



Substitution effects on 1,3-disubstituted imidazol-2-ylidenes and 1,3-diarylimidazol-2-ylidenes revisited: a theoretical study at DFT level

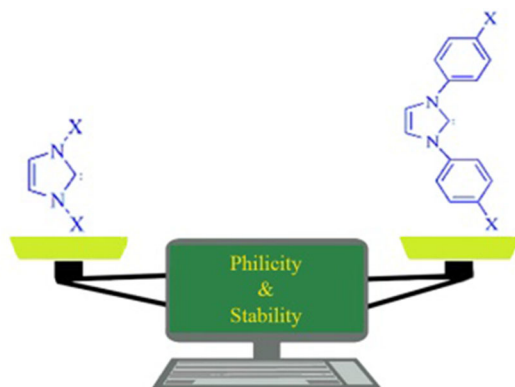
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Abstract

Effect of substituents on philicity and stability of 1,3-disubstituted imidazol-2-ylidenes and 1,3-diarylimidazol-2-ylidenes was assessed using the following calculations: adiabatic electron affinity and adiabatic ionization potential, global electrophilicity and differential orbital energy scales for philicity, and ΔE_{S-T} , ΔE_{Hyd} , ΔE_{iso} , and ΔE_{H-L} for stability, with the aid of density functional theory and the results were then compared with each other. In the case of 1,3-disubstituted imidazol-2-ylidene, the carbene with CH_3 group has the highest nucleophilic character considering all the above scales and the highest thermodynamic stability. 1,3-Diarylimidazol-2-ylidenes with CH_3O and NH_2 groups have high-nucleophilic properties and high-stability; their ΔE_{iso} values are also greater than 377 kJ/mol which means that they may be reasonable synthetic targets. While, the presence of electron donating groups at 1,3-disubstituted imidazol-2-ylidene results in $\Delta E_{iso} > 377$ kJ/mol. Nucleophilicity of 1,3-diarylimidazol-2-ylidenes is, to some extent, greater than that of 1,3-disubstituted imidazol-2-ylidenes.

Graphical abstract



Keywords N-Heterocyclic carbenes · Electrophilic substitutions · Stability · Density functional theory · Carbenes

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Introduction

Carbenes, well-known names to chemists, are neutral divalent species having six electron carbon atoms with two unshared electrons. Classical carbenes are inherently unstable and considered as highly reactive transient intermediates in chemical reactions [1]. As carbene carbon has six electrons, it is assumed to be an electrophilic species, but the increasing number of papers have shown that the philicity of these compounds is strikingly dependent on

substituents attached to the carbene carbon; for example, $(\text{CH}_3\text{O})_2\text{C}:$ and $(\text{Me}_2\text{N})_2\text{C}:$ are both nucleophilic in character [2, 3]. This property may be attributed to 2p–2p π bonding of “vacant” carbenic p orbital of these carbenes with electron pairs of the adjacent Me_2N and CH_3O groups.

One category of carbenes is N-heterocyclic carbenes (NHC), the representative stable and bottled species of which is 1,3-di(adamantyl)imidazol-2-ylidene, first reported by Arduengo et al. 26 years ago; its stability benefits from factors such as electronic, aromatic, and spatial, owing its viability to the mesomeric effects on nitrogen atoms [4]. Several different parameters have been suggested to measure the stability of NHCs; these include: the energy gap between singlet and triplet states ($\Delta E_{\text{S-T}}$), the energy of hydrogenation (ΔE_{Hyd}), the energy of isodesmic reaction (ΔE_{iso}), and finally the energy difference between HOMO and LUMO levels ($\Delta E_{\text{H-L}}$). The first three parameters refer to thermodynamic stability and the last one shows kinetic stability of NHCs. Furthermore, these species have received much attention from scientists, publishing books, and articles [5–15]. Due to their σ donating and π -accepting ability, NHCs can act as excellent ligands in organometallic compounds. In addition, various applications have been found for them, such as polymerization reaction and medicinal uses [16–20]. Su and Chuang predicted that using NHCs skeleton would stabilize triplet ground state of vinylidenes [21]. As a result, reactivity, as well as philicity and stability of these carbenes, are highly important.

As concerns philicity, there are different approaches for obtaining philicity; some of them are summarized in Fig. 1 [22, 23]. The philicity of some carbenes in their singlet ground state was experimentally determined for the first time by insightful studies of Moss and co-workers in 1980 based on the kinetic model of cyclopropanation reaction of some alkenes with carbenes [2, 24]. Therefore, empirical index “ m_{CXY} ” (carbene selectivity index) was born which covered electrophilic, nucleophilic, and ambiphilic

carbenes. Equation (1) correlates this empirical index to the resonance (σ_{R}^+) and inductive (σ_{I}) substituent constants of X and Y in carbene CXY:

$$m_{\text{CXY}} = -1.10 \sum_{\text{X,Y}} \sigma_{\text{R}}^+ + 0.53 \sum_{\text{X,Y}} \sigma_{\text{I}} - 0.31. \quad (1)$$

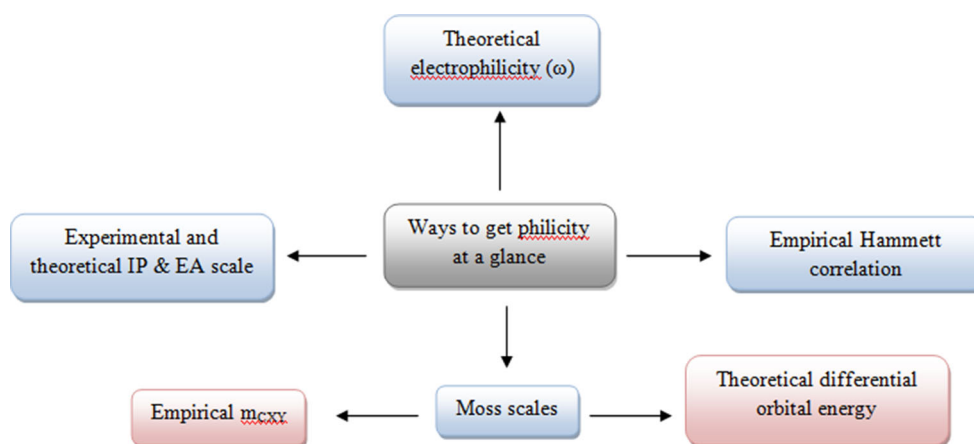
For m_{CXY} values lower than 1.5 the corresponding carbenes are categorized as electrophilic; while nucleophilic ones have values greater than 2.2 m_{CXY} , and ambiphilic carbenes have m_{CXY} in between.

Another approach to obtain philicity is based on frontier molecular orbital (FMO) theory that Moss correlated it with m_{CXY} . Therefore, the differential orbital energy of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of carbenes and alkenes is used in 1,3-dipolar cycloadditions. If the $\Delta \varepsilon_{\text{E}} = \varepsilon_{\text{LUMO}_{\text{carbene}}} - \varepsilon_{\text{HOMO}_{\text{alkene}}}$ is smaller than the $\Delta \varepsilon_{\text{N}} = \varepsilon_{\text{LUMO}_{\text{alkene}}} - \varepsilon_{\text{HOMO}_{\text{carbene}}}$, the corresponding carbene is considered to be an electrophile; the inverse ordering of differential energies makes the carbene to be a nucleophile. An ambiphilic carbene reacts rapidly with both electron-rich and electron-poor alkenes. In this method, with a superficial glance, the philicity of a carbene can be predicted quantitatively and quickly.

In another method, philicity is correlated to ionization potential (IP) and electron affinity (EA). Sander and co-workers have used these parameters and two dimensional scales for evaluating philicity of singlet carbenes as well as triplet ones [3]. Adiabatic ionization potential and adiabatic electron affinity values can be experimentally measured by negative ion photoelectron spectroscopy (NIPES) [25–27]. These data may then be compared with the calculated ones to assess the theoretical methods. An advantage of Sander’s method is that EA and IP can be calculated for any carbene and does not depend (as does m_{CXY}) on specific set of alkenes or carbenes.

Another attractive scale is the theoretical global electrophilicity, ω , defined recently by Parr et al. [28]:

Fig. 1 Ways to get philicity at a glance



$$\omega = \mu^2/2\eta, \quad (2)$$

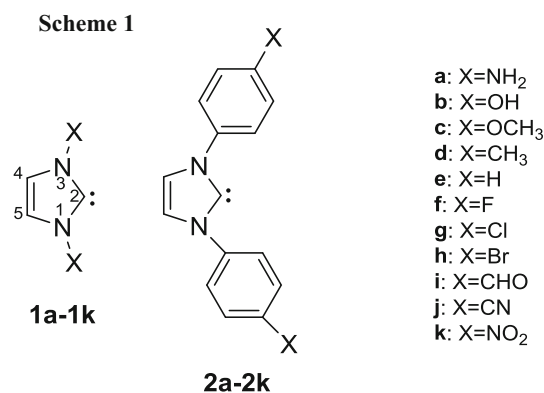
where μ is the electronic chemical potential and η is the chemical hardness. Perez in her paper compared ω of carbenes with their empirical m_{CXY} and found a good agreement between the theoretical and experimental philicity of the investigated species [29]. Global electrophilicity index and m_{CXY} have an inverse order with respect to each other, i.e., a large amount of ω means a high electrophilicity. Based on Perez considerations, nucleophilic carbenes have ω values lower than 1 eV, electrophilic ones showing ω values between 1.21 and 2.40 eV (MeCF and phCCN, respectively), while for the case where $\omega \approx 1$ eV the carbenes are characterized as ambiphilic.

Recently, local electrophilicity (ω_c) and ω of the Group 15 analogues of NHCs have been studied and it was concluded that the “ene” center of these analogues is ambiphilic [30]. It was also found that ligation properties of these compounds would be affected dramatically by the nature of the substituents.

Empirical Hammett correlation is another method for determining philicity of CXY against a series of ring-substituted styrenes by drawing $\log k_X/k_H$ of the addition reaction versus σ constants [31, 32]. However, a question arises as whether this method could determine philicity of carbenes. The answer is affirmative; but how?

If the Hammett ρ value is negative, positive charge will develop on alkene carbon. Therefore, electron-releasing groups lower the energy of the transition state and stabilize it. As a result CF_2 will have an electrophilic character. A positive ρ value shows that a negative charge develops during the addition reaction, mitigated by electron withdrawing phenyl-moiety substituents, leading to the acceleration of the reaction; for example, benzocyclobutenylidene [33] and bicyclo[3.2.1]octa-2,6-dien-4-ylidene [34] are known to be nucleophilic with ρ values + 1.57 and + 0.25, respectively. In the case of ambiphilic carbenes, one encounters a broken Hammett plot at $\sigma = 0.0$. This means that the reaction mechanism changes during the reaction affected by substituents.

The above discussion on importance of predicting philicity and stability of carbenes, prompted us to evaluate substitution effect on these properties for 1,3-disubstituted imidazol-2-ylidenes (1) and 1,3-diarylimidazol-2-ylidenes (2) and make a comparison between the obtained parameters (Scheme 1).



Results and discussion

As the nature of substituent has a remarkable effect on philicity and stability, we decided to evaluate these effect for 1,3-diarylimidazol-2-ylidenes and 1,3-disubstituted imidazol-2-ylidenes; for philicity the following three approaches were considered: adiabatic *IP* and *EA* scales, ω and differential orbital energy. For stability of NHCs, ΔE_{S-T} , ΔE_{Hyd} , ΔE_{iso} , and ΔE_{H-L} were computed using DFT method.

1,3-Disubstituted imidazol-2-ylidenes (1)

The electron donating substituents lead to small *IP* and the lowest and negative *EA* values of the titled carbenes (Table 1). For the substituent CH₃ (with positive inductive effect, + *I*), the corresponding carbene has the most nucleophilic character with *EA* = − 0.51 eV and *IP* = 7.74 eV which may be attributed to its σ -electron donating properties and the positive hyperconjugation of CH₃ (these data agree with those reported by Sander [3]). For substituents NH₂, OCH₃, OH (with − *I* and the positive resonance effect, + *R*) and also *H*, we encounter close nucleophilicities (*EA* = − 0.43, *IP* = 8.09; *EA* = − 0.46, *IP* = 8.35; *EA* = − 0.47, *IP* = 8.83; and *EA* = − 0.46, *IP* = 8.21 eV, respectively). In the case of halogenated species when X = Br, we encounter the highest value of *EA* (2.37 eV) and low *IP* (8.51 eV), while *EA* for X = F, drops to 1.82 eV showing a decrease in carbene electrophilicity. The *IP* increases from 8.51 eV for X = Br to 9.65 eV for X = F, from which one can guess that the corresponding carbene of the latter substituent is both less electrophilic and less nucleophilic with respect to the former. The substituent NO₂ (with *EA* = 1.84 eV and *IP* = 9.92 eV of the corresponding carbene), induces the same philicity as for X = F, which is in accordance with electron withdrawing character of these substituents. Therefore, as Sander has stated, calculated *EA* and *IP* values make it possible to

Table 1 DFT parameters, philicity values of 1,3-disubstituted imidazol-2-ylidene **1**

Entry	X	Carbene	IP/eV	EA/eV	μ/eV	η/eV	ω/eV	N/eV	ΔN_{max}
1	NH ₂	1a	8.09	-0.43	-3.83	8.52	1.72	3.09	0.45
2	OH	1b	8.83	-0.47	-4.18	9.30	1.88	2.65	0.45
3	OCH ₃	1c	8.35	-0.46	-3.94	8.80	1.77	2.88	0.45
4	CH ₃ ^a	1d	7.74	-0.51	-3.61	8.26	1.58	3.6	0.43
5	H ^b	1e	8.21	-0.46	-3.87	8.68	1.73	3.41	0.44
6	F	1f	9.65	1.82	-5.73	7.84	4.20	1.89	0.73
7	Cl	1g	8.83	2.20	-5.52	6.62	4.59	2.51	0.83
8	Br	1h	8.51	2.37	-5.44	6.14	4.82	2.7	0.88
9	CHO	1i	8.92	0.64	-4.78	8.28	2.76	2.47	0.57
10	CN	1j	9.84	0.53	-5.19	9.32	2.89	1.47	0.55
11	NO ₂	1k	9.92	1.84	-5.88	8.08	4.27	1.63	0.72

^a EA (calculated) = -0.52 eV; IP (calculated) = 8.15 eV; IP (experimental) = 7.68 eV [3], ω = 0.83 eV [35]

^b ω = 1.52 eV [36]

identify three classes of carbenes, i.e., (1) strongly nucleophilic carbenes at the bottom right part of the diagram exhibit a small or negative EA and a low IP (**1d**). (2) For $X = NO_2$ the carbene has the highest EA and IP , being extremely electrophilic with no nucleophilicity. (3) Carbenes such as **1h** with a high EA and low IP , it is predicted to have a small singlet–triplet energy gap and hence a triplet ground state (Fig. 2).

Notably, the order of ω for electron donating groups is as follows $CH_3 < NH_2 \cong H \leq OCH_3 < OH$ indicating that inductive effect is significant (Table 1). Kassaei has reported $\omega = 0.83$ eV for $X = CH_3$ by calculating μ and η from the following equations [37]:

$$\mu \approx (E_{HOMO} + E_{LUMO})/2, \quad (3)$$

$$\eta \approx E_{LUMO} - E_{HOMO}. \quad (4)$$

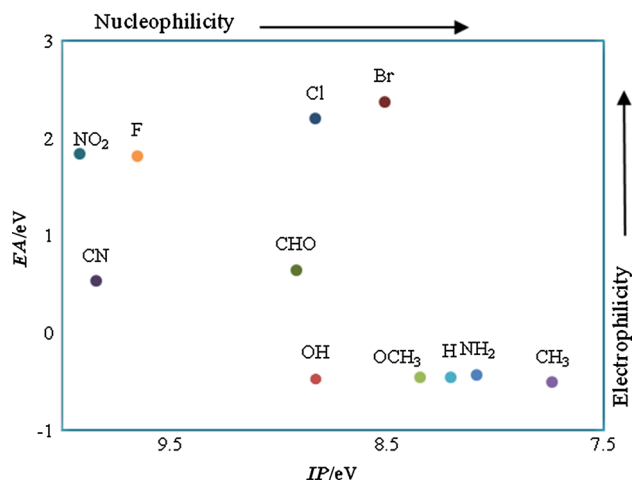


Fig. 2 Calculated IP and EA of NHC **1** at the B3LYP/6-311++G** basis set

This value agrees with our value ($\omega = 0.82$ eV) obtained from $E_{HOMO} = -5.89$ eV, $E_{LUMO} = -0.22$ eV. On the other hand, halogenated species have almost the same ω values. The NO_2 substituent leads to high ω value because of its σ and π -withdrawing character. Species with high ω values have high μ (around 5.42 eV) and high ΔN_{max} (around 0.71 e).

The philicity of singlet state of these carbenes was determined with the aid of differential orbital energy. When $\Delta\epsilon_E$ value is always bigger than the $\Delta\epsilon_N$ value, substituted carbenes are nucleophilic in character; electrophilic carbenes have the inverse ordering of differential orbital energies. If $\Delta\epsilon_E$ for alkenes having electron withdrawing substitution is bigger than $\Delta\epsilon_N$ and also when $\Delta\epsilon_E$ for electron donating substitution on the alkene is smaller than $\Delta\epsilon_N$ the carbene will be considered as ambiphile.

In this regard, interaction of these singlet carbenes with several alkenes was studied (Table 2). When $X = CH_3$ the carbene is suggested to be nucleophile, which is in agreement with the previously mentioned scales. For $X = NH_2$ the carbene is suggested to have nucleophilic character upon addition reaction with most alkenes; however, toward $(CH_3)_2C=C(CH_3)_2$ it would be predicted to behave as electrophilic if it occurred. In the case of NO_2 substituent, $\Delta\epsilon_E$ is always smaller than $\Delta\epsilon_N$, and therefore, so the corresponding carbene has electrophilic character. Carbenes having halogen and CHO substituents act as ambiphilic toward alkenes.

Stability of carbenes can be assessed by ΔE_{S-T} , ΔE_{Hyd} , ΔE_{iso} , and ΔE_{H-L} . Singlet–triplet energy gap is of special importance due to its great influence in the course of carbene reactions. A great ΔE_{S-T} indicates that singlet state is more stable than triplet state and vice versa. As a result, the

Table 2 Differential orbital energies for carbene/alkene addition 1,3-disubstituted imidazol-2-ylidene **1**

X	Alkene and differential orbital energies/eV											
	(CH ₃) ₂ C=C(CH ₃) ₂		(CH ₃) ₂ C=CHCH ₃		(CH ₃) ₂ C=CH ₂		H ₃ CC=CCH ₃		CH ₂ =CHCOOCH ₃		CH ₂ =CHCN	
	$\Delta\epsilon_E$	$\Delta\epsilon_N$	$\Delta\epsilon_E$	$\Delta\epsilon_N$	$\Delta\epsilon_E$	$\Delta\epsilon_N$	$\Delta\epsilon_E$	$\Delta\epsilon_N$	$\Delta\epsilon_E$	$\Delta\epsilon_N$	$\Delta\epsilon_E$	$\Delta\epsilon_N$
NH ₂	5.72	5.91	5.96	5.94	6.37	5.93	6.25	6.08	7.43	4.48	7.79	4.16
OH	6.01	6.57	6.25	6.60	6.66	6.59	6.54	6.74	7.72	5.14	8.08	4.82
OCH ₃	5.95	6.34	6.19	6.37	6.60	6.36	6.48	6.51	7.66	4.91	8.02	4.59
CH ₃	5.96	5.62	6.20	5.65	6.61	5.64	6.49	5.79	7.67	4.19	8.03	3.87
H	5.83	5.81	6.07	5.84	6.48	5.83	6.36	5.98	7.54	4.38	7.90	4.06
F	5.28	7.33	5.52	7.36	5.93	7.35	5.81	7.50	6.99	5.90	7.35	5.58
Cl	3.90	6.71	4.14	6.74	4.55	6.73	4.43	6.88	5.61	5.28	5.97	4.96
Br	3.25	6.52	3.49	6.55	3.90	6.54	3.78	6.69	4.96	5.09	5.32	4.77
CHO	3.89	6.93	4.13	6.96	4.54	6.95	4.42	7.10	5.60	5.50	5.96	5.18
CN	4.17	7.75	4.41	7.78	4.82	7.77	4.70	7.92	5.88	6.32	6.24	6.00
NO ₂	2.72	7.59	2.96	7.62	3.37	7.61	3.25	7.76	4.43	6.16	4.79	5.84

$$\Delta\epsilon_E = \epsilon\text{LUMO}_{\text{carbene}} - \epsilon\text{HOMO}_{\text{alkene}}$$

$$\Delta\epsilon_N = \epsilon\text{LUMO}_{\text{alkene}} - \epsilon\text{HOMO}_{\text{carbene}}$$

Table 3 Thermodynamic stability factors in kJ/mol and $\Delta E_{\text{H-L}}$ in eV of carbenes **1**

Entry	X	Carbene	$\Delta E_{\text{S-T}}$	ΔE_{iso}	ΔE_{Hyd}	$\Delta E_{\text{H-L}}$
1	NH ₂	1a	351.0	451.16	- 94.06	6.2
2	OH	1b	330.9	431.01	- 114.14	6.7
3	OCH ₃	1c	300.8	402.63	- 142.63	6.4
4	CH ₃	1d	351.5	460.99	- 84.27	5.7
5	H	1e	348.9	460.07	- 85.19	5.7
6	F	1f	284.1	347.81	- 197.40	6.7
7	Cl	1g	197.1	368.53	- 176.73	4.7
8	Br	1h	148.9	357.65	- 187.61	3.9
9	CHO	1i	250.6	350.87	- 194.39	4.7
10	CN	1j	300.0	373.67	- 171.59	6.0
11	NO ₂	1k	242.7	332.67	- 212.55	4.4

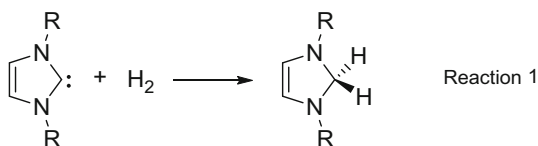
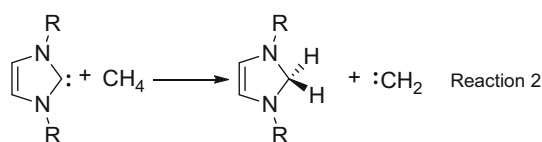
highest stability is exhibited by **1d** (351.5 kJ/mol) (Table 3).

Heat of hydrogenation can be judged by reaction 1 (Scheme 2). This parameter is negative for all investigated

carbenes; the smaller the magnitude of ΔE_{Hyd} the more stable the carbene. Accordingly **1d** is the most stable and **1k** is the least stable of investigated carbene.

Another suitable and economic way of assessing the stability of singlet carbenes is endothermicity of isodesmic reaction 2 (Scheme 3); the higher ΔE_{iso} , the higher the stability. Therefore, carbene **1d** with $\Delta E_{\text{iso}} = 460.99$ kJ/mol has the highest stability. The higher stability of CH₃ substituted carbene with respect to those carbenes with NH₂, OH, and OCH₃ substituents may be attributed to the +I effect and the positive hyperconjugation of CH₃. As stated by Nyulászai, the synthesis of those carbenes with ΔE_{iso} larger than 377 kJ/mol would be feasible [38]. Accordingly, only those carbenes with electron donating substituents have $\Delta E_{\text{iso}} > 377$ kJ/mol. Therefore, **1a-1e** is included in this category.

Kinetic stability can be assessed by the energy difference between HOMO and LUMO orbitals ($\Delta E_{\text{H-L}}$) [39]. The greater difference will result in a more stable carbene; OH and F substituted carbenes with largest $\Delta E_{\text{H-L}}$ values (6.7 eV for both) are the most stable ones, and Br substituted carbene ($\Delta E_{\text{H-L}} = 3.9$ eV) is the least stable species.

Scheme 2**Scheme 3**

The selected geometrical parameters of singlet and triplet states of these carbenes are summarized in Table S1 of the Supplementary Material.

1,3-Diarylimidazol-2-ylidenes (2)

First, the EA and IP of studied carbenes vary between -0.38 to 2.02 and 6.53 – 8.42 eV, respectively (Table 4). Comparing the EA values for halogen substituted species (F: -0.01 eV, Cl: 0.24 eV, Br: 0.29 eV) shows that for fluorine the corresponding carbene is much less electrophilic in character. The IP parameters, however, cannot be taken as a basis of carbene philicity for F, Cl and Br, since there is no significant difference between their IP values. CH_3O and NH_2 substituted carbenes with negative, small and close values of EA (-0.38 and -0.20 eV, respectively) are more efficient in reducing EA than halogens analogues indicating high nucleophilicity of their corresponding carbenes. The EA and IP values for $X = NO_2$ substituted carbene (2.02 and 8.42 eV, respectively) are the highest, showing that such species are the most electrophilic of the studied carbenes. The results obtained from IP values for CH_3O , NH_2 and NO_2 substituents are consistent with those of EA values. The compilation of the calculated EA and IP values of these carbenes can be seen in Fig. 3.

The values of electrophilicity index of nucleophilic 1,3-diarylimidazol-2-ylidenes (**2**) range from 1.48 eV for $X = CH_3O$ group to 1.70 eV for $X = OH$ (Table 4). High π -electron-releasing and low σ -withdrawing effect of $X = CH_3O$ and $X = NH_2$ ($\omega = 1.49$ eV, $\mu = -3.16$ eV) make the corresponding carbenes to be the most nucleophilic of these NHCs (**2**); electrophilic carbenes, show higher ω values from 3.13 eV for $X = CHO$ to 4.25 eV for $X = NO_2$. It should be noted that for $X = NO_2$ the carbene is predicted to be the most electrophilic species, displaying

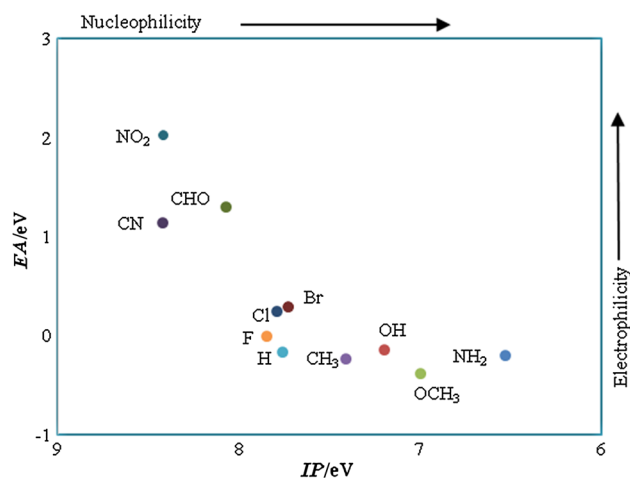


Fig. 3 Calculated IP and EA of NHC **2** at the B3LYP/6-311++G** basis set

the highest μ and ΔN_{max} values (-5.22 eV and 0.81 e, respectively). Inspection of ω values of halogenated species indicates that these carbenes have almost similar philicity index with ΔN_{max} values around 0.50 e.

Differential orbital energy predicts that NH_2 substituted 1,3-diarylimidazol-2-ylidene acts as a nucleophile because $\Delta\epsilon_N$ is always smaller than $\Delta\epsilon_E$ (Table 5). When $X = H, F, Cl, Br, CN,$ and CHO the corresponding carbenes may behave as ambiphile. The carbene with NO_2 as substituent has electrophilic character toward all indicated alkenes.

Ignoring some deviations, carbenes **2** with π -donating groups have the great ΔE_{S-T} , and therefore, the high-stability (Table 6). The NH_2 substituted carbene **2a** with the highest values of ΔE_{iso} and ΔE_{Hyd} (445.39 and -99.87 kJ/mol, respectively) is the most stable of all these species.

In this series, **2b** and **2f** ($\Delta E_{H-L} = 5.3$ eV) are the most kinetically stable carbenes and **2k**, in all aspects, has both the lowest thermodynamic and kinetic stability.

Table 4 DFT parameters, philicity values of 1,3-diarylimidazol-2-ylidene **2**

Entry	X	Carbene	IP/eV	EA/eV	μ/eV	η/eV	ω/eV	N/eV	ΔN_{max}
1	NH_2	2a	6.53	-0.20	-3.16	6.72	1.49	4.00	0.47
2	OH	2b	7.20	-0.14	-3.53	7.34	1.70	3.47	0.48
3	OCH_3	2c	7.00	-0.38	-3.31	7.38	1.48	3.61	0.45
4	CH_3	2d	7.41	-0.24	-3.58	7.64	1.68	3.44	0.47
5	H ^a	2e	7.76	-0.17	-3.79	7.94	1.81	3.32	0.47
6	F	2f	7.85	-0.01	-3.92	7.86	1.95	3.09	0.50
7	Cl	2g	7.79	0.24	-4.01	7.56	2.13	3.02	0.53
8	Br	2h	7.73	0.29	-4.01	7.44	2.16	3.01	0.54
9	CHO	2i	8.07	1.30	-4.68	6.76	3.24	2.53	0.69
10	CN	2j	8.42	1.14	-4.77	7.28	3.13	2.72	0.65
11	NO_2	2k	8.42	2.02	-5.22	6.40	4.25	2.39	0.81

^a $\omega = 1.27$ eV [35]

Table 5 Differential orbital energies for carbene/alkene addition 1,3-diarylimidazol-2-ylidene **2**

X	Alkene and differential orbital energies/eV											
	(CH ₃) ₂ C=C(CH ₃) ₂		(CH ₃) ₂ C=CHCH ₃		(CH ₃) ₂ C=CH ₂		H ₃ CC=CCH ₃		CH ₂ =CHCOOCH ₃		CH ₂ =CHCN	
	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$
NH ₂	5.69	5.22	5.93	5.25	6.34	5.24	6.22	5.39	7.40	3.79	7.76	3.47
OH	5.44	5.75	5.68	5.78	6.09	5.77	5.97	5.92	7.15	4.32	7.51	4.00
OCH ₃	5.54	5.61	5.78	5.64	6.19	5.63	6.07	5.78	7.25	4.18	7.61	3.86
CH ₃	5.37	5.78	5.61	5.81	6.02	5.80	5.90	5.95	7.08	4.35	7.44	4.03
H	5.22	5.90	5.46	5.93	5.87	5.92	5.75	6.07	6.93	4.47	7.29	4.15
F	5.09	6.13	5.33	6.16	5.74	6.15	5.62	6.30	6.80	4.70	7.16	4.38
Cl	4.86	6.20	5.10	6.23	5.51	6.22	5.39	6.37	6.57	4.77	6.93	4.45
Br	4.82	6.21	5.06	6.24	5.47	6.23	5.35	6.38	6.53	4.78	6.89	4.46
CHO	3.74	6.50	3.98	6.53	4.39	6.52	4.27	6.67	5.45	5.07	5.81	4.75
CN	3.90	6.69	4.14	6.72	4.55	6.71	4.43	6.86	5.61	5.26	5.97	4.94
NO ₂	3.03	6.83	3.27	6.86	3.68	6.85	3.56	7.00	4.74	5.40	5.10	5.08

Table 6 Thermodynamic stability factors in kJ/mol and ΔE_{H-L} in eV of carbenes **2**

Entry	X	Carbene	ΔE_{S-T}	ΔE_{iso}	ΔE_{Hyd}	ΔE_{H-L}
1	NH ₂	2a	309.6	445.39	- 99.87	5.0
2	OH	2b	310.9	442.58	- 102.59	5.3
3	OCH ₃	2c	310.4	442.42	- 102.80	5.2
4	CH ₃	2d	308.8	433.25	- 112.01	5.2
5	H	2e	301.7	429.03	- 116.19	5.2
6	F	2f	305.8	434.88	- 110.37	5.3
7	Cl	2g	300.8	429.19	- 116.06	5.1
8	Br	2h	299.6	427.48	- 117.78	5.1
9	CHO	2i	279.1	409.49	- 135.77	4.3
10	CN	2j	286.2	413.29	- 131.96	4.7
11	NO ₂	2k	274.0	405.97	- 139.28	3.9

The selected geometrical parameters of singlet and triplet states of these carbenes are given in Table S2 of the Supplementary Material.

Conclusion

If one desires to compare the nucleophilicity and stability of carbene species **1** and **2**, he/she will find that in the case of NHCs **1**, the carbene **1d** has the highest nucleophilicity and thermodynamic stability considering all calculated scales, which may be attributed to the +I effect and the positive hyperconjugation of CH₃; in addition, **1k** has the highest electrophilicity in these carbenes. As regards

carbenes series **2**, **2a** (due to its +R) has the highest nucleophilicity and thermodynamic stability, and **2k** has the highest electrophilicity and the least stability.

As has been stated by Nyulászai, the synthesis of those carbenes with ΔE_{iso} greater than 377 kJ/mol would be feasible. Accordingly, all investigated aryl substituted carbenes may be prepared in laboratory. This feasibility may also be pertained only to those carbenes of series **1** with electron donating substituents having $\Delta E_{iso} > 377$ kJ/mol. In all NHCs **2**, (with electron donating or electron withdrawing groups) resonance is established. Nucleophilicities of carbenes **2**, to some extent, are greater than those of carbenes **1**, probably due to the presence of phenyl-moiety.

Theoretical and computational details

Density functional theory was used to fully optimize all molecules and calculate single point energy of neutral, anion and cation of carbenes without any symmetry constraint at B3LYP level of theory with 6-311++G** basis set using Spartan' 10 program [35]. All the structures of 1,3-disubstituted imidazol-2-ylidene were determined to be at their minimum by applying real frequency calculations. Chemical potential μ , chemical hardness η , and the additional electronic charge ΔN_{max} were obtained using the following equations [28]:

$$\mu = -(IP + EA)/2, \quad (5)$$

$$\eta = IP - EA, \quad (6)$$

$$\Delta N_{max} = -\frac{\mu}{\eta}. \quad (7)$$

It should be noted that tetracyanoethylene was chosen as the reference for calculating nucleophilicity, $N = E_{\text{HOMO}(\text{Nu})} - E_{\text{HOMO}(\text{TCNE})}$ [40].

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