathbf{2_{\textit{t}-butyl}}$ | - | 24.18 | 108.10 |

The HOMO plots of abnormal carbenes ($\mathbf{2_R}$) and normal carbenes ($\mathbf{1_R}$) suggest a $\sigma^2$ configuration $\mathbf{1_R}$ and $\mathbf{2_R}$ carbenes with the electron density dispersed in the plan of the molecule (Fig. 8).

The nucleus independent chemical shift (NICS) calculated at 0.5, 1, 1.5, 2, 2.5 and 3 Å above the ring center for singlet carbenes $\mathbf{1_R}$ and $\mathbf{2_R}$, at M06/6-311++G** level of theory. The results of our calculations indicate that every $\mathbf{2_R}$ (except $\mathbf{2_{methyl}}$) emerges more aromatic than its corresponding normal $\mathbf{1_R}$ isomer. This is attributed to the higher nucleus independent chemical shifts (NICS) of the former, calculated at 1 Å above the ring center (Table 8).

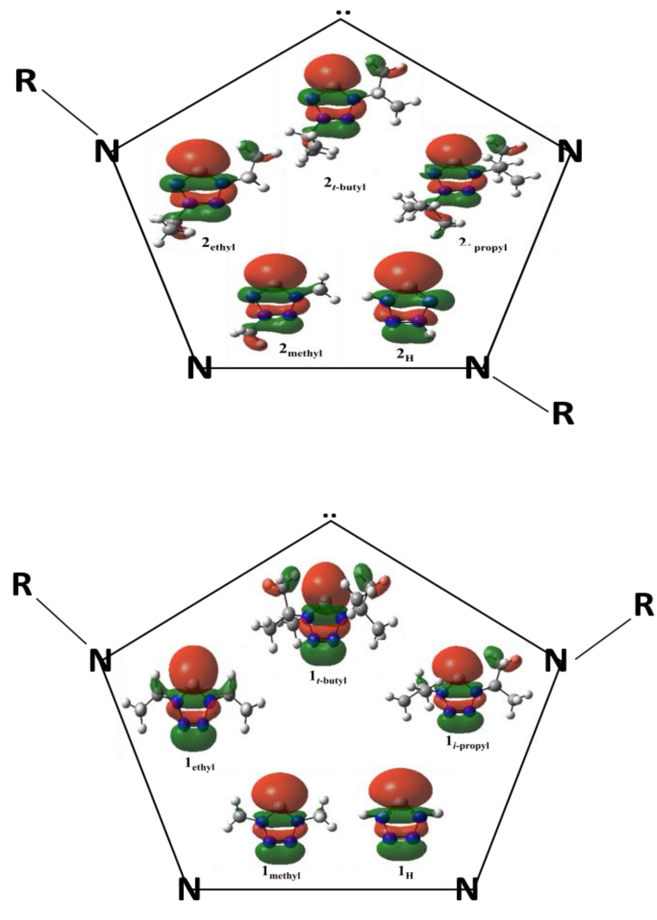


**Fig. 8** The HOMO plots of abnormal carbenes ($\mathbf{2_R}$) and normal carbenes ($\mathbf{1_R}$).

**Table 8.** The nucleus independent chemical shift (NICS) calculated at 0.5, 1, 1.5, 2, 2.5 and 3 Å above the ring center for singlet carbenes $\mathbf{1_R}$ and $\mathbf{2_R}$, at M06/6-311++G** level of theory

| **NHCs** | $\mathbf{1_H}$ | $\mathbf{1_{methyl}}$ | $\mathbf{1_{ethyl}}$ | $\mathbf{1_{\textit{i}\text{-propyl}}}$ | $\mathbf{1_{\textit{t}\text{-butyl}}}$ |
|---|---|---|---|---|---|
| **NICS (0)** | 15.8516 | 11.0169 | 13.7409 | 13.4075 | 12.9468 |
| **NICS (0.5)** | 17.0321 | 13.6992 | 15.6866 | 15.3113 | 15.2318 |
| **NICS (1)** | 13.7891 | 12.0629 | 12.9938 | 13.0070 | 13.1394 |
| **NICS (1.5)** | 8.4059 | 7.5054 | 7.9754 | 8.0719 | 8.1563 |
| **NICS (2)** | 4.8216 | 4.3560 | 4.5942 | 4.6746 | 4.7151 |
| **NICS (2.5)** | 2.8586 | 2.6031 | 2.7266 | 2.7678 | 2.7854 |
| **NICS (3)** | 1.7845 | 1.6312 | 1.7048 | 1.7071 | 1.7124 |

| **NHCs** | $\mathbf{2_H}$ | $\mathbf{2_{methyl}}$ | $\mathbf{2_{ethyl}}$ | $\mathbf{2_{\textit{i}\text{-propyl}}}$ | $\mathbf{2_{\textit{t}\text{-butyl}}}$ |
|---|---|---|---|---|---|
| **NICS (0)** | 15.3955 | 17.7510 | 13.0120 | 13.0014 | 12.4720 |
| **NICS (0.5)** | 17.1728 | 16.5541 | 16.6071 | 15.8060 | 14.9951 |
| **NICS (1)** | 14.2325 | 11.5566 | 14.6339 | 13.7023 | 13.1527 |
| **NICS (1.5)** | 8.7848 | 6.8859 | 8.4078 | 8.4875 | 8.3561 |
| **NICS (2)** | 5.0740 | 4.0291 | 4.4348 | 4.8776 | 4.9127 |
| **NICS (2.5)** | 3.0188 | 2.4406 | 2.5019 | 2.8738 | 2.9210 |
| **NICS (3)** | 1.8896 | 1.5450 | 1.5302 | 1.7731 | 1.8080 |

## 4 Conclusions

A comparison is made between *N* of 1,4-disubstituted, "normal", tetrazol-5-ylidens ($\mathbf{1_R}$), and their 1,3-disubstituted, "mesoionic, or abnormal", isomers ($\mathbf{2_R}$), at the M06/6-311++G** level of theory; where R = H, methyl, ethyl, *i*-propyl, and *t*-butyl. Also acetaldehyde is used as a target molecule for probing real nucleophilic reactions as functions of the size of substituents, at same level of theory. The results of our calculations indicate that every abnormal $\mathbf{2_R}$ is more nucleophilic than its corresponding normal $\mathbf{1_R}$ isomer for exhibiting a larger *N* and a smaller $\Delta G^{\ddagger}$. In addition, *N* increases as the size of the substituent increases that it shows this parameter only cover substituents σ-donor abilities, while the kinetically results ($\Delta G^{\ddagger}$) simultaneously include both σ-donor abilities and steric effects. Our calculated global electrophilicity ($\omega$ / eV) takes on a trend with an exactly opposite direction from *N*. Stabilities of $\mathbf{1_R}$ and $\mathbf{2_R}$ carbenic species are presumed to be related to their singlet-triplet energy gaps ($\Delta E_{S\text{-}T}$, kcal/mol). Every normal $\mathbf{1_R}$ appears more stable but less nucleophilic than its corresponding abnormal $\mathbf{2_R}$ isomer. Hence, nucleophilicity of an isomeric carbene appears to be indirectly proportional to $\Delta E_{S\text{-}T}$. Another words, the less stable is a carbene, the more nucleophilic it may be. Among the ten species scrutinized ($\mathbf{1_R}$ and $\mathbf{2_R}$), $\mathbf{1_{methyl}}$ and $\mathbf{2_{methyl}}$ stand out for their highest degrees of puckering. In contrast, the most planar species turn out to be the $\mathbf{1_H}$ and $\mathbf{2_H}$. According to our calculation the angle (N—$C_{carbene}$—N) is increased from normal to abnormal carbenes. Likewise, nucleophilicity is increased from normal to abnormal carbenes. Interestingly, except for nonplanar $\mathbf{1_{methyl}}$, the trend of (N—$\hat{C}_{carbene}$—N) angle for planar species is $\mathbf{1_{\textit{t}\text{-butyl}}}$ > $\mathbf{1_{\textit{i}\text{-propyl}}}$ > $\mathbf{1_{ethyl}}$ > $\mathbf{1_H}$. Similarly, the highest carbenic angle in abnormal $\mathbf{2_R}$ carbenes is for nonplanar $\mathbf{2_{methyl}}$. Except for the latter, the trend of (N—$\hat{C}_{carbene}$—N) angle for planar abnormal species is $\mathbf{2_{\textit{t}\text{-butyl}}}$ > $\mathbf{2_{\textit{i}\text{-propyl}}}$ > $\mathbf{2_{ethyl}}$ > $\mathbf{2_H}$. These trends also appear consistent with that of their nucleophilicity values. The normal $\mathbf{1_{\textit{t}\text{-butyl}}}$ as well as other normal molecules follows in order of increasing donor strength. Among normal carbenes, $\mathbf{1_{methyl}}$ shows the higher $\Delta E_{PA}$ = -49.47 kcal/mol because it has a small singlet-triplet energy separations. Similarly in abnormal carbenes the highest $\Delta E_{PA}$ is found for $\mathbf{2_{methyl}}$, with $\Delta E_{PA}$ = -75.49 kcal/mol; while the lowest $\Delta E_{PA}$ are found for $\mathbf{1_H}$ with 56.21 kcal/mol in normal and for $\mathbf{2_{ethyl}}$ = -58.76 in abnormal. In the head-to-head form, $\mathbf{1_{\textit{t}\text{-butyl}}}$ does not dimerize, while all other normal $\mathbf{1_R}$ carbenes, plus abnormal $\mathbf{2_{methyl}}$ may form doubly bonded (head-to-head) dimers. Finally, bulky substituted $\mathbf{1}_{t\text{-butyl}}$ emerges as the least probable candidate for dimerization. For all our carbenes (except $\mathbf{1_{methyl}}$ and $\mathbf{2_{methyl}}$), cyclic bridged path is probable for being endothermic. We showed above that the electrophilicity of carbenes continuously decreases with their decreasing stability from $\mathbf{1_R}$ to $\mathbf{2_R}$ and an increasing nucleophilicity is seen from $\mathbf{2_R}$ to $\mathbf{1_R}$.

## Acknowledgements

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**Graphical Abstract**

Nucleophilicity of both normal (**$1_R$**) and abnormal (**$2_R$**) N-heterocyclic carbene (NHC); every **$2_R$** showing a higher nucleophilicity than its corresponding **$1_R$** isomer (R = H, methyl, ethyl, *i*-propyl, and *t*-butyl)