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A density functional theory study on the stability and ligand properties of the different substituted phenyl carbenes

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In regard to the worldwide interest in synthesis and application of stable carbenes, DFT calculations (B3LYP/6-311++G**//B3LYP/6-31+G* levels) are employed to reach at a series of phenyl carbenes. The singlet-triplet energy separations (ΔE_{S-T}), HOMO-LUMO energy gaps ($\Delta E_{HOMO-LUMO}$), as well as philicity indices (N and ω) and basicity of these carbenes are compared and contrasted with the synthesized N-heterocyclic carbenes. The investigations reveal that F, Cl, Br, NMe₂ and PMe₂ stabilize singlet states more than their corresponding triplet states. The reactivity of the species is discussed in terms of nucleophilicity, electrophilicity and proton affinity. This detailed study offers new insights into the chemistry of these classes of carbenes.

Key words: Stability, phenyl carbenes, nucleophilicity and electrophilicity, proton affinity, DFT.

INTRODUCTION

Carbenes are usually short lived reactive species (Bertrand, 2002 and Regitz, 1989). They are neutral compounds featuring a divalent carbon atom, having two non bonded electrons, either with parallel (that is, triplet (Wassermann, 1970a, b; Herzberg and Johns, 1971) or paired spins (that is, singlet) (for pertinent books on carbene chemistry, (Kirmse, 1971; Regitz, 1989; Jones and Moss, 1973; Moss and Jones, 1975; Brinker, 1994; Moss et al., 2004; Bertrand, 2002). These reactive intermediates are frequently characterized using infrared (IR), UV-visible and in the case of triplets, electron paramagnetic resonance (EPR) spectroscopy (Bertrand, 2002; Kirmse, 1971; Moss and Jones, 1975; Sander, 1993). In methylene, the parent of all carbenes (CH₂) which has a triplet ground state, indicated by electron spin resonance (ESR) studies (Milligan, 1985; Wasserman, 1970; Bernheim, 1970), four electrons are involved in the C-H bonds. The orbital occupation of the last two electrons defines the specific electronic state of methylene. If we assume a bent structure, we can use the

simple model of a sp^2 -hybridized carbon. The four bonding electron occupy two of these sp^2 hybrids and the p -orbital available for the last two electrons. Placing one electron in each of these orbitals with their spins aligned creates a triplet state.

The electronic structure of phenylcarbene is analogous to that of methylene. To obtain the lowest energy states, the two nonbonding electrons can be placed into two molecular orbitals that are similar to the two MOs of methylene. Again, the in-plane MO has significant s -character and is lower in energy than the p -orbital. Unlike the case in methylene, the neighboring phenyl group can donate electron density into this p -orbital, especially in the singlet state where this orbital is empty (Bachrach, 2007).

Now, we are pleased to report the results of our density functional theory (DFT) calculations on the stability, multiplicity and reactivity of some substituted derivatives of phenylcarbene (Ph-C-H, 1), including Ph-C-F (2), Ph-C-Cl (3), Ph-C-Br (4), Ph-C-CH₃ (5), Ph-C-SiH₃ (6), Ph-C-NMe₂ (7), Ph-C-PMe₂ (8) and Ph-C-Ph (9). We studied the effects of π -donor/ σ -acceptor (N(CH₃)₂) and π -donor/ σ -donor (P(CH₃)₂) and also halogens (F, Cl, Br), CH₃, SiH₃ and Ph substituents on the singlet-triplet energy gaps (ΔE_{S-T}) of phenyl carbene.

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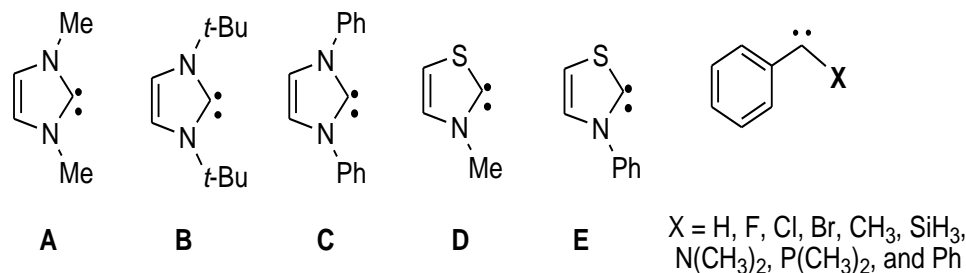


Figure 1. Scrutinized carbenes studied in this work.

COMPUTATIONAL METHOD

DFT (Parr and Yang, 1989) is a general computational method that is frequently used in computing properties of molecules (Mollamin et al., 2011). The Becke 3 Lee-Yang-Parr (B3LYP) functional (Becke, 1993; Parr and Yang, 1989) with 6-31+G* split-valance basis set was used in this work. In the present study, density functional theory method has been used to fully optimize the geometries of carbenes. Becke's three parameter exact exchange functional (B3) (Becke, 1999, 1996) combined with gradient corrected correlation functional of Lee-Yang-Parr (LYP) (Lee, 1988; Adamo and Barone, 1997) of DFT method has been employed to optimize the molecules using the standard 6-31+G* Pople's basis sets (Rassolov, 1998). The improved energetic results are obtained by the single point calculations at higher levels of theory, including B3LYP/6-311++G**.

All calculations are carried out using the Gaussian 98 package (Frisch et al., 1998). Harmonic vibrational frequencies are computed in order to characterize the stationary points as minima, representing equilibrium structures, and to evaluate zero-point vibrational energies. Also, the natural bond orbital (NBO) population analyses (Glendening et al., 2003) on optimized structures are accomplished at B3LYP/6-311++G** level and atoms in molecules (AIM) (Bader, 1990) analyses are accomplished at B3LYP/6-311G** level. The nucleophilicity index, N , which was recently introduced by Domingo et al. (2008) is calculated as $N = E_{\text{HOMO}}(\text{Nu}) - E_{\text{HOMO}}(\text{TCE})$, where tetracyanoethylene (TCE) is chosen as the reference. The global electrophilicity, ω , (Parr et al., 1999) is also calculated following the expression, $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu \approx (E_{\text{HOMO}} + E_{\text{LUMO}})/2$) and η is the chemical hardness ($\eta = E_{\text{LUMO}} - E_{\text{HOMO}}$) (Parr and Pearson, 1983; Parr and Yang, 1989). PAs for the singlet-ground-state divalent species are calculated and compared to some synthesized N-heterocyclic carbenes (NHCs) at B3LYP/6-311++G**//B3LYP/6-31+G*.

RESULTS AND DISCUSSION

The studied carbenes along with some stable synthesized carbenes are as shown in Figure 1. The selected optimized geometrical parameters of the studied carbenes are given in Table 1.

Relationship between structure and ground state multiplicities

The structure, stability and reactivity of carbenes are very dependent on the electron configuration of the carbenic

center. Our calculations indicate that the nitrogen and phosphorus atoms and fluorine, chlorine and bromine atoms stabilizes the singlet state of carbene to the extent that $\Delta E_{\text{S-T}}$ is found as large as 25.9, 3.35, 23.8, 15.7 and 15.1 kcal/mol, respectively (Table 2).

Singlet-triplet energy separation through optimized geometries and substituent effects through AIM analysis

The calculated harmonic vibrational frequencies using analytical second derivative at B3LYP/6-31+G* level of theory indicated that all the optimized structures are at stationary points, corresponding to local minima in the potential energy surface without any imaginary frequencies. Although, the $\text{C}_{\text{phenyl}}\text{-C}_{\text{carbene}}$ bond length of both singlet and triplet states of our structures are shorter than a typical C-C bond (1.393 to 1.467 versus 1.540 Å) (Tables 1 and 2). Going from singlet to triplet carbenes, the divalent angle of the latter become larger. Evidently, smaller divalent angle imposes more p character to the covalent bonding orbitals which is compensated with the 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 of the σ - π gap leading to the favorable singlet and unfavorable triplet states.

The relative stability of the p and the s orbitals is determined by the nature of the substituents adjacent to the carbenic center. This means that, at least for carbon, we can control the multiplicity of the molecule by choosing appropriate substituents. Carbon and other members of the 2nd row of the periodic table are "special" because of the relatively small energy differences and size differences between the 2s and the 2p orbitals.

Because of these properties, the parent carbene CH_2 has a triplet ground state. In practice, it is much easier to use substituents to favor singlet carbenes than triplet ground states, so both multiplicities are possible for carbon but not for most other elements. The presence of electronegative groups induces positive charges on the carbenic centers with fewer values for the singlet states due to the lone pair conjugation with the empty carbenic

Table 1. Principal geometrical parameters for the singlet (s) and triplet (t) (in parentheses) states of the scrutinized carbenes at B3LYP/6-31+G*.

X	Point group	C _{phenyl} -C _{Carbene}	C _{Carbene} -X	C _{phenyl} -C _{Carbene} -X
H	C _s /C ₁ (C _s /C ₁)	1.439 (1.393)	1.111 (1.083)	106.84 (135.31)
F	C _s /C ₁ (C _s /C ₁)	1.462 (1.460)	1.352 (1.355)	108.13 (108.25)
Cl	C _s /C ₁ (C _s /C ₁)	1.454 (1.452)	1.758 (1.761)	112.49 (112.57)
Br	C _s /C ₁ (C _s /C ₁)	1.448 (1.445)	1.912 (1.919)	113.25 (113.31)
CH ₃	C _s /C ₁ (C _s /C ₁)	1.446 (1.397)	1.481 (1.471)	117.14 (136.95)
SiH ₃	C _s /C ₁ (C _s /C ₁)	1.428 (1.394)	1.863 (1.815)	126.36 (159.05)
NMe ₂	C _s /C ₁ (C _s /C ₁)	1.467 (1.410)	1.310 (1.372)	117.84 (128.50)
PMe ₂	C _s /C ₁ (C _s /C ₁)	1.450 (1.404)	1.626 (1.762)	128.74 (138.13)
Phenyl	C ₂ /C ₁ (C ₂ /C ₁)	1.435 (1.404)	1.435 (1.404)	119.27 (142.66)

Table 2. Calculated singlet-triplet energy gaps (ΔE_{S-T} , kcal/mol) along with the smallest calculated vibrational frequencies (ν_{\min} , cm⁻¹) for the singlet and triplet (in parentheses) states at B3LYP/6-311++G**/B3LYP/6-31+G*.

X	E _S (a.u.)	E _T (a.u.)	ΔE_{S-T} (kcal/mol)	$\nu_{\min S}$ (cm ⁻¹)	$\nu_{\min T}$ (cm ⁻¹)
methylene	-39.1467379	-39.1660972	-12.2	1426.3	1076.2
H	-270.2919891	-270.300144	-5.1	183.4	201.9
F	-369.5907372	-369.552668	23.9	106.9	132.6
Cl	-729.9409498	-729.915617	15.7	72.5	78.2
Br	-2843.861017	-2843.83753	15.1	117.9	121.3
CH ₃	-309.6278405	-309.635861	-5.1	77.2	58.3
SiH ₃	-561.0152208	-561.038582	-17.0	27.4	28.2
NMe ₂	-404.364459	-404.323167	25.9	32.7	46.0
PMe ₂	-690.9607962	-690.955451	3.4	36.6	33.9
Phenyl	-501.4214049	-501.429343	-5.0	58.0	43.7

p-orbital. This stabilization effect is easily detectable in terms of atoms in molecules (AIM) (Merceron-Saffon, 2003) theory (Table 3). Comparing the values calculated for X = F, Cl, Br, the resulted ρ values indicate stronger bonds for singlets rather than triplet 0.244, 0.188 and 0.155 a.u., respectively for X = F, Cl, Br.

The parent 1 is a triplet ground state with the singlet-triplet energy gap ($\Delta E_{S-T} = E_T - E_S$) of -5.1 kcal/mol and the divalent angle of 106.84° (Tables 1 and 2). In 2, 3 and 4, F, Cl and Br substituent, which have a *p*-orbital, raises the vacancy 2p orbital of the carbene, by increasing the separation of the 2p and spⁿ (σ) orbitals. The ground-state of (F, Cl, Br)-substituted carbene becomes singlet. But it is not about 6. On the basis of Pauling electronegativities, electropositive Si is considered as a σ -donor substituent which is anticipated to induce a small gap between s and p orbitals leading to a ground state triplet carbene. The calculated negative ΔE_{S-T} for 6 fulfills this expectation with the highest gap obtained for 6 (Table 2). Evidently, the supreme wide divalent angle of the triplet state 6 compared to the other structures is a prominent reason for the observed phenomena (Table 1). The negative charge on the carbenic center of 6 is the

result of Si σ -donation. The less charge on the carbenic center of the singlet state of 6 compared to the corresponding triplet (-0.348 versus 0.677) is related to the effect of hyperconjugation in the former, as stated by Nemirowski and Schreiner (Conejero, 2004). Evidently, Si-C_{carbene} bond is weaker than C-C_{carbene} one. The resulted $\nabla^2\rho$ value for Si-C_{carbene} bond of 6 shows the ionic character of these bonds (Table 3).

Although, the electropositive phosphorous is σ -donor, but the presence of an electron lone pair also engenders a *p*-donor substituent. The accumulation of these two characteristics, leads to the singlet ground states for 8 and 9 but with the smallest ΔE_{S-T} among 2, 3, 4 and 7 (Table 2). The less charge on the carbenic centers of the triplet state of 8 and 9 among all carbenes clearly indicate σ -donation of phosphino substituents (Table 4). However, the negative charges on the corresponding singlet states indicate concurrent *p*-donating. Consequently, we can strongly claim that in our studied carbenes, phosphorus atoms choose the role of *p*-donor substituents (Merceron-Saffon, 2002, 2003; Conejero, 2004).

The accurate determination of the energy separation, ΔE_{S-T} , between singlet and triplet carbenes has long

Table 3. Topological parameters of the bond critical point (BCP) for the singlet (s) and triplet (t) (in parentheses) states of the scrutinized carbenes at the B3LYP/6-311G**/B3LYP/6-31+G*.

X	BCP	ρ (a.u.)	$\nabla^2\rho$ (a.u.)	λ_1 (a.u.)	λ_2 (a.u.)	λ_3 (a.u.)
H	H-C:	0.250 (0.258)	-0.716 (-0.756)	-0.676 (-0.673)	-0.605 (-0.665)	0.565 (0.582)
F	F-C:	0.244 (0.243)	0.210 (0.294)	-0.615 (-0.432)	-0.288 (-0.354)	0.111 (0.108)
Cl	Cl-C:	0.188 (0.187)	-0.236 (-0.222)	-0.301 (-0.222)	-0.275 (-0.268)	0.340 (0.333)
Br	Br-C:	0.155 (0.152)	-0.115 (-0.110)	-0.202 (-0.196)	-0.196 (-0.185)	0.283 (0.271)
CH ₃	C-C:	0.248 (0.258)	-0.507 (-0.616)	-0.473 (-0.494)	-0.438 (-0.464)	0.404 (0.342)
SiH ₃	Si-C:	0.106 (0.105)	0.229 (0.349)	-0.119 (-0.125)	-0.114 (-0.125)	0.463 (0.600)
NMe ₂	N-C:	0.313 (0.286)	-0.509 (-0.651)	-0.678 (-0.540)	-0.537 (-0.493)	0.705 (0.382)
PMe ₂	P-C:	0.262 (0.195)	-0.771 (0.352)	-0.677 (-0.296)	-0.669 (0.183)	0.575 (0.832)
Phenyl	C-C:	0.271 (0.281)	-0.623 (-0.655)	-0.534 (-0.533)	-0.487 (-0.489)	0.398 (0.368)

^aHere, $\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$ is an eigen value of the Hessian matrix of ρ .

Table 4. Ranges of NBO atomic charges of carbene (C) and heteroatom (Y) for the scrutinized carbenes at B3LYP/6-311++G**/B3LYP/6-31+G*.

Species	C _{Carbene}	Y
1	-0.124 (0.841)	0.0824 (0.067)
2	0.366 (1.048)	-0.372 (-0.108)
3	-0.026 (0.831)	-0.020 (0.098)
4	-0.095 (0.782)	0.046 (0.144)
5	0.0726 (0.893)	-0.724 (-0.382)
6	-0.348 (0.677)	0.754 (0.379)
7	0.125 (0.804)	-0.426 (-0.156)
8	-0.563 (0.595)	1.083 (0.464)
9	0.0566 (0.814)	-0.197 (-0.169)

challenged experimentalists and theoreticians alike. 6 had a triplet ground state with a wide carbene bond angle of 159.05° which had eased the promotion of an electron from σ to p -orbital in favor of the triplet state. Quantitatively, Schleyer et al. (1996) showed that the energy of triplet methylene drops below that of singlet state if the carbene bond angle is enlarged over 104° (Sulzbach, 1996). Now, our calculated wide carbene bond angle of 159.05° (Table 1) puts triplet Ph-C-SiH₃ 16.98 kcal/mol lower in energy than its singlet 6 (Table 2).

The ionic P-C_{carbene} bond of triplet 8 is in front of covalent bonds of phenylcarbenes. Compared to the large ΔE_{S-T} of 7, the small ΔE_{S-T} of 8 show less p -donation of phosphorous compared to nitrogen stem from the energetic cost required to achieve planar environment (~30 to 35 kcal/mol for phosphorus versus ~5 kcal/mol for nitrogen) (Bouhadir and Bourissou, 2004). Amino substituents are well known for the significant singlet state stabilization through p -donating/ σ -accepting interactions. The presence of electronegative amino group induces positive charges on the carbenic centers of 5 with fewer values for the singlet states due to the lone pair conjugation with the empty carbonic p orbital.

Evidently, the σ -acceptor substituents (Pauling electronegativities (EN)): (C = 2.5, N = 3.0) are anticipated to induce a large gap between σ - and p -orbitals in favor of the singlet state (Hirai, 2009).

This stabilization effect is easily detectable in terms of AIM theory (Table 3). According to the topological analysis of electron density in the theory of AIM, ρ is used to describe the strength of a bond. In general, the larger the value of ρ is, the stronger the bond is. The $\nabla^2\rho$ describes the characteristic of the bond. Where $\nabla^2\rho < 0$, the bond is considered covalent while with $\nabla^2\rho > 0$ the bond belongs to the ionic one. Compared to the parent phenylcarbene, the resulted ρ values indicate stronger bonds for both singlet and triplet 5 ($\rho = 0.313$ and 0.286 a.u. for 5 (s) and 5 (t), respectively, versus 0.250 and 0.258 a.u. for 1 (s) and 1 (t), respectively). Hence, the presence of p -donor/ σ -acceptor amino group enlarges the ΔE_{S-T} of 5 to 25.91 kcal/mol.

The order of singlet-triplet energy gaps (ΔE_{S-T}) is (5.1 kcal/mol), (5.1 kcal mol⁻¹) > (5.0 kcal/mol), respectively for 1, 5 and 9 at B3LYP/6-311++G** (Table 2). In all cases, the triplet is predicted to be the ground state. For some of them, it is in accordance with the experiment (Jones and Moss, 2004). Complete active space-space self-consistent-field SCF (CASSCF) predicts an energy difference of about 10 kcal/mol, and correction for dynamic correlation increases the gap (Schreiner et al., 1996). These values are in accordance with other high-level computations. DFT (Matzinger et al., 1996; Wong and Wentrup, 1996; Platz et al., 2004) and CCSD(T) (Matzinger et al., 1996; Wong and Wentrup, 1996) calculations place the gap at about 5 kcal/mol. Unfortunately, singlet phenylcarbene has not been spectroscopically observed, and the singlet-triplet gap has not been measured (Bachrach, 2007; Platz et al., 2004).

The NBO atomic charges

Resonance effects are best understood in terms of the p -acidity or basicity of the substituent adjacent to the

Table 5. The nucleophilicity (N), the global electrophilicity (ω) indices and proton affinity (PA) for all the singlet scrutinized carbenes compared to the synthesized NHCs.

Structure	HOMO (a.u.)	LUMO (a.u.)	$\Delta E_{\text{HOMO-LUMO}}$	η (eV)	N (eV)	ω (eV)	PA (kcal/mol)
2	-0.2347	-0.1123	4.72	4.721	3.07	3.35	253.47
3	-0.2253	-0.1219	4.72	4.724	3.33	3.96	258.09
4	-0.2224	-0.1241	4.71	4.714	3.41	4.15	258.79
7	-0.1905	-0.0319	4.32	4.317	4.27	1.06	274.77
8	-0.1903	-0.0554	3.67	3.671	4.28	1.52	271.92
A	-0.21693	-0.00817	131.00	-	3.56	0.83	267.98
B	-0.20902	-0.01098	124.27	-	3.77	0.83	276.33
C	-0.22738	-0.03619	119.97	-	3.27	1.24	270.59
D	-0.23188	-0.02357	130.71	-	3.15	1.07	256.74
E	-0.23474	-0.04272	120.49	-	3.07	1.36	259.99

carbenic center. Pauling suggested in 1980 that substituents with opposing effects would stabilize singlet carbenes, because it would populate the vacant p -orbital while avoiding the build-up of excessive charge at the carbon atom. This is known as “Push-Pull” substitution and it can be done in a variety of ways. These types of substitution patterns have allowed the isolation of numerous stable singlet carbenes and carbenoids with a large variation in structural and reactivity characteristics.

The stabilization of the carbene center by substituents may result in negative or less positive partial atomic charges on the carbene centers. The lower positive atomic charge of +0.125 on the singlet state of 7 as compared to the 0.804 on its corresponding triplet state indicates stabilization of the former caused by hyperconjugation (Table 3). Increase of the carbene atomic charge from 0.125 in 7 (s) to + 0.162 in 2 (s) shows that such a stabilizing effect slightly decreases (Table 4). Due to the higher electronegativities of fluorine atom than chlorine and bromine, it is anticipated to place partial positive atomic charges on their adjacent carbene centers. Yet, stabilization by π -donor fluorine substituent places less positive partial atomic charge on the singlet carbene centers than their corresponding triplet states (+0.366 versus +1.048 for 2 and -0.026 versus +0.831 for 3 and -0.095 versus +0.782 for 4 (Table 4).

The σ -donority of electropositive silicon and phosphorus atoms (on the basis of Pauling electronegativity; $EN_{\text{Si}} = 1.8$ and $EN_{\text{P}} = 2.2$), expectedly induce negative charges on the carbene centers. Nevertheless, the synergistic π -donating stabilizing effect of the phosphorus atom is clearly shown in the negative charges on the singlets relative to positive charge on their triplet states (-0.348 versus +0.677 for the 6 and -0.563 versus +0.595 for 8).

Nucleophilicity, electrophilicity and proton affinity

The chemical hardness (η) and chemical potential (μ) have been determined for all of our carbenes using the highest occupied molecular orbital (HOMO) and lowest

unoccupied molecular orbital (LUMO) energies at B3LYP/6-311++G** level of theory. The chemical hardness (η) and chemical potential (μ) are important tools to study the relative stabilities of different conformers of a molecular system. The chemical hardness parameter received much attention after the invention of Pearson's maximum hardness principle (Pearson, 1973), which states that the minimum energy structure has the maximum chemical hardness. The maximum hardness principle (MHP) is able to predict the most stable structure whose chemical hardness is found to be 4.317 eV in 7. The calculated chemical hardness values in 2, 3 and 4 are more or less similar to that of 7 and indicate that there is no considerable change in molecular orbital energies of these structures.

The nucleophilicity (N) and the global electrophilicity (ω) indices as well as the PAs for the singlet ground state divalent species are calculated at B3LYP/6-311++G**/B3LYP/6-31+G* level and compared and contrasted with a wide variety of synthesized N-heterocyclic carbenes (Table 5). The gas-phase proton affinities of carbenes (PA, the negative of the enthalpies of their protonation reactions) are an accepted criterion for discussing the basicity of carbenes (Maxwell et al., 1992). The increasing trend of nucleophilicity, electrophilicity and basicity is followed in F-, Cl- and Br-phenyl carbenes. All the electronegative substituents decrease the nucleophilicity. Compared to NHCs A to E, our phenyl carbenes show higher nucleophilicities and electrophilities. Specifically, 7 and 8 are the most nucleophilic species studied in this work with $N = 4.58$ (compare to the 3.07 to 3.77 range obtained for NHCs A to E). Among each kind of structurally different carbenes, 8 indicates the highest N values (4.28 eV) while 2 show the lowest values (3.07 eV).

Group 15 (P and N) (8 and 7) are the most nucleophilic species among substituted carbenes. The higher calculated N values for all the species relative to the calculated ω ones introduce them as nucleophiles. However, halogens (Br, Cl and F) are considered as the most electrophiles with ω values higher than the others

(4.15, 3.96 and 3.35 eV for 4, 3 and 2, respectively). Indeed, 8 is the most nucleophilic and the least electrophilic species.

Conclusion

Employing B3LYP/6-31+G* calculations, nine phenyl carbenes were studied. All thermodynamic parameters including relative energies, ΔE_{S-T} and $\Delta E_{HOMO-LUMO}$ support the stability of the singlet states of 2, 3, 4, 7 and 8. To investigate the ligand properties of the carbenes, the nucleophilicity (N) and electrophilicity (ω) indices are calculated at B3LYP/6-311++G** for our scrutinized phenyl carbenes. 8 and 4 possesses a higher nucleophilicity index: $N = 4.28$ and higher electrophilicity index: $\omega = 4.15$, respectively. Indeed, our phenyl carbenes seem more nucleophilic than some of the synthesized NHCs. NHCs with the proton affinity more than 255 kcal/mol appears as the basic as our studied carbenes.

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