

Different substituted phenyl carbenes / silylenes/ germylenes: a survey of stability

Fereshteh Naderi^{*1}, Rahimeh Bagheri¹, Mohammad Yari²

¹ Department of Chemistry, Shahr-e Qods Branch, Islamic Azad University, Tehran, Iran

² Department of Chemistry, Islamshahr Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

The effects of halogens; fluorine, chlorine and bromine, on the stability and multiplicity of phenyl carbenes / silylenes/ germylenes structures are compared and contrasted at B3LYP/6-311++G**//B3LYP/6-31+G* level. The singlet-triplet energy gaps, ΔE_{S-T} , values for all the above species increase through fluorinated up, ΔE_{S-TS} and $\Delta E_{HOMO-LUMOS}$ support the stability of the singlet states inspite of their corresponding triplet states. The investigations reveal that F, Cl and Br stabilize singlet states more than their corresponding triplet states. The reactivity of the species is discussed in terms of nucleophilicity and electrophilicity. This detailed study offers new insights into the chemistry of these classes of carbenes / silylenes/ germylenes.

Keywords: Stability; Fluorine; Energy gap; Triplet state

INTRODUCTION

Carbenes are usually short lived reactive species. They are neutral compounds featuring a divalent carbon atom, having two nonbonded electrons, either with parallel (that is, triplet) or paired spins (that is, singlet) (for pertinent books on carbene chemistry. These reactive intermediates are frequently characterized using infrared (IR), UV-visible and in the case of triplets, electron paramagnetic resonance (EPR) spectroscopy. In methylene, the parent of all carbenes (CH₂) which has a triplet ground state, indicated by electron spin resonance (ESR) studies [1-5], 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 synthesis and experimental characterization of the silicon and germanium analogues of methylene (CH₂) were a considerable challenge because of their intrinsic kinetic instabilities. In the last decade of the twentieth century, remarkable progress has been made in the chemistry of

low-coordinate compounds of heavier Group 14 elements [6].

Following the successful synthesis and isolation of the first stable silene and disilene in 1981, a variety of low-coordinated silicon compounds such as Si=Pn (Pn=N, P, As), Si=Ch (Ch=S, Se),

^{*}Corresponding author: fnaderi2@yahoo.com

1-silaallenes, silabenzene, 2-silanaphthalene, and tetrasila-1,3-butadiene have been synthesized as stable compounds by taking advantage of kinetic stabilization with bulky substituents (so called steric protection) and most of them are structurally well-characterized [7-11]. Although it has been recognized theoretically that germynes should be much more stable than silylenes. The first isolable diaminogermynes $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ge}$: were synthesized by Harris and Lappert in 1974. In 1999, Kira et al. have applied their original helmet-like bidentate ligand to the kinetic stabilization of a germylene and succeeded in the synthesis and isolation of very stable dialkylgermylene [12]. The simple carbenes are π -electron-deficient and σ -electron rich, so that they are effectively stabilized by π -electron donor, σ -electron-acceptor substituents.

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 phenyl carbene, phenyl silylene and phenyl germynes including, Ph-X-F, Ph-X-Cl and Ph-X-Br where X is C, Si and Ge.

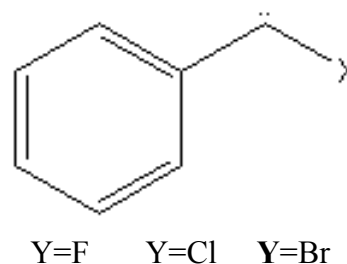
COMPUTATIONAL METHODS

Full geometry optimizations are accomplished without any symmetry constraints using hybrid functional B3LYP and the 6-31+G* basis set, employing the Gaussian 98 code [13]. The applied basis set comprises Pople's well-known 6-31G* basis set [14] and an extra plus due to the importance of diffuse functions [15, 16]. To obtain more accurate energetic data, single point calculations are performed at the B3LYP/6-311+G* level [17]. Vibrational frequencies are calculated to establish the nature of stationary points as true minima [18]. The nucleophilicity

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

RESULTS AND DISCUSSION

The studied phenyl carbene / silylene / germylene are as shown in Scheme 1. The selected optimized geometrical parameters of the studied phenyl carbene / silylene / germylene are given in Table 1.



Scheme 1. Carbenes / silylenes / germynes discussed in this article.

Relationship between structure and ground state multiplicities

The structure, stability and reactivity of phenyl carbene / silylene / germylene are very dependent on the electron configuration of the center. In contrast to the carbon atom, the heavier group 14 atoms have a low ability to form hybrid orbitals. They therefore prefer the $(ns)^2(np)^2$ valence electron configurations in their divalent species [22]. Since two electrons remain as a singlet pair in the ns orbital, the ground state of silylene and germylene is a singlet, unlike the case of carbene where the ground state is a triplet (Scheme 1) [23].

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

| Y | Point group | C _{Phenyl} -X | X-Y | C _{Phenyl} - X - Y |
|---------|--|------------------------|---------------|-----------------------------|
| F(C) | C _s /C ₁ (C _s /C ₁) | 1.462 (1.460) | 1.352 (1.355) | 108.13 (108.25) |
| F(Si) | C _s /C ₁ (C _s /C ₁) | 1.892 (1.866) | 1.658 (1.643) | 99.06 (113.39) |
| F(Ge) | C _s /C ₁ (C _s /C ₁) | 1.939 (1.927) | 1.797 (1.783) | 96.92 (110.32) |
| Cl(C) | C _s /C ₁ (C _s /C ₁) | 1.454(1.452) | 1.758(1.761) | 112.49(112.57) |
| Cl(Si) | C _s /C ₁ (C _s /C ₁) | 1.892 (1.868) | 2.133 (2.090) | 101.39 (116.97) |
| Cl(Ge) | C _s /C ₁ (C _s /C ₁) | 1.945 (1.927) | 2.252 (2.209) | 99.84 (115.85) |
| Br(C) | C _s /C ₁ (C _s /C ₁) | 1.448(1.445) | 1.912(1.919) | 113.25(113.31) |
| Br(Si) | C _s /C ₁ (C _s /C ₁) | 1.891 (1.867) | 2.288 (2.239) | 101.65 (117.48) |
| Br(Ge) | C _s /C ₁ (C _s /C ₁) | 1.944 (1.925) | 2.399 (2.354) | 99.93 (115.40) |

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*

| Y | E _S (a.u.) | E _T (a.u.) | ΔE_{S-T} (kcal/mol) | $\nu_{\min S}$ (cm ⁻¹) | $\nu_{\min T}$ (cm ⁻¹) |
|---------|-----------------------|-----------------------|--------------------------------|------------------------------------|------------------------------------|
| F(C) | -369.591 | -396.553 | 23.85 | 106.9 | 132.6 |
| F(Si) | -621.023 | -620.953 | 44.1 | 76.1 | 64.8 |
| F(Ge) | -2406.559 | -2406.481 | 49.5 | 98.2 | 91.7 |
| Cl(C) | -729.941 | -729.916 | 15.69 | 72.5 | 78.2 |
| Cl(Si) | -981.363 | -981.302 | 38.8 | 54.9 | 43.4 |
| Cl(Ge) | -2766.912 | -2766.841 | 44.9 | 73.2 | 57.3 |
| Br(C) | -2843.861 | -2843.837 | 15.06 | 121.3 | 117.9 |
| Br(Si) | -3092.8901 | -3092.831 | 37.5 | 65.0 | 59.6 |
| Br(Ge) | -4878.443 | -4878.374 | 43.4 | 76.9 | 61.9 |

On the basis of theoretical calculations, the singlet-triplet energy differences ΔE_{S-T} for silylene and germlyene, [$\Delta E_{S-T} = E(\text{triplet}) - E(\text{singlet})$], are found to be 44.1, 38.8 and 37.5 kcal/mol for F, Cl and Br substituent of silylene and 49.5, 44.9 and 43.4 kcal/mol for F, Cl and Br substituent of germlyene respectively. These values for F, Cl and Br substituent of carbene are 23.9, 15.7 and 15.1 kcal/mol respectively. These are very smaller than former. That of phenyl carbene is estimated as -5.1 kcal/mol.

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. The C_{phenyl}-C_{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). Although C_{phenyl}-Si_{silylene} and C_{phenyl}-Ge_{germylene} of both singlet and triplet states of our structures are almost the same as a typical C-Si or C-Ge bond (Table 1). Going from singlet to triplet phenyl carbene/silylene/germylene, 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 / silylene / germylene. 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 carbene / silylene / germylene center. In practice, it is much easier to use substituents to favor singlet carbene / silylene / germylene than triplet ground states, so both multiplicities are possible for carbon, silicon and germanium but not for most other elements. The presence of electronegative groups induces positive charges on the carbenic / silylenic / germylenic centers with fewer values for the singlet states due to the lone pair conjugation with the empty carbenic / silylenic / germylenic p-orbital. This stabilization effect is easily detectable in terms of atoms in molecules (AIM) [24] 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 F substituent of carbene ($\rho = 0.244$ and 0.243 a.u. for Ph-C-F (singlet) and Ph-C-F (triplet)), followed by Cl and Br substituent of carbene ($\rho = 0.188$ and 0.187 a.u. for Ph-C-Cl (singlet) and Ph-C-Cl (triplet) and $\rho = 0.155$ and 0.152 a.u. for Ph-C-Br (singlet) and Ph-C-Br (triplet)). Comparing the values calculated for X = F, Cl and Br, the resulted ρ values indicate stronger bonds for singlets rather than triplet 0.244 , 0.188 and 0.155 a.u. In values calculated for X = F, Cl and Br, the resulted ρ values indicate stronger bonds for carbenes rather than silylenes and germylenes. These values are 0.110 , 0.856 and 0.788 a.u. for singlet silylene and 0.114 , 0.810 and 0.737 a.u. for singlet germylene for X = F, Cl and Br respectively, because of more electronegativity of carbon versus silicon and germanium.

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

| Y | BCP | ρ (a.u.) | $\nabla^2\rho$ (a.u.) | λ_3 (a.u.) | λ_2 (a.u.) | λ_1 (a.u.) |
|--------|--------|---------------|-----------------------|--------------------|--------------------|--------------------|
| F(C) | F-C: | 0.244 (0.243) | 0.210 (0.294) | -0.615 (-0.432) | -0.288 (-0.354) | 0.111(0.108) |
| F(Si) | F-Si: | 0.111 (0.114) | 4.250 (4.317) | 4.336 (4.446) | -0.086 (-0.128) | -0.0002(-0.0002) |
| F(Ge) | F-Ge: | 0.114 (0.115) | -2.813 (-2.821) | -3.560 (-3.568) | 0.748 (0.752) | -0.0007 (-0.0007) |
| Cl(C) | Cl-C: | 0.188(0.187) | -0.236(-0.222) | -0.301(-0.222) | -0.275(-0.268) | 0.340(0.333) |
| Cl(Si) | Cl-Si: | 0.856 (0.908) | 2.803 (2.975) | 3.727 (3.789) | -0.924 (-0.814) | -0.0004 (-0.0003) |
| Cl(Ge) | Cl-Ge: | 0.810 (0.872) | 3.428 (3.507) | 3.366 (3.527) | 0.063 (-0.019) | -0.0003 (-0.0003) |
| Br(C) | Br-C: | 0.155(0.152) | -0.115(-0.110) | -0.202(-0.196) | -0.196(-0.185) | 0.283(0.271) |
| Br(Si) | Br-Si: | 0.788 (0.839) | -1.084 (1.317) | -2.547 (2.559) | 1.463 (-1.242) | -0.0002 (-0.0002) |
| Br(Ge) | Br-Ge: | 0.737(0.792) | 1.842 (1.993) | 2.535 (2.625) | -0.693 (-0.631) | -0.0002 (-0.0003) |

F, Cl and Br substituent, which have a *p*-orbital, raises the vacancy 2*p* orbital of the carbene, by increasing the separation of the 2*p* and *sp*ⁿ (σ) orbital.

The accurate determination of the energy separation, ΔE_{S-T} , between singlet and triplet carbenes has long challenged experimentalists and theoreticians alike. F substituent had a singlet ground state with a narrow carbene / silylene / germylene bond angle of 108, 99 and 97°. ΔE_{S-T} for F substituents are more than the other ΔE_{S-T} , 24, 44 and 49 (kcal/mol) for F substituent of carbene / silylene / germylene, which made the promotion of an electron from σ to *p*-orbital difficult in favor of the singlet 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°. Now, our calculated carbene bond angle (Table 1) puts singlet F substituent of carbene lower in energy than its triplet (Table 2).

The order of singlet-triplet energy gaps (ΔE_{S-T}) are 23.9, 15.7 and 15.1 kcal/mol respectively for F, Cl and Br substituent of carbenes and 44.1, 38.8 and 37.5 kcal/mol respectively for F, Cl and Br substituent of silylenes and finally 49.5, 44.9 and 43.4 at kcal/mol respectively for F, Cl and Br substituent of germylenes (Table 2). In all cases, the singlet 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. These values are in accordance with other high-level computations. DFT and CCSD(T) 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 [25, 26].

The NBO atomic charges

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

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

| Species | X | C _{Phenyl} | Y |
|---------|---------------|---------------------|----------------|
| F(C) | 0.366(1.048) | -0.625(-0.528) | -0.372(-0.108) |
| F(Si) | 1.216(1.163) | -0.654(-0.544) | -0.696(-0.663) |
| F(Ge) | 1.209(1.057) | -0.636(-0.454) | -0.703(-0.656) |
| Cl(C) | -0.026(0.831) | -0.629(-0.621) | -0.020(0.098) |
| Cl(Si) | 0.938(0.855) | -0.631(-0.527) | -0.456(-0.382) |
| Cl(Ge) | 0.961(0.795) | -0.608(-0.451) | -0.489(-0.396) |
| Br(C) | -0.095(0.782) | -0.632(-0.537) | -0.046(-0.144) |
| Br(Si) | 0.861(0.765) | -0.629(-0.527) | -0.381(-0.291) |
| Br(Ge) | 0.884(0.712) | -0.605(-0.455) | -0.414(-0.307) |

The stabilization of the carbene center by substituents may result in negative or less positive partial atomic charges on the carbene centers. 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 F substituent of carbenes and -0.026 versus +0.831 for Cl substituent and -0.095 versus +0.782 for Br substituent of carbenes (Table 4). Since in silylenes and germylenes the electronegativity of C_{phenyl} and substituents are more than silicon and germanium silylene and germylene center by substituents result in positive partial atomic charges on the silylene and germylene centers.

Nucleophilicity, electrophilicity

The chemical hardness (η) and chemical potential (μ) have been determined for all of our carbenes, silylene and germylene 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, which states that the minimum energy structure has the maximum chemical hardness.

The calculated chemical hardness values in F, Cl and Br substituent of carbenes are more or less similar to each other and indicate that there is no considerable change in molecular orbital energies of these structures. The chemical hardness values in F, Cl and Br substituent of silylenes and germylenes are lower. The nucleophilicity (N) and the global electrophilicity (ω) indices 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 increasing trend of nucleophilicity, electrophilicity and basicity is followed in F-, Cl- and Br-phenyl carbenes, silylenes and germylenes. All the electronegative substituents decrease the nucleophilicity. Compared to NHCs A to E, our phenyl carbenes show higher nucleophilicities and electrophilities. However, bromine, Br, is considered as the largest substituent with ω values higher than the others (4.15, 3.17 and 3.31 eV for Br substituent of carbenes, silylenes and germylenes, respectively). Indeed, these species are the most nucleophilic and the least electrophilic species.

Table 5. The nucleophilicity (N) and global electrophilicity (ω) for all the singlet scrutinized carbene / silylene / germylene

| Structure | HOMO(a.u.) | LUMO(a.u.) | $\Delta E_{\text{HOMO-LUMO}}(\text{eV})$ | η (eV) | N(eV) | ω (eV) |
|-----------|------------|------------|--|-------------|-------|---------------|
| F(C) | -0.2347 | -0.1123 | 4.72 | 4.721 | 3.07 | 3.35 |
| F(Si) | -0.2426 | -0.0980 | 3.93 | 3.934 | 2.86 | 2.73 |
| F(Ge) | -0.2503 | -0.1043 | 3.97 | 3.972 | 2.65 | 2.93 |
| Cl(C) | -0.2253 | -0.1219 | 4.72 | 4.724 | 3.33 | 3.96 |
| Cl(Si) | -0.2442 | -0.1084 | 4.80 | 4.798 | 2.81 | 3.11 |
| Cl(Ge) | -0.2507 | -0.1122 | 3.76 | 3.763 | 2.64 | 3.23 |
| Br(C) | -0.2224 | -0.1241 | 4.71 | 4.714 | 3.41 | 4.15 |
| Br(Si) | -0.2414 | -0.1095 | 3.59 | 3.589 | 2.89 | 3.17 |
| Br(Ge) | -0.2504 | -0.1112 | 3.79 | 3.787 | 2.64 | 3.19 |

CONCLUSION

Employing B3LYP/6-31+G* calculations, nine phenyl carbenes / silylene / germylene were studied. All thermodynamic parameters including relative energies, ΔE_{S-TS} and $\Delta E_{HOMO-LUMO}$ support the stability of the singlet states of them. To investigate the ligand properties of the carbenes, silylene and germylene the nucleophilicity (N) and electrophilicity (ω) indices are calculated at B3LYP/6-311++G** for our scrutinized phenyl carbenes / silylene / germylene. Br, Cl and F substituents of carbene possess a higher nucleophilicity index and higher electrophilicity index, respectively. Indeed, our phenyl carbenes seem more nucleophilic than our phenyl silylenes and germylenes.

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