

Study of Electronic Effects on Normal vs. Abnormal Tetrazol-5-ylidenes at DFT

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ABSTRACT: We present electronic effects on stability (ΔE_{S-T}), nucleophilicity (N), global electrophilicity (ω), and band gaps ($\Delta E_{HOMO-LUMO}$) of 36 novel 1,4- and 1,3-tetrazole-5-ylidenes, 1 and 2, respectively. A union of three sets of "normal" $1_{W,W}$, $1_{D,D}$, and $1_{D,W}$ are compared to another union of four sets of "abnormal" $2_{W,W}$, $2_{D,D}$, $2_{D,W}$ and $2_{W,D}$ NHCs, electron-withdrawing substituents (W) and electron-donating ones (D). Every 1 is more stable and shows a larger bandgap than its corresponding 2. In addition, philicities, N and ω , of every 2 appear larger than that of the corresponding 1 isomer. Carbenes with W groups increase electrophilicity while D ones increase nucleophilicity and in pull-push groups, W groups in carbene center increase electrophilicity. All our NHCs give doubly bonded head-to-head dimers except for 5 species.

KEYWORDS: Tetrazolyliidenes; Band gap; Singlet-triplet energy gap; Electronic effects.

INTRODUCTION

Carbenes are sextet neutral divalent carbon species. The two nonbonding-unpaired electrons of a triplet carbene have parallel spins with a linear or bent geometry, while those of a closed shell singlet carbene appear anti-parallel in an σ or $2p_{\pi}$ orbital. In contrast, a singlet open shell carbene has one of its two-nonbonding electrons in σ and the other in a $2p_{\pi}$ orbital. Carbenes ordinarily are unstable reactive intermediates with very short lifetimes. To access stability of carbenes, substantial efforts have been made to determine their singlet-triplet energy gap [$\Delta E_{S-T} = E(\text{triplet}) - E(\text{singlet})$] [1]. Arduengo and co-workers reported the first stable N-heterocyclic carbene (NHC), which became commercially available in 1991 [2]. The latter owed its viability to the electronic effects of the two neighboring α -nitrogen atoms plus the steric protection of its adamantyl groups. Subsequently, many reports appeared probing electronic and steric effects on the stability of other

NHCs [2-14]. The electronic stabilization factors included a π -donation into the carbene out-of-plane p orbital by the electron-rich π -system (N-C=C-N) and a π -electronegativity effect. NHCs are usually defined as σ -basic/ π^* -acidic ligands. The frontier molecular orbital (MO) pattern shows the carbene lone pair generally is the highest occupied molecular orbital (HOMO) and gives σ -donicity property to the NHC. The pattern of the π MOs depends on the nature of the backbone, as well as on the presence of a 3rd N atom, as in triazoles. One of the lowest unoccupied molecular orbitals (LUMOs) generally corresponds to a π^* MO strongly localized on the carbene atom, and gives π -acidity property to the NHC. Filled π MOs are generally lower in energy than the carbene lone pair and give weak π -donicity property to the NHC [15].

Normal carbenes appear less nucleophilic than their corresponding abnormal isomers, for R = H, methyl, ethyl,

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i-propyl, and *t*-butyl [7]. The substituent constant σ_m of Hammett [16] has recently been correlated to various thermodynamic parameters of divalents [17]. Sketching σ_m against a desired Divalent Thermodynamic Parameter (DTP) may give a linear correlation factor ρ . A positive value of ρ means that DTP responds to substituents in the same sense as benzoic acid ionization; *i.e.*, electron withdrawing groups increase DTP. If $\rho > 1$, then DTP is more sensitive to the effect of the substituent than benzoic acid dissociation. If $0 < \rho < 1$, then electron-withdrawing groups still increase DTP but less than in benzoic acid dissociation. A negative ρ means that electron-donating groups increase DTP.

A small ρ often means that a triplet divalent with a free radical nature is involved with little charge separation [18]. Allenes are found to racemize by passing over their corresponding planar singlet carbenic transition states (R=H, F, Cl, Br, I, OH, NH₂, CN and NO₂) [19]. The height of the energy barrier relates to the topology of R which is the highest in *para* and lowest in the *ortho*. Steric effects may explain the lower linearity of the free energy relationships found for the latter. Moreover, D groups highly increase the rate of the above enantiomeric interconversions. Following our recent report on steric effects on nucleophilicity of NHCs at DFT [7], here we are interested to know how N of (1) and (2) are influenced by electronic effects. Hence, we have probed electron withdrawing substituents (W = NO₂, CN, CO₂H, Cl, CF₃, F, and CO₂Me) plus electron donating ones (D = TMS, NMe₂, NH₂, OMe, and OH), at M06 (Fig. 1). All optimized structures are stability singlet state and they have C₁ point group (except: 1_{NH₂,NH₂} (C_s), 1_{NMe₂,NMe₂} (C_s), 1_{CO₂H,CO₂H} (C₂), 1_{CO₂Me,CO₂Me} (C₂), and 1_{CN,CN} (C_s)) (Fig. 1).

We have studied correlation between N, ω , and ΔE_{S-T} of **1** and **2** against their corresponding Hammett substituent constants (σ_m), they give poor linear correlation factors ($R^2 = 0.3-0.7$, see supplementary information).

COMPUTATIONAL METHODS

For all structures, geometry optimizations are carried out with the Gaussian 98 program at the M06 level, and the 6-311++G** basis set [20-22]. Triplet multiplicity structures are optimized through unrestricted broken spin-symmetry UM06/6-311++G** method. M06 density functional methods are available in the DFT for both restricted (for singlet close-shell) and unrestricted

(for triplet states). The nature of all optimized structures is determined by calculating the harmonic vibrational frequencies (minima with no imaginary frequency (keyword: FREQ = NORAMAN)). The frequency calculations also provide thermodynamic parameters such as the zero-point vibrational energy, thermal correction, enthalpies, and Gibbs free energies at 298.15 K and 1.0 atm. Nucleophilicity index, N , [23] is calculated as $N = E_{\text{HOMO}(\text{Nu})} - E_{\text{HOMO}(\text{TCNE})}$, where HOMO(Nu) and HOMO(TCNE) are the highest occupied molecular orbitals of NHCs and the reference tetracyanoethylene, respectively. The global electrophilicity (ω) [24] is also calculated using the expression, $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2$) and η is the chemical hardness ($\eta = E_{\text{LUMO}} - E_{\text{HOMO}}$) [25].

RESULTS AND DISCUSSION

We have compared and contrasted normal 1,4-disubstituted tetrazol-5-ylidens (**1**), with abnormal 1,3-disubstituted tetrazol-5-ylidens (**2**), at M06/6-311++G** level of theory. Electron withdrawing groups (W) employed consist of NO₂, CN, CO₂H, Cl, CF₃, F, and CO₂Me. Electron donating groups (D) used are TMS, NMe₂, NH₂, OMe, and OH. In addition, push-pull groups (D,W) used are (NH₂,CO₂Me), (NH₂,CN), (OMe,CN), and (OMe,CO₂Me); while pull-push groups (W,D) used are (CN,NH₂), (CN,OMe), (CO₂Me,OMe), and (CO₂Me,NH₂) (Fig. 1). Singlet-triplet energy gaps ($\Delta E_{S-T} = E_T - E_S$), proton affinity (PA), dimerization (ΔE_{dim}), nucleophilicity (N), electrophilicity (ω), band gap ($\Delta E_{\text{HOMO-LUMO}} = E_{\text{LUMO}} - E_{\text{HOMO}}$) and isodesmic reactions are reported. We used acetaldehyde derivatives as a target molecule for probing real nucleophilic reactions at same level of theory by the substituents.

Addition reactions of (1) and (2) with acetaldehyde in the gas phase are characterized by Gibbs's free energy ΔG (kcal/mol). This data showed that every (2) is more stable than its corresponding (1) (Table 1, Fig. 2). The unanticipated stability of free NHC would arise mainly from substantial σ -charge transfer from the carbenic carbon to the more electronegative neighboring nitrogen atoms. So, π -donation would only play a minor role. Related theoretical and experimental studies have also suggested that there is a cyclic electron stabilization, conferring the imidazol-2-ylidenes a certain aromatic character. Directly, the essential stabilizing role

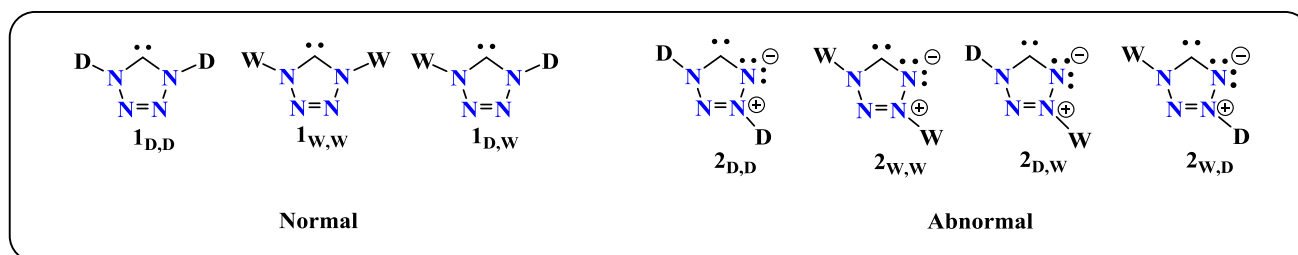


Fig. 1: Scrutinized carbenes including three sets normal $1_{W,W}$, $1_{D,D}$ and $1_{D,W}$, and four sets abnormal $2_{W,W}$, $2_{D,D}$, $2_{D,W}$ and $2_{W,D}$; for $D = \text{TMS}, \text{NMe}_2, \text{NH}_2, \text{OMe}, \text{and OH}$; while $W = \text{NO}_2, \text{CN}, \text{CO}_2\text{H}, \text{Cl}, \text{CF}_3, \text{F}, \text{and CO}_2\text{Me}$.

of the C=C bond in imidazol-2-ylidenes has been induced for a long time. The classical explanation using a thermodynamic stabilization of the carbenes via cyclic 6π -electron delocalization had reviewed after the isolation of the first imidazolin-2-ylidenes in 1995. It was then clear that such a delocalization would only be an additional stabilizing reason, and that the electron donation of the nitrogen atoms would be necessary and sufficient for stabilizing the free carbene. On the other hand, Arduengo suggested a kinetic stabilization provided by the double bond. It has stated as critical for achieving an electron repulsion strong enough to prevent any electrophilic reactivity of the carbene [26].

Schleyer and co-workers have used the Nucleus Independent Chemical Shift (NICS) as a new magnetic-based aromaticity parameter [27]. The NICS is a method of computational that calculates the absolute magnetic shielding at the center of a ring. The shielding values report with a reversed sign to make them compatible with the chemical shift conventions of NMR spectroscopy [28]. The negative NICS values indicate aromaticity and positive values antiaromaticity. NICS's are calculated at 0.5, 1, 1.5, and 2 Å above the ring center for singlet carbenes (1) and (2), at M06/6-311++G** level of theory. The results of our calculations indicate that every (2) (except $2_{\text{TMS},\text{TMS}}$, $2_{\text{CO}_2\text{H},\text{CO}_2\text{H}}$, $2_{\text{CO}_2\text{Me},\text{CO}_2\text{Me}}$, $2_{\text{CF}_3,\text{CF}_3}$, $2_{\text{NO}_2,\text{NO}_2}$) emerges more aromatic than its corresponding normal (1) isomer in $1_{D,D}$ and $1_{W,W}$ groups but in $2_{D,W}$ is more aromatic than its corresponding 1(except $2_{\text{NH}_2,\text{CN}}$). This is attributed to the higher NICS of the former, calculated at 1Å above the ring center (Table 1).

Substituent effects on philicities (N and ω), band and energy gaps

The nucleophilicity index, N , which was introduced by Domingo *et al* [24] is a crucial factor for coordination

of NHCs to transition metal complexes. Here, we have calculated N and global electrophilicity (ω) indices for our singlet ground state carbenes, at M06/6-311++G**. The results of our calculations indicate that every abnormal (2) is more nucleophilic than its corresponding normal (1) isomer (Table 1). For instance, in the abnormal $2_{D,D}$ set, $2_{\text{TMS},\text{TMS}}$ ($N = 3.52$ eV) exerts more nucleophilicity than its corresponding normal $1_{\text{TMS},\text{TMS}}$ isomer ($N = 2.67$ eV). In the abnormal $2_{W,W}$ set, $2_{\text{CO}_2\text{Me},\text{CO}_2\text{Me}}$ ($N = 2.67$ eV) exerts more nucleophilicity than its corresponding normal $1_{\text{CO}_2\text{Me},\text{CO}_2\text{Me}}$ isomer ($N = 1.57$ eV). Likewise, abnormal $2_{\text{CO}_2\text{Me},\text{NH}_2}$ ($N = 2.69$ eV) and $2_{\text{NH}_2,\text{CO}_2\text{Me}}$ ($N = 2.55$ eV) exert more nucleophilicity than its corresponding normal $1_{\text{NH}_2,\text{CO}_2\text{Me}}$ isomer ($N = 1.972$ eV). The band gap of every (2) appears narrower than its corresponding (1) (Table 1). Carbenes with electron withdrawing groups increase electrophilicity while electron donating ones increase nucleophilicity and in pull-push groups, electron withdrawing group in carbene center increase electrophilicity. The N increases in going from OH to OMe (1.36 to 1.55), NH_2 to NMe_2 , CO_2H to CO_2Me , CN to CF_3 , (OMe,CN) to (OMe, CO_2Me) and (NH_2,CN) to ($\text{NH}_2,\text{CO}_2\text{Me}$) in (1) and (2) (Table1). Hence, N increases as a function of the size of the substituent (W or D). Between normal and abnormal TMS is more nucleophilic than other donor groups, $\text{TMS} > \text{NMe}_2 > \text{NH}_2 > \text{OMe} > \text{OH}$ (Table 1). Similarly, beyond this phenomenon lays several views: a) The orders of our calculated N values appear consistent with the trend of the σ -donor abilities of the employed substituents: $\text{TMS} > \text{NMe}_2 > \text{NH}_2 > \text{OMe} > \text{OH}$. In electron withdrawing sets, N values appear consistent with the trend of the π -acceptor abilities of the employed substituents. Hence, the trend of N values in normal $1_{W,W}$ set is: $\text{F} > \text{Cl} > \text{CO}_2\text{Me} > \text{CF}_3 > \text{NO}_2 > \text{CN} > \text{CO}_2\text{H}$. This trend in abnormal $2_{W,W}$ set appears as: $\text{CO}_2\text{Me} > \text{Cl} > \text{NO}_2 > \text{F}$

Table 1: Nucleophilicity (N), and electrophilicity (ω), singlet–triplet energy gaps (ΔE_{S-T} , kcal/mol), band gaps between HOMO and LUMO orbitals ($\Delta E_{HOMO-LUMO}$, kcal/mol), the smallest calculated vibrational frequencies (ν_{min} , cm^{-1}), proton affinities (PA, kcal/mol), the nucleus independent chemical shift (NICS) calculated at 1 Å above the ring center, and carbene charge for singlet states of scrutinized NHCs, at M06/6-311++G.**

Set	NHCs	N	ω	ΔE_{S-T}	$\Delta E_{HOMO-LUMO}$	ν_{min}	PA	NICS(1)	Carbene charge
$1_{D,D}$	$1_{OH,OH}$	1.36	1.78	84.16	151.23	133.13	219.27	-11.97	0.10
	$1_{OMe,OMe}$	1.55	1.48	89.37	157.50	66.14	227.94	-12.17	0.11
	$1_{NH_2,NH_2}$	1.77	1.55	86.39	148.72	85.59	233.78	-12.26	0.12
	$1_{NMe_2,NMe_2}$	2.23	1.44	85.00	140.56	25.72	242.27	-12.70	0.12
	$1_{TMS,TMS}$	2.67	1.44	86.09	128.89	24.23	253.82	-13.55	0.13
$1_{W,W}$	$1_{F,F}$	2.09	1.74	54.12	133.22	217.48	194.82	-12.09	0.12
	$1_{Cl,Cl}$	1.63	1.68	44.63	147.46	139.93	213.67	-12.07	0.19
	$1_{CO_2H,CO_2H}$	-0.08	2.56	86.61	163.15	66.93	210.73	-12.09	0.10
	$1_{CO_2Me,CO_2Me}$	1.57	1.84	70.80	143.38	28.15	228.35	-11.92	0.24
	$1_{CN,CN}$	0.00	2.96	64.93	150.29	98.77	187.05	-13.19	0.31
	$1_{CF_3,CF_3}$	0.73	2.25	80.05	151.86	17.79	205.65	-12.49	0.25
	$1_{NO_2,NO_2}$	0.47	3.59	66.68	126.06	34.68	208.70	-11.77	0.23
$1_{D,W}$	$1_{OMe,CN}$	0.77	2.28	79.73	149.84	76.99	209.14	-12.45	0.20
	$1_{OMe,CO_2Me}$	1.56	1.82	47.24	144.62	38.24	228.18	-12.03	0.19
	$1_{NH_2,CN}$	0.88	2.16	81.38	150.89	111.98	211.38	-12.42	0.20
	$1_{NH_2,CO_2Me}$	1.72	1.73	87.21	143.46	41.46	230.97	-12.11	0.17
$2_{D,D}$	$2_{OH,OH}$	2.00	1.77	54.57	134.66	157.98	233.56	-11.62	0.02
	$2_{OMe,OMe}$	2.53	1.54	51.75	128.64	31.91	245.49	-11.80	0.06
	$2_{NH_2,NH_2}$	2.72	1.64	55.57	120.48	115.76	246.44	-11.85	0.06
	$2_{NMe_2,NMe_2}$	3.13	1.43	57.34	116.78	33.07	258.01	-12.06	0.08
	$2_{TMS,TMS}$	3.52	1.46	54.36	105.73	09.36	270.62	-13.95	0.05
$2_{W,W}$	$2_{F,F}$	1.69	1.35	45.11	148.72	230.28	214.75	-11.69	0.09
	$2_{Cl,Cl}$	2.04	1.52	22.70	145.58	149.60	231.85	-12.01	0.13
	$2_{CO_2H,CO_2H}$	1.28	3.45	33.98	89.17	69.98	215.49	-12.67	0.07
	$2_{CO_2Me,CO_2Me}$	2.67	2.89	40.19	97.89	26.68	244.39	-12.29	0.12
	$2_{CN,CN}$	1.36	4.98	39.24	93.56	112.84	214.52	-13.19	0.18
	$2_{CF_3,CF_3}$	1.36	3.14	43.07	106.05	23.76	227.62	-13.15	0.14
	$2_{NO_2,NO_2}$	1.88	4.96	34.16	84.15	32.88	232.92	-11.94	0.13
$2_{D,W}$	$2_{OMe,CN}$	1.75	3.08	48.10	108.10	58.29	228.97	-12.62	0.05
	$2_{OMe,CO_2Me}$	2.46	2.36	49.03	107.26	37.35	244.91	-12.19	0.01
	$2_{NH_2,CN}$	1.84	3.06	49.39	106.49	125.43	228.55	-12.24	0.06
	$2_{NH_2,CO_2Me}$	2.55	2.36	50.05	105.27	46.13	246.76	-12.43	0.03
$2_{W,D}$	$2_{CN,OMe}$	1.82	2.58	47.42	116.78	52.39	228.40	-11.91	0.15
	$2_{CN,NH_2}$	1.92	2.61	51.16	114.02	129.19	230.25	-11.68	0.15
	$2_{CO_2Me,OMe}$	2.61	1.99	44.95	113.00	18.13	247.52	-11.59	0.13
	$2_{CO_2Me,NH_2}$	2.69	2.02	47.16	109.92	45.34	249.22	-11.77	0.13

$\text{CF}_3 \approx \text{CN} > \text{CO}_2\text{H}$. In the pull-push sets ($1_{\text{W,D}}$, $2_{\text{W,D}}$ and $2_{\text{D,W}}$) the trend of N values is $(\text{CO}_2\text{Me}, \text{NH}_2) > (\text{CO}_2\text{Me}, \text{OMe}) > (\text{CN}, \text{NH}_2) > (\text{CN}, \text{OMe}) > (\text{NH}_2, \text{CO}_2\text{Me}) > (\text{OMe}, \text{CO}_2\text{Me}) > (\text{NH}_2, \text{CN}) > (\text{OMe}, \text{CN})$. b) For each species N is directly proportional to the energy of its highest occupied molecular orbital (E_{HOMO}) [25]. Our calculated global electrophilicity (ω/eV) [24,25] takes on a trend with an exactly opposite direction from N . Every (2) appears less electrophilic than its corresponding (1) isomer (Table 1). In comparison to the nucleophilicity indexes that only cover substituents σ -donor abilities, here the results simultaneously include the latter plus electronic effects. The trends of reactivity indicate that $1_{\text{TMS,TMS}}$ and $2_{\text{TMS,TMS}}$ are more reactive than other species in their corresponding (1) and (2) donor series, respectively. These data indicate that both $1_{\text{D,D}}$ and $2_{\text{D,D}}$ show relatively higher stability and nucleophilicity with a rather low electrophilicity (Table 1). On the other hand, every (2) is presumably less stable than its corresponding (1) for exhibiting a smaller $\Delta E_{\text{S-T}}$ (Table 1).

For instance, $2_{\text{NMe}_2, \text{NMe}_2}$ with $\Delta E_{\text{S-T}} = 57.34$ kcal/mol is assumed less stable than $1_{\text{NMe}_2, \text{NMe}_2}$ ($\Delta E_{\text{S-T}} = 85.00$ kcal/mol). Likewise, $2_{\text{F,F}}$ with $\Delta E_{\text{S-T}} = 45.11$ kcal/mol appears less stable than $1_{\text{F,F}}$ ($\Delta E_{\text{S-T}} = 54.12$ kcal/mol), while $2_{\text{NH}_2, \text{CO}_2\text{Me}}$ with $\Delta E_{\text{S-T}} = 50.05$ kcal/mol and $2_{\text{CO}_2\text{Me}, \text{NH}_2}$ ($\Delta E_{\text{S-T}} = 47.16$ kcal/mol) appear less stable than $1_{\text{NH}_2, \text{CO}_2\text{Me}}$ ($\Delta E_{\text{S-T}} = 87.21$ kcal/mol). Hence, nucleophilicity of an isomeric carbene appears to be indirectly proportional to $\Delta E_{\text{S-T}}$. On the other, the less stable is a carbene, the more nucleophilic it may be. Among normal carbenes, $1_{\text{OMe}, \text{OMe}}$ ($\Delta E_{\text{S-T}} = 89.37$ kcal/mol) appears as the most stable in $1_{\text{D,D}}$ sets, while $1_{\text{CO}_2\text{H}, \text{CO}_2\text{H}}$ ($\Delta E_{\text{S-T}} = 86.61$ kcal/mol) and $1_{\text{NH}_2, \text{CO}_2\text{Me}}$ ($\Delta E_{\text{S-T}} = 87.21$ kcal/mol) are the most stable in $1_{\text{W,W}}$ and $1_{\text{D,W}}$, respectively. In contrast, the least stable of all normal carbenes is $1_{\text{Cl}, \text{Cl}}$ with $\Delta E_{\text{S-T}} = 44.63$ kcal/mol (Table 1). Similarly in abnormal carbenes, $2_{\text{NMe}_2, \text{NMe}_2}$ ($\Delta E_{\text{S-T}} = 57.34$ kcal/mol) appears as the most stable in $2_{\text{D,D}}$ sets, while $2_{\text{F,F}}$ ($\Delta E_{\text{S-T}} = 45.11$ kcal/mol) and $2_{\text{NH}_2, \text{CO}_2\text{Me}}$ ($\Delta E_{\text{S-T}} = 50.05$ kcal/mol) and $2_{\text{CN}, \text{NH}_2}$ ($\Delta E_{\text{S-T}} = 51.16$ kcal/mol) are the most stable in $2_{\text{W,W}}$, $2_{\text{D,W}}$, and $2_{\text{W,D}}$ respectively. In contrast, the least stable of all abnormal carbenes is $2_{\text{Cl}, \text{Cl}}$ with $\Delta E_{\text{S-T}} = 22.70$ kcal/mol (Table 1). Higher $\Delta E_{\text{S-T}}$ correlates with lower carbenic charge on normal carbenes (1). It is not true for abnormal carbenes (2) (Table 1). An inverse relationship is often anticipated between the electrophilic and nucleophilic character of a molecule,

which is indeed found in the case of our carbenes. Hoffmann, Schleyer, and Schaefer have emphasized that a molecule may be called "stable" if its computed smallest vibrational frequency (ν_{min}) is at least 100 cm^{-1} [26]. In this work the following show ν_{min} more than 100 cm^{-1} : $1_{\text{Cl}, \text{Cl}}$ (139.93 cm^{-1}), $1_{\text{F}, \text{F}}$ (217.48 cm^{-1}), $1_{\text{CN}, \text{CN}}$ (98.77 cm^{-1}), $1_{\text{NH}_2, \text{CN}}$ (111.98 cm^{-1}), $2_{\text{OH}, \text{OH}}$ (157.98 cm^{-1}), $2_{\text{F}, \text{F}}$ (230.28 cm^{-1}), $2_{\text{Cl}, \text{Cl}}$ (149.6 cm^{-1}), $2_{\text{CN}, \text{CN}}$ (112.42 cm^{-1}), and $2_{\text{NH}_2, \text{CN}}$ (125.43 cm^{-1}) (Table 1). In terms of $\Delta E_{\text{S-T}}$, stability of both (1) and (2) species appear dependent on the electronic effects of the substituents.

The important reason to explain the stability of the singlet state is the inductive effect of the σ -withdrawing amine group substituents, which stabilizes the σ orbital on the carbenic center. This stabilization of the σ orbital increases the $E_{\text{S-T}}$'s gap, and thus the single state is favored. p_π donation from the N atoms into the vacant p_π orbital of the carbene C atom explain more stabilization [29].

Relative stability

NHCs tendency to coordinate to carbon-electrophiles has made act as organocatalysts [30]. At M06/6-311++G^{**} level of theory, acetaldehyde derivative was used as a target molecule for probing real nucleophilic reactions. Every abnormal (2) acts more nucleophilic than its corresponding normal (1) isomer in donor sets, since every (2) turns out more reactive than its corresponding (1) for exhibiting a smaller ΔG^\ddagger (Table 2, Fig. 2). The relative stability of the studied series (n, ab and pull-push) are analyzed using isodesmic reactions (Fig. 2). The corresponding calculated Gibbs free energy values (ΔG^{2-4}) are given in Table 2. First, we compare the studied series with the corresponding five-membered Arduengo-type counterparts (Fig. 2). The tetrazolydene structures (normal and abnormal) in electron withdrawing, releasing and pull-push groups are less stable than NHC species (strongly negative magnitudes of ΔG^2 are found). The largest differences in stability are predicted for $1_{\text{W,W}}$ and $2_{\text{W,W}}$. However, negative ΔG^3 values are seen for $1_{\text{W,W}}$ and $2_{\text{W,W}}$; that show they are not stability but other groups are more stability than saturated five-membered Arduengo-type. This is supported by the more negative absolute NICS values predicted for stable series. There are negative ΔG^4 values for some $1_{\text{W,W}}$ and $2_{\text{W,W}}$ too; in other groups ΔG^4 is positive that show they are more stable than linear diaminocarbene. These results evidence that the studied species can generally be synthesized, or at least used as ligands in metal complexes.

Table 2: M06/6-311++G calculated for singlet ground states (kcal/mol) of isodesmic reactions for comparing stability of carbenes.**

Set	NHCs	ΔG^1	ΔG^2	ΔG^3	ΔG^4	Set	NHCs	ΔG^1	ΔG^2	ΔG^3	ΔG^4
1 _{D,D}	1 _{OH,OH}	3.12	-12.16	0.82	1.65	2 _{D,D}	2 _{OH,OH}	8.52	-4.29	8.69	9.52
	1 _{OMe,OMe}	40.05	-6.13	6.85	7.68		2 _{OMe,OMe}	54.88	-9.55	3.43	4.26
	1 _{NH2,NH2}	21.18	-6.72	6.27	7.09		2 _{NH2,NH2}	24.69	-0.58	12.40	13.22
	1 _{NMe2,NMe2}	40.48	-0.53	12.45	13.28		2 _{NMe2,NMe2}	54.54	-0.89	12.09	12.92
	1 _{TMS,TMS}	-3.21	2.42	15.40	16.23		2 _{TMS,TMS}	-3.49	3.84	16.82	17.64
1 _{w,w}	1 _{F,F}	-	-17.22	-4.24	-3.41	2 _{w,w}	2 _{F,F}	43.21	-22.88	-9.90	-9.07
	1 _{Cl,Cl}	30.67	-11.25	1.74	2.56		2 _{Cl,Cl}	60.45	-2.90	10.08	10.90
	1 _{CO2H,CO2H}	-	-20.16	-7.18	-6.35		2 _{CO2H,CO2H}	-	-16.24	-3.25	-2.43
	1 _{CO2Me,CO2Me}	-	-19.44	-6.46	-5.64		2 _{CO2Me,CO2Me}	-	-9.57	3.41	4.23
	1 _{CN,CN}	22.54	-20.60	-7.61	-6.79		2 _{CN,CN}	47.20	-12.08	0.90	1.72
	1 _{CF3,CF3}	32.94	-12.61	0.37	1.20		2 _{CF3,CF3}	50.89	-9.12	3.86	4.68
	1 _{NO2,NO2}	27.84	-23.14	-10.16	-9.33		2 _{NO2,NO2}	44.92	-19.00	-6.01	-5.19
1 _{D,w}	1 _{OMe,CN}	29.09	-13.78	-0.79	0.03	2 _{D,w}	2 _{OMe,CN}	58.96	-2.99	9.99	10.82
	1 _{OMe,CO2Me}	35.09	-14.01	-1.03	-0.21		2 _{OMe,CO2Me}	55.37	-2.02	10.97	11.79
	1 _{NH2,CN}	24.87	-9.89	3.09	3.91		2 _{NH2,CN}	20.45	3.92	16.90	17.72
	1 _{NH2,CO2Me}	22.89	-10.83	2.15	2.97		2 _{NH2,CO2Me}	19.69	4.83	17.81	18.64
						2 _{w,D}	2 _{CN,OMe}	46.01	-12.13	0.86	1.68
							2 _{CN,NH2}	46.45	-11.95	1.03	1.86
							2 _{CO2Me,OMe}	48.22	-11.36	1.63	2.45
							2 _{CO2Me,NH2}	48.18	-13.16	-0.17	0.65

Dimerization

Dimerization is considered as one of the most important reactions of carbenes. In the classic dimerization mechanism of singlet carbenes, the filled *s* orbital of each carbene was anticipated to interact with the empty *p* orbital of the other [31]. Alder *et al.* showed that most dimers are formed by proton catalyzed or possibly metal ion-catalyzed routes [32]. 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. The dimerization includes the attack of the lone pair of one carbene center on the empty p_π orbital of a second carbene (one of the electrons of the σ -HOMO carbene lone pair to the π^* -LUMO centered on the carbenic C atom). Imidazolidinylidenes need sterically demanding ligands to prevent their dimerization

to tetraazafulvalenes, imidazolyliidenes display a thermodynamically unfavorable dimerization even for small ligands such as methyl groups. The dimerization reaction has to be kinetically prevented by steric protection. Similarly, this appears that a suitable increase of the steric bulk of the R substituent on the N atoms is key in attaining stable saturated or aromatic monomeric NHCs [33-34].

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 M06311++G**(Fig. 3). In the head-to-head form, 1_{NH2,CO2Me}, 2_{Cl,Cl}, 2_{NO2,NO2} and 2_{OMe,CO2Me} do not dimerize, while all other carbenes form doubly bonded (head-to-head) dimers (Table 3).

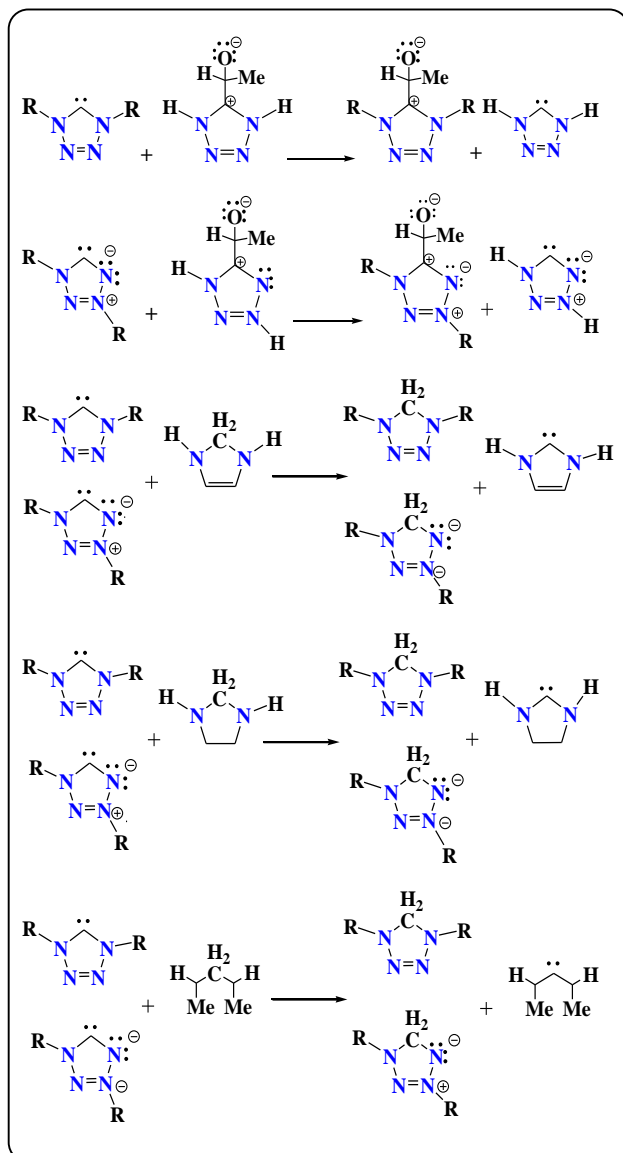


Fig. 2: Isodesmic reactions involving seven sets of *N*-Heterocyclic Carbenes (NHCs) in 1_R and 2_R , at M06/6-311++G**.

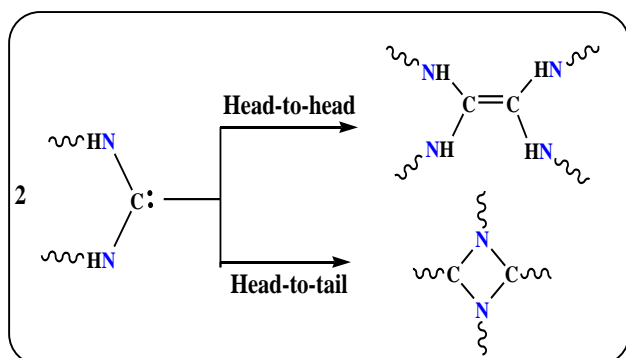


Fig. 3: Possible dimerization forms of carbenes.

In accord with the Carter, Goddard, Malrieu, and Trinquier model, doubly bonded dimers are expected to form if the sum of their ΔE_{S-T} values ($\sum \Delta E_{S-T}$) is smaller than the double bond energy of the dimer (ΔE_{dim}) [35-38]. Interestingly, the $\sum \Delta E_{S-T}$ values for our scrutinized carbenes are considerably greater than the related double bond energies. This diminishes the possibility of their head-to-head dimerization. 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 $2_{\text{CO}_2\text{Me},\text{CO}_2\text{Me}}$), cyclic bridged path is probable for being endothermic (see $\Delta E_{\text{dim}2}$ values in Table 3). Apeloig *et al.* reported that with increasing singlet–triplet energy separation, the energy of dimerization linearly decreases [39]. We showed above that the ω of carbenes continuously decreases with their decreasing stability from (1) to (2) and an increasing nucleophilicity from (2) to (1) (Table 1).

Proton Affinity (PA)

Singlet carbenes can be viewed as the conjugate bases of the corresponding secondary carbocations. So, the $\text{p}K_a$ and proton affinity of diaminocarbenes are of fundamental interest. Due to side reactions attempts to measure the $\text{p}K_a$ of non-aromatic diaminocarbenes on the same scale have not been successful. At present the only way to evaluate the basicity of various diaminocarbenes is from calculated proton affinities (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 carbenic atom. The NHCs are strong bases [28] and because ε (σ -HOMO) correlates not only to the first proton affinity, but more generally to the donor strength of the respective NHC. Hence is possible to rank the carbenes according to their donor strength based on the first proton affinities and the ε (σ -HOMO) values. Among normal carbenes, $1_{\text{TMS},\text{TMS}}$ (PA = -253.82 kcal/mol) (because it has a small HOMO–LUMO energy gap in donor group,) appears as the highest in $1_{\text{D,D}}$ sets, while $1_{\text{CO}_2\text{Me},\text{CO}_2\text{Me}}$ (PA = -228.35 kcal/mol) and $1_{\text{NH}_2,\text{CO}_2\text{Me}}$ (PA = -230.97 kcal/mol) (because it has a big singlet–triplet energy gap) are the highest in $1_{\text{W,W}}$ and $1_{\text{D,W}}$ sets, respectively. Similarly, in abnormal carbenes, $2_{\text{TMS},\text{TMS}}$ (PA = -270.62 kcal/mol) appears as the highest in $2_{\text{D,D}}$ sets, while $2_{\text{CO}_2\text{Me},\text{CO}_2\text{Me}}$ (PA = -244.39 kcal/mol) and $2_{\text{CO}_2\text{Me},\text{NH}_2}$ (PA = -249.22 kcal/mol) are the highest in $2_{\text{W,W}}$, $2_{\text{D,W}}$, and $2_{\text{W,D}}$ respectively (Table 1).

Table 3: M06/6-311++G calculated dimerization energies leading to doubly bonded (ΔE_{dim1}) and cyclic bridged (ΔE_{dim2}) dimers for singlet ground states (kcal/mol), sum of ΔE_{S-T} values ($\sum \Delta E_{S-T}$ /kcal/mol) for singlet carbenes 1_{X,X} and 2_{X,X}.**

Set	NHCs	ΔE_{dimer1}	ΔE_{dimer2}	$\sum \Delta E_{S-T}$	Set	NHCs	ΔE_{dimer1}	ΔE_{dimer2}	$\sum \Delta E_{S-T}$
1 _{D,D}	1 _{OH,OH}	-6.51	-	168.32	2 _{D,D}	2 _{OH,OH}	-90.92	69.93	109.14
	1 _{OMe,OMe}	-10.66	-	178.75		2 _{OMe,OMe}	-28.96	70.53	103.50
	1 _{NH2,NH2}	-3.61	-	172.78		2 _{NH2,NH2}	-19.22	81.70	111.14
	1 _{NMe2,NMe2}	-1.64	-	170.01		2 _{NMe2,NMe2}	-12.34	86.11	114.67
	1 _{TMS,TMS}	22.66	-	172.17		2 _{TMS,TMS}	-3.08	111.24	108.71
1 _{W,W}	1 _{F,F}	-22.33	-	108.23	2 _{W,W}	2 _{F,F}	-117.43	-	90.22
	1 _{Cl,Cl}	-21.88	-	89.26		2 _{Cl,Cl}	-	-	45.40
	1 _{CO2H,CO2H}	-19.97	-	173.23		2 _{CO2H,CO2H}	-17.02	-	67.95
	1 _{CO2Me,CO2Me}	-22.56	-	141.60		2 _{CO2Me,CO2Me}	-38.50	-16.61	80.38
	1 _{CN,CN}	-14.41	-	129.86		2 _{CN,CN}	-26.19	107.54	78.49
	1 _{CF3,CF3}	-4.26	-	160.10		2 _{CF3,CF3}	-21.81	92.93	86.14
	1 _{NO2,NO2}	-28.12	-	133.36		2 _{NO2,NO2}	-	-	14.29
1 _{D,W}	1 _{OMe,CN}	-17.43	-	165.53	2 _{D,W}	2 _{OMe,CN}	-	67.95	91.28
	1 _{OMe,CO2Me}	-12.76	-	156.69		2 _{OMe,CO2Me}	-	-	91.64
	1 _{NH2,CN}	-16.2	-	162.28		2 _{NH2,CN}	-15.93	-	96.48
	1 _{NH2,CO2Me}	-	-	175.74		2 _{NH2,CO2Me}	-16.88	95.98	97.46
				2 _{W,D}	2 _{CN,OMe}	-29.99	95.68	86.53	
					2 _{CN,NH2}	-29.65	-	98.28	
					2 _{CO2Me,OMe}	-28.56	94.43	81.89	
					2 _{CO2Me,NH2}	-26.81	97.58	86.89	

Molecular geometric parameters on Nucleophilicity (*N*)

In abnormal carbenes (2), \tilde{C}_5-N_1 bond lengths are larger than those of normal carbenes (1), but \tilde{C}_5-N_4 bond lengths are shorter for showing double bond character (Table 4). In (1), bond lengths are similar because of molecular symmetry. A smaller divalent angle imposes more *p* character to the covalent sp^2 bonding orbitals, which compensates with more *s* character of the non-bonding σ orbital of the carbene [40].

This causes lowering of the σ orbital energy and enlargement $\sigma-p_\pi$ gap, leading to the favorable singlet and rather unstable triplet state [41]. So, the more *s* character of σ orbital causes its shrinking and lowers the nucleophilicity [42,43]. In (2) carbenic bond angles are longer than those in (1). Carbenic bond angles decrease as the size of substitutions increase: $1_{OMe,OMe} > 1_{OH,OH}$; $1_{F,F} > 1_{Cl,Cl}$;(Table 3). In contrast, in 2 carbenic bond angles,

lengths, and *N* are larger than those in (1) while the reverse is true for ΔE_{S-T} . Abnormal carbene 2_{OH,OH} shows a wider carbenic bond angle ($N_1-\hat{C}_5-N_4 = 101.38^\circ$) and a higher nucleophilicity ($N = 2.00$) than its corresponding normal carbene 1_{OH,OH} ($N_1-\hat{C}_5-N_4 = 96.55^\circ$ and $N = 1.36$, respectively) (Tables 1 and 4). These results are consistent with the higher HOMO energy displayed by every (2) compared to its corresponding (1) (Table 1). In addition, higher stability (ΔE_{S-T}) and band gaps ($\Delta E_{HOMO-LUMO}$) are demonstrated by every (1) compared to its corresponding (2) (Tables 1). The widest carbenic bond angle ($N_1-\hat{C}_5-N_4$) and the highest *N* in normal sets are seen for 1_{TMS,TMS} (101.62°). The trend of angle size and *N* in D,D set is $1_{TMS,TMS} > 1_{NMe2,NMe2} > 1_{NH2,NH2} > 1_{OMe,OMe} > 1_{OH,OH}$. This is similar to that of 2_{D,D} set: $2_{TMS,TMS} > 2_{NMe2,NMe2} > 2_{NH2,NH2} > 2_{OMe,OMe} > 2_{OH,OH}$.

Table 4: Geometrical parameters including, carbenic bond lengths ($N_1-\overset{\cdot\cdot}{C}_5$, $\overset{\cdot\cdot}{C}_5-N_4$, Å), carbenic bond angles ($N_1-\overset{\cdot\cdot}{C}_5-N_4$, deg), and dihedral angle ($N_1-\overset{\cdot\cdot}{C}_5-N_4-N_3$, D) in degrees for seven sets of N-Heterocyclic Carbenes (NHCs), at M06/6-311++G** level of theory.

Set	NHCs	$\overset{\cdot\cdot}{C}_5-N_1$	$\overset{\cdot\cdot}{C}_5-N_4$	$N_1-\overset{\cdot\cdot}{C}_5-N_4$	D	Set	NHCs	$\overset{\cdot\cdot}{C}_5-N_1$	$\overset{\cdot\cdot}{C}_5-N_4$	$N_1-\overset{\cdot\cdot}{C}_5-N_4$	D
$1_{D,D}$	$1_{OH,OH}$	1.35	1.35	96.55	1.64	$2_{D,D}$	$2_{OH,OH}$	1.36	1.36	101.38	0.01
	$1_{OMe,OMe}$	1.35	1.35	96.76	0.53		$2_{OMe,OMe}$	1.37	1.36	101.58	0.84
	$1_{NH_2,NH_2}$	1.35	1.35	98.68	0.00		$2_{NH_2,NH_2}$	1.38	1.35	102.42	-0.53
	$1_{NMe_2,NMe_2}$	1.35	1.35	98.96	0.00		$2_{NMe_2,NMe_2}$	1.37	1.35	103.07	-0.42
	$1_{TMS,TMS}$	1.36	1.36	101.62	0.05		$2_{TMS,TMS}$	1.39	1.35	103.51	0.00
$1_{W,W}$	$1_{F,F}$	1.34	1.34	94.07	-0.05	$2_{W,W}$	$2_{F,F}$	1.36	1.37	96.45	0.00
	$1_{Cl,Cl}$	1.35	1.35	96.80	-0.04		$2_{Cl,Cl}$	1.39	1.35	101.85	0.00
	$1_{CO_2H,CO_2H}$	1.35	1.35	100.22	0.00		$2_{CO_2H,CO_2H}$	1.40	1.33	102.60	-0.02
	$1_{CO_2Me,CO_2Me}$	1.35	1.35	99.15	-0.02		$2_{CO_2Me,CO_2Me}$	1.41	1.34	102.39	0.16
	$1_{CN,CN}$	1.35	1.35	99.08	0.00		$2_{CN,CN}$	1.42	1.33	102.46	-0.03
	$1_{CF_3,CF_3}$	1.35	1.35	98.29	-0.21		$2_{CF_3,CF_3}$	1.40	1.35	101.77	0.93
	$1_{NO_2,NO_2}$	1.34	1.34	96.68	-0.01		$2_{NO_2,NO_2}$	1.39	1.36	100.96	-0.01
$1_{D,W}$	$1_{OMe,CN}$	1.34	1.36	97.90	-0.19	$2_{D,W}$	$2_{OMe,CN}$	1.40	1.33	102.27	0.00
	$1_{OMe,CO_2Me}$	1.34	1.36	97.95	-0.12		$2_{OMe,CO_2Me}$	1.40	1.34	101.31	0.00
	$1_{NH_2,CN}$	1.35	1.36	98.90	-0.01		$2_{NH_2,CN}$	1.41	1.33	102.79	-0.07
	$1_{NH_2,CO_2Me}$	1.34	1.36	98.93	0.00		$2_{NH_2,CO_2Me}$	1.41	1.34	101.92	-0.09
$2_{W,D}$	$2_{CN,OMe}$	1.40	1.35	101.86	-0.01	$2_{W,D}$	$2_{CN,NH_2}$	1.40	1.35	102.08	0.05
	$2_{CN,NH_2}$	1.40	1.35	102.08	0.05		$2_{CO_2Me,OMe}$	1.40	1.35	102.54	0.00
	$2_{CO_2Me,OMe}$	1.40	1.35	102.54	0.00		$2_{CO_2Me,NH_2}$	1.40	1.35	102.69	0.04
	$2_{CO_2Me,NH_2}$	1.40	1.35	102.69	0.04						

CONCLUSIONS

A comparison is made between N of 1,4-disubstituted, "normal", tetrazol-5-ylidens (1), and their 1,3-disubstituted, "mesoionic, or abnormal", isomers (2), at the M06/6-311++G** level of theory: The employed ylidenes ($1_{W,W}$, $1_{D,D}$ and $1_{D,W}$, respectively) are compared and contrasted to another union of four sets of "abnormal" $1_{D,3D^-}$, $1_{W,3W^-}$, $1_{W,3D^-}$ and $1_{D,3W}$ -tetrazol-5-ylidenes ($2_{W,W}$, $2_{D,D}$, $2_{D,W}$ and $2_{W,D}$, respectively).

Acetaldehyde derivative is used as a target molecule for probing real nucleophilic reactions at same level of theory. The results of our calculations indicate that every abnormal (2) is more nucleophilic than its corresponding normal (1) isomer. Our calculated global electrophilicity (ω/eV) takes on a trend with an exactly opposite direction from N . Stabilities of (1) and (2) carbenic species

electron withdrawing (W) substituents are CN, CF₃, CO₂H, CO₂Me, NO₂, F, and Cl. Electron donating (D) ones include OH, OMe, NH₂, NMe₂, and TMS. A union of three sets of "normal" $1_{W,4W^-}$, $1_{D,4D^-}$ and $1_{W,4D}$ -tetrazol-5-

are presumed to be related to their singlet-triplet energy gaps (ΔE_{S-T} , kcal/mol). Every normal (1) appears more stable but less nucleophilic than its corresponding abnormal (2) isomer. Hence, N of a set of carbene appears to be indirectly proportional to their ΔE_{S-T} . According to our calculation the angle ($N_1-\overset{\cdot\cdot}{C}_5-N_4$) is increased from normal to abnormal carbenes. Likewise, N is increased from normal to abnormal carbenes. Among normal carbenes, $1_{TMS,TMS}$ shows the higher PA = -253.82 kcal/mol because of small HOMO-LUMO energy gap and $1_{CO_2Me,CO_2Me}$ PA = -228.35 kcal/mol and $1_{NH_2,CO_2Me}$ PA = -230.97 kcal/mol

because of large singlet-triplet energy gap and in abnormal forms $2_{\text{NMe}_2, \text{NMe}_2}$ and $2_{\text{TMS}, \text{TMS}}$ show the higher PA = -270.62 kcal/mol, $2_{\text{CO}_2\text{Me}, \text{CO}_2\text{Me}}$ PA = -244.39 kcal/mol and $2_{\text{NH}_2, \text{CO}_2\text{Me}}$ PA = -246.76 kcal/mol; while the lowest PA's are found for $1_{\text{OH}, \text{OH}}$ and $2_{\text{OH}, \text{OH}}$ in donor groups and $1_{\text{CN}, \text{CN}}$ and $2_{\text{CN}, \text{CN}}$ in withdrawing groups, $1_{\text{OMe}, \text{CN}}$ and $2_{\text{NH}_2, \text{CN}}$ in pull-push groups. $1_{\text{NH}_2, \text{CO}_2\text{Me}}$, $2_{\text{Cl}, \text{Cl}}$, $2_{\text{NO}_2, \text{NO}_2}$ and $2_{\text{OMe}, \text{CO}_2\text{Me}}$ do not dimerize, while all other carbenes form doubly bonded (head-to-head) dimers. For all our carbenes (except $2_{\text{CO}_2\text{Me}, \text{CO}_2\text{Me}}$), cyclic bridged path is probable for being endothermic. We showed above that the electrophilicity of carbenes continuously decreases with their decreasing stability from (1) to (2) and an increasing nucleophilicity from (2) to (1). Carbenes with electron withdrawing groups increase electrophilicity while electron donating ones increase nucleophilicity and in pull-push groups, electron withdrawing group in carbene centre increase electrophilicity.

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