

Original Research Article

Decoding Substituent-Controlled Singlet-Triplet Signatures of Silylenes: A DFT Study on Divalent Silicon Species

Mehdi Nabati* 

Independent Researcher (Computational Chemistry and Drug Design), Tehran, Iran



Citation M. Nabati, Decoding Substituent-Controlled Singlet-Triplet Signatures of Silylenes: A DFT Study on Divalent Silicon Species. *J. Pharm. Sci. Comput. Chem.* **2026**, 2(1), 75-90.

 <https://doi.org/10.48309/jpscc.2026.574776.1039>



Article info:

Submitted: 2026-02-09

Revised: 2026-03-20

Accepted: 2026-03-26

ID: JPSCC-2602-1039

Article Podcast: [Click here](#)

Keywords:

Silylenes, Singlet-triplet energy gap, Density functional theory, Molecular electrostatic potential, Global reactivity descriptors

ABSTRACT

The electronic structure and singlet-triplet characteristics of a series of divalent silicon species, SiR_2 ($\text{R} = \text{H, F, Cl, Br, Me, Et, iPr, tBu, Ph}$), were systematically investigated using density functional theory (DFT). Geometry optimizations and frequency analyses confirmed all stationary points as true minima. The effects of substituents on structural parameters, energetics, charge distribution, polarizability, and spectroscopic signatures were analyzed in both singlet and triplet states. Singlet-triplet energy gaps corrected for zero-point energy reveal a pronounced preference for the singlet state across the entire series, with strong substituent dependence. Frontier molecular orbital analysis and global reactivity descriptors highlight substantial variations in electrophilicity and chemical softness induced by both substituent identity and spin state. Molecular electrostatic potential (MEP) maps clearly demonstrate the ambiphilic nature of singlet silylenes, characterized by well-separated electrophilic and nucleophilic regions, in contrast to the more diffuse electronic distribution of triplet species. Furthermore, calculated ^{29}Si NMR parameters and NBO analyses provide direct spectroscopic and orbital-level fingerprints distinguishing the two spin states. Overall, this study offers a comprehensive substituent-controlled framework for understanding singlet-triplet electronic signatures in silylenes, providing valuable insights for their reactivity and experimental identification.

Introduction

Silicon-containing compounds play a central role across a broad spectrum of scientific and technological fields, ranging from medicinal chemistry [1] and advanced materials to industrial catalysis and semiconductor technology [2]. In pharmaceutical research, the strategic incorporation of silicon into organic frameworks has emerged as a powerful approach to modulate lipophilicity, metabolic stability, and bioavailability, often leading to improved pharmacokinetic profiles compared to their carbon analogues [3-6]. In parallel, silicon-based

materials constitute the backbone of modern electronics and semiconductor industries, where their tunable electronic properties enable precise control over conductivity and device performance [7-9]. Moreover, organosilicon compounds are indispensable in synthetic chemistry, serving as versatile reagents, intermediates, and catalysts in a wide variety of transformations. The unique electronic structure of silicon, characterized by its ability to engage in hyperconjugation, σ - π interactions, and flexible coordination environments, underpins the remarkable diversity of its chemical behavior [10-12].

*Corresponding Author: Mehdi Nabati (mnabati@gmail.com)

Among silicon-centered reactive intermediates, silylenes ($R_2Si:$), the silicon analogues of carbenes, occupy a particularly intriguing position. As divalent silicon species featuring a lone pair and a vacant p-orbital, silylenes exhibit rich and highly tunable electronic structures that can exist in either singlet or triplet spin states. Unlike carbenes, however, silylenes display a pronounced sensitivity to substituent effects, relativistic contributions, and σ -donor/ π -acceptor interactions, leading to substantial variations in their stability, geometry, and reactivity. Over the past decades, advances in steric and electronic stabilization strategies have enabled the isolation of selected silylene derivatives, revealing their potential as ligands, catalysts, and reactive intermediates in bond activation processes. Nevertheless, the fundamental factors governing their electronic structure and spin-state preferences remain far from fully understood [13-18].

A comprehensive understanding of silylenes requires a multidimensional investigation that goes beyond simple energetic considerations. Properties such as singlet-triplet energy gaps, charge distribution, hybridization at the silicon center, molecular geometry, and response to external perturbations collectively determine their chemical behavior. Reactivity descriptors derived from conceptual DFT, including Fukui functions and global reactivity indices, provide valuable insight into their nucleophilic and electrophilic tendencies. At the same time, MEP surfaces, dipole moments, and polarizabilities offer complementary perspectives on charge delocalization and substituent-controlled electronic effects. Vibrational properties, particularly silicon-substituent stretching modes, further reflect bond strengths and structural flexibility, making them essential for correlating electronic structure with observable spectroscopic signatures [19,20].

Despite their fundamental and applied importance, the experimental investigation of silylenes remains severely limited due to their intrinsically short lifetimes and high reactivity, which often render direct spectroscopic characterization difficult or even impossible. In this context, computational chemistry provides an indispensable and often the only viable route to access detailed information about their

structure and properties. While previous theoretical studies have addressed selected silylene systems, they are frequently restricted to a narrow set of substituents or focus on isolated properties, offering an incomplete picture of substituent-controlled trends [21-24]. In the present work, we perform a systematic and unified DFT investigation of a diverse series of silylenes bearing halogen, alkyl, and phenyl substituents. Our study encompasses an extensive set of descriptors, including electronic structure, singlet-triplet behavior, reactivity indices, stability trends, polarizability, dipole moments, silicon hybridization, substituent bond angles, electronegativity effects, charge distribution, MEP maps, and vibrational characteristics of silicon-centered bonds. Particular emphasis is placed on ^{29}Si NMR signatures, which are experimentally inaccessible for most silylenes due to their fleeting nature, yet provide exceptionally sensitive probes of the electronic environment at the silicon center. By integrating these complementary analyses, this work offers a coherent and in-depth perspective on the substituent-controlled signatures of divalent silicon species, filling critical gaps in the current literature and establishing reliable structure-property relationships for this important class of compounds.

Computational methods

All quantum chemical calculations were performed using Gaussian 16 software [25]. While molecular visualization, electrostatic potential mapping, and vibrational mode analysis were conducted with GaussView 6.0.16 [26]. Geometry optimizations for all silylene derivatives were carried out in both singlet and triplet spin states using the B3LYP hybrid density functional in combination with the 6-311++G(d,p) basis set. Frequency calculations were performed at the same level of theory to confirm that the optimized structures correspond to true minima on the potential energy surface and to obtain zero-point energy corrections, vibrational spectra, and thermodynamic properties.

Electronic structure analyses included the evaluation of frontier molecular orbitals,

Mulliken and natural population charges, and natural bond orbital (NBO) analysis to probe the bonding characteristics and lone pair distribution at the silicon center. The singlet–triplet energy gaps were determined from the single-point energies of the optimized geometries of each spin state, providing a quantitative measure of the relative stability of the spin states across different substituents.

To investigate reactivity trends, global reactivity descriptors including ionization potentials (IP), electron affinities, electronegativity, chemical hardness, softness, and electrophilicity indices were calculated. Local reactivity indices were evaluated using Fukui functions obtained from finite-difference approximations, employing single-point calculations for the neutral, cationic, and anionic species at the optimized geometries. MEP maps were generated from Merz–Kollman charges with an IOp grid fine-tuning to provide accurate visualization of the charge distribution and regions of nucleophilic and electrophilic susceptibility.

Polarizabilities and dipole moments were extracted from the frequency calculations, while NMR shielding constants, including ^{29}Si NMR, were computed using the GIAO method at the optimized geometries, providing insight into the electronic environment of the silicon atom that is otherwise experimentally inaccessible due to the short-lived nature of silylenes. Vibrational analyses were further employed to characterize the Si–X stretching modes (X = H, F, Cl, Br, Me, Et,

ipr, tBu, Ph) and their correlation with electronic properties and substituent effects.

Overall, this comprehensive computational protocol allows for a multifaceted investigation of silylene derivatives, systematically assessing the influence of various halogen, alkyl, and aryl substituents on their electronic structure, reactivity, stability, polarizability, dipole moment, geometry, charge distribution, MEP profiles, vibrational characteristics, and NMR signatures, thereby providing a coherent framework for understanding the substituent-controlled properties of divalent silicon species.

Results and Discussion

Structural characteristics of singlet and triplet silylenes

Table 1 summarizes the optimized Si–X bond lengths and X–Si–X bond angles for a series of substituted silylenes in both singlet and triplet electronic states, as obtained from DFT geometry optimizations. The investigated systems include the parent silylene (SiH_2), halogen-substituted derivatives (SiF_2 , SiCl_2 , and SiBr_2), and carbon-based substituents ranging from small alkyl groups to sterically demanding alkyl and aryl ligands. The comparative presentation of singlet and triplet geometrical parameters provides direct insight into the substituent-controlled structural signatures associated with the singlet–triplet electronic dichotomy in divalent silicon species.

Table 1. Optimized Si–X bond lengths and X–Si–X bond angles (Å, degree) for singlet and triplet silylenes calculated at the DFT level

Molecules	Si–X bond length (Å)		X–Si–X bond angle (degree)	
	Singlet state	Triplet state	Singlet state	Triplet state
SiH_2	1.530	1.490	91.208	118.405
SiF_2	1.616	1.620	100.955	116.444
SiCl_2	2.109	2.083	102.221	119.177
SiBr_2	2.263	2.235	103.034	123.074
SiMe_2	1.922	1.914	97.758	118.952
SiEt_2	1.932	1.927	98.608	118.968
$\text{Si}(\text{ipr})_2$	1.939	1.944	99.398	118.382
$\text{Si}(\text{tBu})_2$	1.962	1.968	109.165	123.576
SiPh_2	1.903	1.869	103.100	120.372

Comparison of Si–X bond lengths

The optimized Si–X bond lengths for both singlet and triplet states reveal a pronounced

dependence on the electronic nature and steric demand of the substituents. For SiH_2 , the singlet state exhibits a longer Si–H bond (1.530 Å) compared to the triplet state (1.490 Å),

reflecting the presence of a localized lone pair in the singlet configuration that weakens the $\sigma(\text{Si-H})$ bonds. In the case of halogen-substituted silylenes (SiF_2 , SiCl_2 , and SiBr_2), a gradual increase in Si-X bond length is observed with increasing atomic size of the substituent ($\text{F} < \text{Cl} < \text{Br}$) in both spin states. Notably, for SiCl_2 and SiBr_2 , the Si-X bonds are slightly shorter in the triplet state than in the singlet state, consistent with enhanced σ -bonding and reduced lone-pair repulsion in the triplet configuration. For alkyl-substituted silylenes (SiMe_2 , SiEt_2 , $\text{Si}(i\text{Pr})_2$, and $\text{Si}(t\text{Bu})_2$), the Si-C bond lengths increase moderately with increasing substituent bulk. In most cases, the triplet state exhibits marginally longer Si-C bonds than the singlet state, particularly for sterically demanding groups such as $i\text{Pr}$ and $t\text{Bu}$. This trend suggests that steric congestion in the triplet state partially counteracts the bond-shortening effect expected from increased radical character. Interestingly, SiPh_2 displays a shorter Si-C bond length in the triplet state compared to the singlet state, which can be attributed to π -interactions between the phenyl rings and the silicon center, leading to partial delocalization of unpaired electrons in the triplet configuration.

Comparison of X-Si-X bond angles

A clear and systematic difference is observed between the X-Si-X bond angles of singlet and triplet silylenes. For all investigated systems, the singlet states adopt significantly more acute bond angles than their corresponding triplet states. In SiH_2 , the singlet X-Si-X angle is close to 90° (91.2°), characteristic of a bent geometry stabilized by an sp^2 -like lone pair on silicon, whereas the triplet state exhibits a much more open angle (118.4°), approaching a diradical configuration.

A similar trend is found for halogenated silylenes, where the singlet bond angles gradually increase from SiF_2 to SiBr_2 , reflecting reduced electronegativity and increased steric repulsion of heavier halogens. Nevertheless, in all cases, the triplet geometries display

substantially larger bond angles (≈ 116 – 123°), indicating a transition toward an sp -hybridized silicon center with minimized lone-pair repulsion. For alkyl-substituted silylenes, steric effects become more pronounced. While singlet-state bond angles remain below 100° for smaller alkyl groups (Me , Et , $i\text{Pr}$), a marked increase is observed for $\text{Si}(t\text{Bu})_2$, where the singlet angle reaches 109.2° . This widening reflects significant steric crowding that forces the molecule toward a more open geometry, partially resembling triplet-like characteristics. In all cases, the triplet states maintain consistently large bond angles, typically around 118 – 124° , demonstrating that electronic configuration dominates over substituent effects in determining the overall angular geometry of triplet silylenes. The structural analysis clearly demonstrates that the singlet-triplet electronic configuration is the primary factor governing the geometry of silylenes, while substituent effects modulate these trends through electronic and steric contributions. Singlet silylenes are characterized by shorter X-Si-X angles and bond-length patterns indicative of a localized lone pair, whereas triplet silylenes consistently adopt more open geometries with reduced angular strain. The gradual evolution of both bond lengths and bond angles across different substituents highlights the delicate interplay between lone-pair stabilization, radical character, and steric effects in controlling the structural signatures of divalent silicon species.

Singlet-triplet energetics of substituted silylenes

Table 2 presents the electronic energies corrected for zero-point vibrational energy (ZPE) for both singlet and triplet states of the investigated silylenes, along with the corresponding singlet-triplet energy gaps ($\Delta E_{\text{S-T}}$). These energetic parameters provide a quantitative measure of the relative stability of the two spin states and allow direct assessment of substituent effects on the singlet-triplet balance in divalent silicon species.

Table 2. Electronic energies corrected for zero-point vibrational energy ($E^{\text{elec+ZPE}}$) and singlet–triplet energy gaps ($\Delta E_{\text{S-T}}$) of substituted silylenes (kcal/mol)

Molecules	$E_{\text{S}}^{\text{elec+ZPE}}$ (kcal/mol)	$E_{\text{T}}^{\text{elec+ZPE}}$ (kcal/mol)	$\Delta E_{\text{S-T}}$ (kcal/mol)
SiH ₂	-182356.509	-182336.554	+19.955
SiF ₂	-307011.408	-306935.960	+75.448
SiCl ₂	-759253.670	-759200.724	+52.946
SiBr ₂	-3409241.804	-3409194.537	+47.267
SiMe ₂	-231681.871	-231649.710	+32.161
SiEt ₂	-280981.376	-280958.896	+22.480
Si(<i>i</i> Pr) ₂	-330287.324	-330264.168	+23.156
Si(<i>t</i> Bu) ₂	-379588.957	-379569.127	+19.830
SiPh ₂	-472251.896	-472225.801	+26.095

Definition of energies and formula

The reported energies correspond to the sum of the electronic energy and the zero-point vibrational energy, obtained from harmonic frequency calculations performed at the optimized geometries. The singlet–triplet energy gap was calculated according to the following expression:

$$\Delta E_{\text{S-T}} = E_{\text{T}}^{\text{elec+ZPE}} - E_{\text{S}}^{\text{elec+ZPE}}$$

A positive value of $\Delta E_{\text{S-T}}$ indicates that the singlet state is energetically more stable than the triplet state, whereas a negative value would imply triplet-state stabilization [27].

Comparison of singlet-state energies

The singlet-state energies listed in Table 2 reveal a strong dependence on the nature of the substituents attached to the silicon center. Among the investigated systems, SiF₂ exhibits the most stabilized singlet state, reflected by the largest absolute singlet–triplet energy gap. This pronounced stabilization can be attributed to the strong electron-withdrawing character of fluorine, which enhances lone-pair stabilization at silicon. Halogen-substituted silylenes show a clear trend in singlet stabilization that follows the electronegativity order F > Cl > Br. In contrast, alkyl-substituted silylenes (SiMe₂, SiEt₂, Si(*i*Pr)₂, and Si(*t*Bu)₂) display

comparatively less stabilized singlet states, consistent with the electron-donating nature of alkyl groups, which reduces lone-pair localization at silicon. The phenyl-substituted system, SiPh₂, occupies an intermediate position, reflecting a balance between σ -donation and π -interaction effects.

Comparison of triplet-state energies

The triplet-state energies are consistently higher than the corresponding singlet-state energies for all studied silylenes, indicating that none of the investigated systems exhibits a triplet ground state at the chosen level of theory. The energetic penalty associated with the triplet configuration decreases systematically as the substituents become less electronegative or more sterically demanding.

In particular, alkyl-substituted silylenes show relatively smaller singlet–triplet separations, suggesting partial stabilization of the triplet state through hyperconjugative interactions and steric effects that favor a more open geometry. Nevertheless, even for the most sterically congested system, Si(*t*Bu)₂, the triplet state remains energetically disfavored relative to the singlet state.

Analysis of singlet–triplet energy gaps ($\Delta E_{\text{S-T}}$)

The singlet–triplet energy gaps summarized in Table 2 span a wide range, from approximately 20 to over 75 kcal/mol, underscoring the

decisive role of substituent identity in controlling the electronic structure of silylenes. The largest ΔE_{S-T} value is observed for SiF_2 (+75.4 kcal/mol), highlighting the exceptional stabilization of the singlet state by strongly electronegative substituents. Moderate ΔE_{S-T} values are found for SiCl_2 and SiBr_2 , while alkyl-substituted derivatives exhibit significantly smaller gaps, reflecting increased singlet–triplet competition. The smallest energy separations are obtained for SiH_2 and $\text{Si}(\text{tBu})_2$, indicating that these systems lie closer to the singlet–triplet crossover regime, albeit still favoring singlet ground states. The energetic data presented in Table 2 demonstrate that all investigated silylenes possess singlet ground states, with singlet–triplet separations that are highly sensitive to substituent effects. Electron-withdrawing substituents strongly stabilize the singlet configuration, leading to large ΔE_{S-T} values, whereas electron-donating and sterically demanding groups reduce the singlet–triplet gap and partially stabilize the triplet state. These results establish a clear energetic framework that directly correlates substituent identity with the singlet–triplet landscape of divalent silicon species, providing a critical foundation for the subsequent electronic structure and bonding analyses.

Electric properties and polarizability features of singlet and triplet silylenes

Table 3 summarizes the calculated dipole moments, isotropic polarizabilities (α_{iso}), and

polarizability anisotropies (α_{aniso}) for the investigated silylenes in both singlet and triplet electronic states. These properties provide insight into charge separation, electronic flexibility, and the extent of anisotropic electron distribution induced by substituent effects and spin-state changes.

Comparison of dipole moments

The dipole moments reported in Table 3 exhibit a strong dependence on both the electronic state and the nature of the substituents. In most cases, the singlet states display larger dipole moments than the corresponding triplet states, reflecting enhanced charge separation associated with a localized lone pair at the silicon center.

For the parent silylene SiH_2 , the dipole moment is small in both spin states, approaching zero in the triplet configuration due to its more symmetric geometry. Halogen-substituted silylenes show increased dipole moments, with SiCl_2 exhibiting the largest value among the halogen series in the singlet state.

Alkyl- and aryl-substituted silylenes display relatively large singlet-state dipole moments, with SiPh_2 showing the highest dipole moment of the series. The pronounced dipole in SiPh_2 can be attributed to asymmetric charge delocalization involving σ - and π -interactions between the phenyl rings and the silicon center. Across all systems, the systematic reduction of dipole moments upon singlet–triplet excitation highlights the diminished charge localization in the triplet state.

Table 3. Calculated dipole moments (Debye), isotropic polarizabilities (α_{iso} , Å³), and polarizability anisotropies (α_{aniso} , Å³) of singlet and triplet silylenes

Molecules	Dipole moment (Debye)		α_{iso} (Å ³)		α_{aniso} (Å ³)	
	Singlet state	Triplet state	Singlet state	Triplet state	Singlet state	Triplet state
SiH_2	0.439	0.004	3.696	3.212	1.080	1.042
SiF_2	0.981	1.516	3.516	2.930	0.656	0.578
SiCl_2	1.388	1.071	6.664	6.254	3.982	4.514
SiBr_2	0.909	0.512	8.918	8.638	5.824	6.922
SiMe_2	1.484	0.853	7.406	6.901	1.861	2.619
SiEt_2	1.512	0.926	10.683	10.515	2.282	3.811
$\text{Si}(\text{ipr})_2$	1.515	0.957	14.015	14.043	4.406	6.000
$\text{Si}(\text{tBu})_2$	1.409	0.864	17.195	17.423	5.077	6.683
SiPh_2	2.103	0.735	23.395	24.006	20.294	24.310

Comparison of isotropic polarizabilities (α_{iso})

The isotropic polarizability (α_{iso}) was calculated as the average of the diagonal components of the polarizability tensor, while the polarizability anisotropy (α_{aniso}) [28] was derived from the differences between these tensor components according to the standard definitions shown below.

$$\alpha_{\text{iso}} = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\alpha_{\text{aniso}} = \sqrt{\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{2}}$$

The isotropic polarizability values increase markedly with increasing substituent size and electronic softness. Small substituents such as hydrogen and fluorine yield the lowest α_{iso} values, whereas bulky alkyl and aryl groups lead to substantial enhancement of molecular polarizability.

In general, α_{iso} values are comparable for singlet and triplet states, with only minor differences observed upon spin-state change. Notably, SiPh₂ exhibits the largest α_{iso} values in both spin states, reflecting the highly polarizable π -electron system of the phenyl rings. These trends indicate that isotropic polarizability is predominantly governed by substituent identity rather than electronic spin configuration.

Comparison of polarizability anisotropies (α_{aniso})

The polarizability anisotropy values reported in Table 3 reveal more pronounced differences

between singlet and triplet states than those observed for α_{iso} . In most cases, triplet silylenes display larger α_{aniso} values, indicating increased anisotropy in electron distribution associated with more open geometries and diradical character.

This effect is particularly evident for bulky alkyl- and aryl-substituted systems, such as Si(*t*Bu)₂ and SiPh₂, where steric effects and extended substituent frameworks amplify directional electronic response. The significantly larger α_{aniso} values observed for SiPh₂ highlight the role of conjugated π -systems in enhancing anisotropic polarizability. The electric properties summarized in Table 3 demonstrate that dipole moments are primarily sensitive to spin-state-dependent charge localization, whereas isotropic polarizability is dominated by substituent size and electronic softness. In contrast, polarizability anisotropy serves as a sensitive descriptor of geometric distortion and diradical character in triplet silylenes. Together, these results underscore the complementary roles of dipole moments and polarizability components in capturing the substituent- and spin-state-dependent electronic signatures of divalent silicon species.

Charge distribution and Si-X bond polarity in singlet and triplet silylenes

Table 4 summarizes the Mulliken atomic charges on the silicon atom (q_{Si}) and on the directly bonded substituent atom (q_{X}), together with the resulting Si-X bond polarity ($\Delta q_{\text{Si-X}}$), for a series of substituted silylenes in both singlet and triplet electronic states.

Table 4. Mulliken charge distribution and Si-X bond polarity ($\Delta q_{\text{Si-X}}$) in singlet and triplet silylenes

Molecules	q_{Si}		q_{X}		$\Delta q_{\text{Si-X}}$	
	Singlet state	Triplet state	Singlet state	Triplet state	Singlet state	Triplet state
SiH ₂	+0.232	+0.082	-0.116	-0.041	0.348	0.123
SiF ₂	+0.732	+0.682	-0.366	-0.341	1.098	1.023
SiCl ₂	+0.494	+0.347	-0.247	-0.174	0.741	0.521
SiBr ₂	+0.485	+0.321	-0.243	-0.161	0.728	0.482
SiMe ₂	+0.406	+0.233	-0.567	-0.517	0.973	0.750
SiEt ₂	+0.394	+0.211	-0.408	-0.372	0.802	0.583
Si(<i>i</i> pr) ₂	+0.381	+0.199	-0.270	-0.235	0.651	0.434
Si(<i>t</i> Bu) ₂	+0.376	+0.194	-0.162	-0.123	0.538	0.317
SiPh ₂	+0.240	+0.150	-0.135	-0.077	0.375	0.227

Here, X corresponds to hydrogen in SiH_2 , halogen atoms in halogen-substituted silylenes, and carbon atoms in alkyl- and phenyl-substituted derivatives.

Comparison of silicon atomic charges (q_{Si})

The Mulliken charges on the silicon atom reveal systematic variations depending on both substituent identity and spin state. In all investigated systems, the silicon center carries a positive partial charge, reflecting the electron-deficient nature of divalent silicon.

For halogen-substituted silylenes, the silicon atom exhibits significantly larger positive charges, with SiF_2 showing the highest q_{Si} values due to the strong electron-withdrawing character of fluorine. In contrast, alkyl- and phenyl-substituted silylenes display substantially lower q_{Si} values, consistent with σ -donating and hyperconjugative effects of carbon-based substituents. Across the entire series, the singlet states show consistently higher positive charges on silicon than the corresponding triplet states, indicating stronger charge localization associated with the lone-pair-bearing singlet configuration.

Comparison of substituent atomic charges (q_{X})

The charges on the atoms directly bonded to silicon exhibit trends complementary to those observed for q_{Si} . In halogenated silylenes, the halogen atoms carry pronounced negative charges, which increase in magnitude with increasing electronegativity, reaching a maximum for fluorine.

For alkyl- and phenyl-substituted systems, the carbon atoms bonded to silicon also bear negative charges, although with smaller magnitudes compared to halogens. These reduced negative charges reflect the weaker electronegativity difference between silicon and carbon and the partial delocalization of electron density through σ - and π -interactions. Similar to q_{Si} , the magnitude of q_{X} is generally larger in the singlet state than in the triplet state, indicating enhanced bond polarization in the singlet configuration.

Comparison of Si–X bond polarity ($\Delta q_{\text{Si-X}}$)

The Si–X bond polarity, quantified as $\Delta q_{\text{Si-X}}$, provides a direct measure of charge separation along the Si–X bond. As shown in Table 4, halogen-substituted silylenes exhibit the largest bond polarities, with SiF_2 displaying the highest $\Delta q_{\text{Si-X}}$ values, in line with its strong ionic character.

In contrast, alkyl- and phenyl-substituted silylenes show markedly lower bond polarities, reflecting more covalent Si–C bonding. In all cases, $\Delta q_{\text{Si-X}}$ values are systematically larger for singlet states than for triplet states, highlighting the greater degree of charge separation associated with the localized lone pair in singlet silylenes. The Mulliken charge analysis presented in Table 4 demonstrates that both substituent electronegativity and electronic spin state play key roles in shaping the charge distribution and bond polarity in silylenes. Singlet states consistently exhibit stronger charge localization on the silicon center and higher Si–X bond polarity, whereas triplet states show reduced polarization and more delocalized electron density. These trends provide a clear electronic rationale for the observed differences in singlet–triplet energetics and electric response properties, reinforcing the substituent-controlled nature of the singlet–triplet signatures in divalent silicon species.

Frontier molecular orbital analysis and global reactivity descriptors of singlet and triplet silylenes

Figure 1 illustrates the spatial distributions of the highest occupied molecular orbitals (HOMO) for all investigated silylenes in both singlet and triplet electronic states.

In the singlet state, the HOMO is mainly localized on the silicon center and corresponds to the nonbonding lone pair, whereas the LUMO is predominantly associated with the vacant p-orbital of silicon, indicating pronounced ambiphilic character. In contrast, the triplet state exhibits a different orbital topology, where the frontier orbitals are more delocalized and reflect the presence of two unpaired electrons with reduced donor–acceptor differentiation. Substituent effects strongly influence the extent

of orbital delocalization, particularly in alkyl- and phenyl-substituted silylenes.

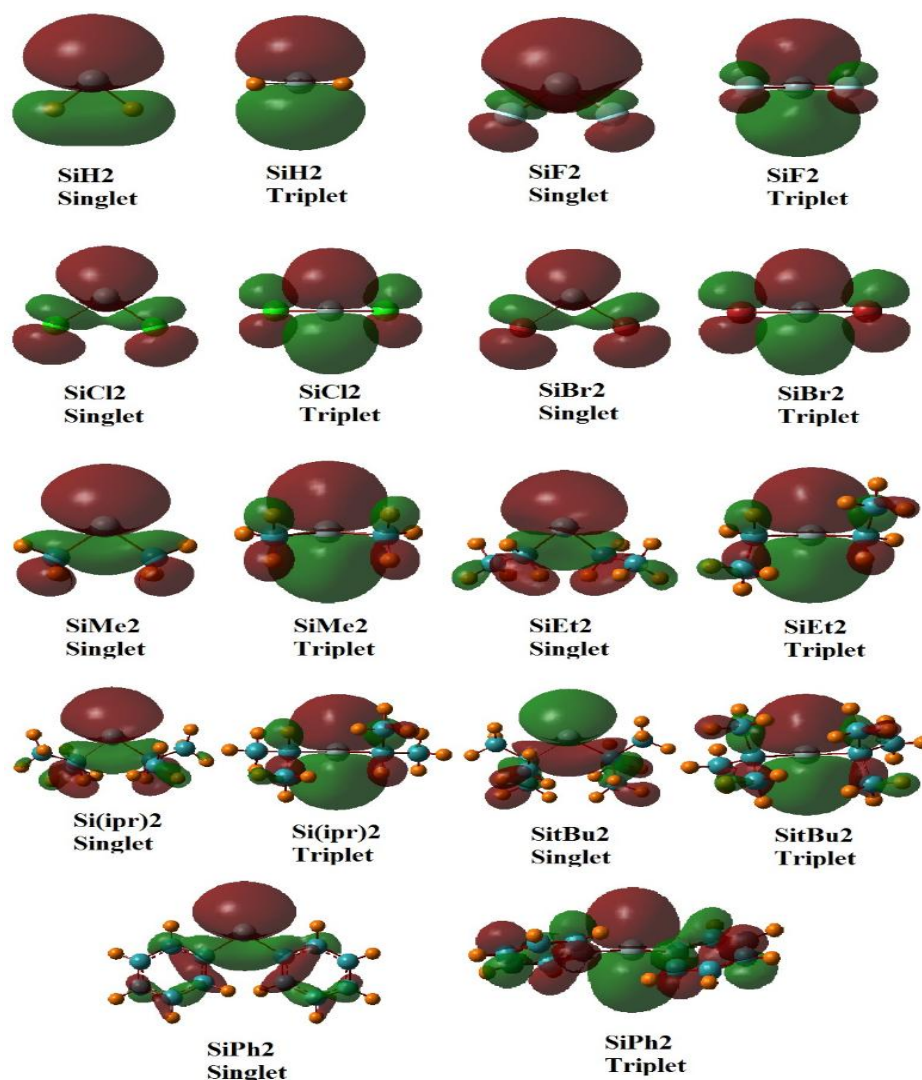


Figure 1. The highest occupied molecular orbitals for all investigated silylenes

Table 5 summarizes the frontier molecular orbital energies and the global reactivity descriptors [29] of the studied silylenes in both singlet and triplet (α form) electronic states, derived within the framework of CDFT.

The global reactivity descriptors were calculated within the framework of CDFT using the frontier molecular orbital energies. The IP and EA were approximated as $IP = -E_{HOMO}$ and $EA = -E_{LUMO}$, respectively. The energy gap was obtained as $\Delta E = E_{LUMO} - E_{HOMO}$. The electronegativity (χ), chemical potential (μ), chemical hardness (η), chemical softness (S), electrophilicity index (ω),

and maximum charge transfer (ΔN_{max}) were evaluated using the following standard relations:

$$IP = -E_{HOMO}$$

$$EA = -E_{LUMO}$$

$$\Delta E = E_{LUMO} - E_{HOMO}$$

$$\chi = \frac{-(E_{LUMO} + E_{HOMO})}{2}$$

$$\mu = \frac{(E_{LUMO} + E_{HOMO})}{2}$$

$$\eta = \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2}$$

$$S = \frac{1}{\eta}$$

$$\omega = \frac{\mu^2}{2\eta}$$

$$\Delta N_{\text{Max}} = \frac{-\mu}{\eta}$$

Table 5. Frontier orbital energies and global reactivity descriptors of singlet and triplet silylenes

SiR ₂	Singlet state										
	HOMO	LUMO	IP	EA	ΔE	χ	μ	η	S	ω	ΔN _{max}
SiH ₂	-0.242	-0.119	0.242	0.119	0.123	0.180	-0.180	0.062	16.129	0.261	2.903
SiF ₂	-0.291	-0.078	0.291	0.078	0.213	0.184	-0.184	0.106	9.434	0.160	1.736
SiCl ₂	-0.284	-0.119	0.284	0.119	0.165	0.202	-0.202	0.083	12.048	0.246	2.434
SiBr ₂	-0.267	-0.117	0.267	0.117	0.150	0.192	-0.192	0.075	13.333	0.246	2.560
SiMe ₂	-0.206	-0.082	0.206	0.082	0.124	0.144	-0.144	0.062	16.129	0.167	2.322
SiEt ₂	-0.202	-0.080	0.202	0.080	0.122	0.141	-0.141	0.061	16.393	0.163	2.311
Si(iPr) ₂	-0.200	-0.077	0.200	0.077	0.123	0.138	-0.138	0.062	16.129	0.154	2.226
Si(tBu) ₂	-0.194	-0.077	0.194	0.077	0.117	0.136	-0.136	0.058	17.241	0.159	2.345
SiPh ₂	-0.205	-0.088	0.205	0.088	0.117	0.146	-0.146	0.058	17.241	0.184	2.517
SiR ₂	Triplet state (α form)										
	HOMO	LUMO	IP	EA	ΔE	χ	μ	η	S	ω	ΔN _{max}
SiH ₂	-0.196	0.041	0.196	-0.041	0.237	0.078	-0.078	0.118	8.474	0.026	0.661
SiF ₂	-0.166	0.012	0.166	-0.012	0.178	0.077	-0.077	0.089	11.236	0.033	0.865
SiCl ₂	-0.189	-0.037	0.189	0.037	0.152	0.113	-0.113	0.076	13.158	0.042	1.487
SiBr ₂	-0.182	-0.048	0.182	0.048	0.134	0.115	-0.115	0.067	14.925	0.099	1.716
SiMe ₂	-0.153	0.053	0.153	-0.053	0.206	0.050	-0.050	0.103	9.709	0.012	0.485
SiEt ₂	-0.154	0.049	0.154	-0.049	0.203	0.052	-0.052	0.102	9.804	0.013	0.510
Si(iPr) ₂	-0.152	0.051	0.152	-0.051	0.203	0.050	-0.050	0.102	9.804	0.012	0.490
Si(tBu) ₂	-0.151	0.038	0.151	-0.038	0.189	0.056	-0.056	0.094	10.638	0.017	0.596
SiPh ₂	-0.153	-0.019	0.153	0.019	0.134	0.086	-0.086	0.067	14.925	0.055	1.284

Comparison of frontier orbital energies (HOMO, LUMO, ΔE)

The HOMO energies of singlet silylenes are consistently lower than those of their triplet counterparts, reflecting increased electronic stabilization in the closed-shell configuration. The LUMO energies in singlet species remain negative for most compounds, whereas positive or near-zero LUMO values are observed in triplet states, indicating reduced electron-accepting ability. Consequently, the HOMO–LUMO energy gap (ΔE) is generally smaller in singlet silylenes, suggesting enhanced chemical reactivity compared to the triplet analogues.

IP and EA

Singlet silylenes exhibit higher IP and positive electron affinities, highlighting their balanced donor–acceptor nature. In contrast, triplet species show reduced IP values and frequently negative EA values, indicating weaker electron-accepting capability and diminished

electrophilic behavior. Substituent effects are evident, with electronegative halogens increasing IP and EA relative to alkyl- and aryl-substituted systems.

Electronegativity (χ) and Chemical Potential (μ)

Electronegativity values are systematically higher for singlet states, while the corresponding chemical potentials are more negative, reflecting greater thermodynamic stability. Triplet silylenes display lower electronegativity and less negative chemical potentials, consistent with their higher-energy, more reactive electronic structures.

Chemical hardness (η) and softness (S)

Singlet silylenes are characterized by lower hardness and higher softness values, indicating increased polarizability and reactivity. In contrast, triplet states show enhanced hardness and reduced softness, suggesting greater

resistance to charge transfer processes. Bulky substituents tend to decrease hardness and increase softness, particularly in the singlet state.

Electrophilicity Index (ω) and $\Delta N_{\max}$

The electrophilicity index is markedly higher for singlet silylenes, confirming their stronger electrophilic character. Correspondingly, $\Delta N_{\max}$ values indicate a higher capacity for charge acceptance in singlet species. Triplet silylenes exhibit significantly lower ω and $\Delta N_{\max}$ values, reflecting diminished electrophilic behavior. frontier molecular orbital analysis and global reactivity descriptors consistently demonstrate that singlet silylenes possess enhanced ambiphilicity, lower HOMO–LUMO gaps, higher electrophilicity, and greater charge-transfer capability compared to their triplet counterparts. These electronic features rationalize the higher chemical reactivity and stabilization of singlet silylenes and underline the critical role of substituent effects in modulating their electronic structure and reactivity.

MEP analysis of singlet and triplet silylenes

The MEP is a powerful tool for visualizing the charge distribution over a molecule and for identifying regions susceptible to electrophilic and nucleophilic attacks. The MEP surface maps the electrostatic potential generated by the nuclei and electron density onto an electron density isosurface, where negative regions (typically shown in red) correspond to electron-rich sites, and positive regions (blue) indicate electron-deficient areas [30].

Figure 2 presents the MEP surfaces of all investigated silylenes in both singlet and triplet electronic states, providing direct insight into substituent- and spin-state-dependent electronic features.

In singlet silylenes, a pronounced negative electrostatic potential is predominantly localized above the silicon center, corresponding to the nonbonding lone pair. Simultaneously, positive potential regions are observed along the Si–X bonding directions, reflecting the electrophilic character associated with the vacant p-orbital on silicon. This clear separation of nucleophilic and electrophilic regions highlights the strong ambiphilic nature of singlet silylenes.

In contrast, the triplet state exhibits a markedly different MEP pattern. The negative potential is more diffuse and less localized on the silicon center, while positive regions become less intense and more evenly distributed. This redistribution is consistent with the presence of two unpaired electrons and reduced donor–acceptor differentiation in the triplet configuration. Substituent effects are clearly evident across the series. Electronegative halogen substituents intensify the positive electrostatic potential around the silicon center, whereas alkyl and phenyl substituents promote charge delocalization, leading to broader and less localized potential regions. Bulky substituents further modulate the MEP by steric shielding of reactive sites, particularly in the singlet state. Overall, MEP analysis confirms that singlet silylenes possess a highly polarized electronic structure with well-defined electrophilic and nucleophilic regions, underpinning their enhanced reactivity and ambiphilic behavior. In contrast, triplet silylenes display more diffuse electrostatic potential distributions, consistent with their reduced polarity and lower electrophilicity. These findings complement the charge distribution, polarizability, and global reactivity analyses, collectively reinforcing the substituent-controlled modulation of singlet–triplet electronic signatures in silylenes.

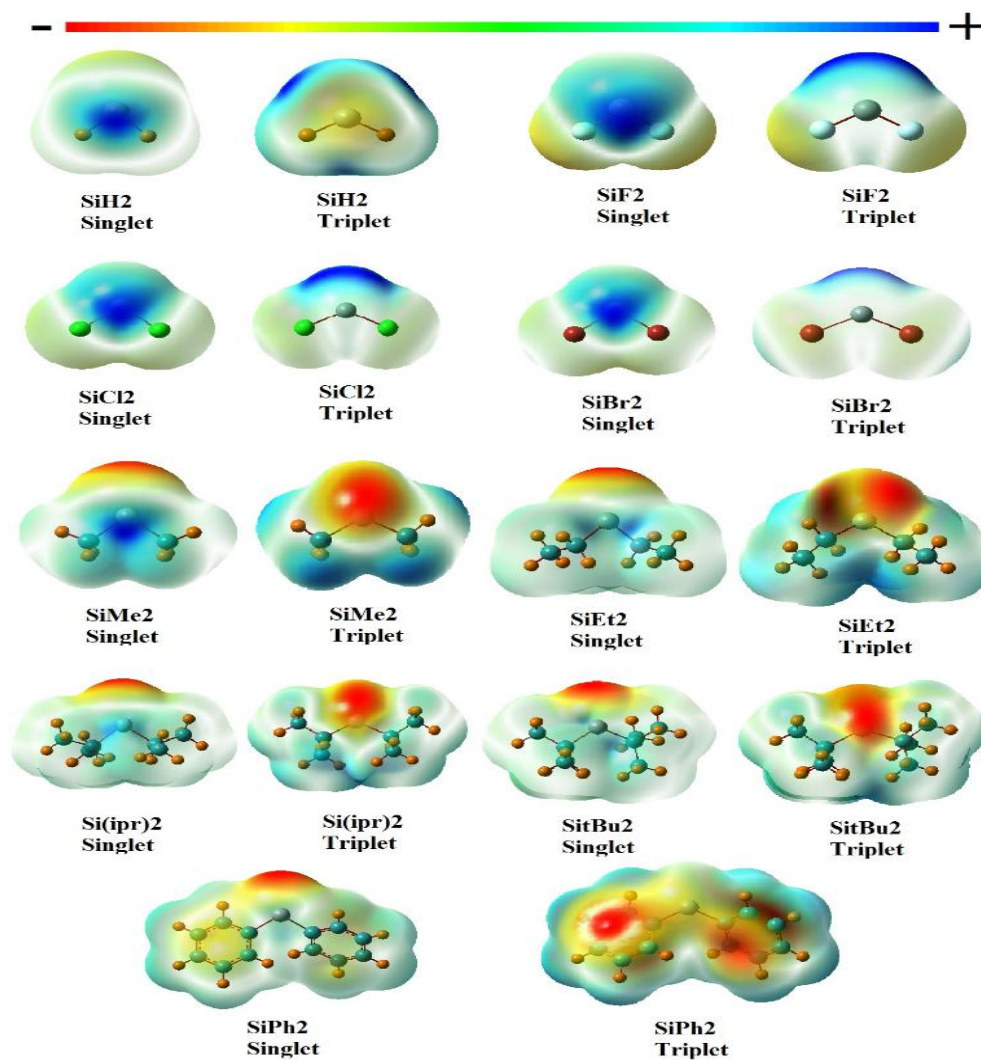


Figure 2. MEP maps of singlet and triplet silylenes

Computed ^{29}Si NMR shielding and chemical shift analysis of singlet and triplet silylenes

Table 6 reports the calculated isotropic ^{29}Si nuclear magnetic shielding constants and the corresponding chemical shifts for all investigated silylenes in both singlet and triplet electronic states. The NMR parameters were computed using the GIAO method, and the chemical shifts were referenced to tetramethylsilane (TMS).

Singlet state

In the singlet silylenes, the ^{29}Si shielding constants exhibit strongly negative values for alkyl- and phenyl-substituted systems, leading

to very large downfield chemical shifts. This pronounced deshielding reflects the presence of a silicon-centered lone pair and a vacant p-orbital, resulting in a highly anisotropic and polarized electronic environment around the silicon nucleus. Among the series, alkyl-substituted silylenes display particularly high chemical shifts, indicating enhanced electron donation toward silicon and increased sensitivity of the silicon nucleus to substituent effects.

Halogen-substituted silylenes show a systematic trend, where increasing halogen size leads to reduced shielding and progressively larger chemical shifts, consistent with increasing σ -withdrawing and π -donating interactions that modulate the electron density at silicon.

Table 6. Calculated ^{29}Si NMR shielding constants and chemical shifts of singlet and triplet silylenes (reference: TMS)

Molecules	Singlet state		Triplet state	
	^{29}Si Shielding (ppm)	^{29}Si Chemical shift (ppm)	^{29}Si Shielding (ppm)	^{29}Si Chemical shift (ppm)
SiH_2	-387.63	800.20	489.92	-77.34
SiF_2	379.92	32.66	251.78	160.80
SiCl_2	122.20	290.38	261.18	151.40
SiBr_2	32.50	380.08	237.50	175.08
SiMe_2	-352.32	764.90	408.21	4.37
SiEt_2	-301.44	714.02	369.66	42.92
$\text{Si}(\text{ipr})_2$	-289.44	702.02	356.22	56.36
$\text{Si}(\text{tBu})_2$	-303.70	716.28	332.20	80.38
SiPh_2	-139.52	552.10	374.89	37.69

Triplet state

In contrast, the triplet silylenes exhibit substantially higher shielding constants and markedly lower chemical shift values. This trend is consistent with the redistribution of electron density in the open-shell configuration, where the absence of a localized lone pair reduces deshielding at the silicon center. The chemical shifts in the triplet state are clustered within a narrower range, indicating diminished substituent sensitivity relative to the singlet state.

Notably, the dramatic singlet–triplet differences in both shielding and chemical shift values highlight the strong dependence of the ^{29}Si NMR response on the electronic spin state. The computed ^{29}Si NMR parameters clearly distinguish between singlet and triplet silylenes. Singlet species exhibit extreme deshielding and large downfield chemical shifts due to their highly polarized and ambiphilic electronic structures, whereas triplet species are significantly more shielded, reflecting a more delocalized and less anisotropic electron distribution. These findings provide a direct spectroscopic signature of singlet–triplet differentiation in silylenes and complement the trends observed in charge distribution, frontier orbital, and MEP analyses.

NBO analysis of silicon hybridization and donor–acceptor interactions in silylenes

Table 7 presents the results of the NBO analysis [31] for the investigated silylenes in both singlet and triplet electronic states. The table summarizes the hybridization of the silicon atom in the Si–X bonds, the hybridization character of the silicon lone pair (LP) in the singlet state, and the stabilization energies associated with $\sigma(\text{Si-X})_1 \rightarrow \sigma^*(\text{Si-X})_2$ donor–acceptor interactions.

Analysis of Si–X bond hybridization

In the singlet state, the Si–X bonds exhibit pronounced sp^nd^m hybridization with significant p-character and measurable d-orbital contributions. This reflects strong angular flexibility and deviation from idealized sp^2 hybridization, consistent with the experimentally observed bent geometries of singlet silylenes. The extent of p- and d-character increases with more electronegative or heavier substituents, indicating enhanced polarization and orbital mixing.

In contrast, the triplet state displays Si–X bonds with near-pure sp hybridization and negligible d-character, suggesting a more linear bonding framework dominated by p-orbital participation. This difference directly reflects the fundamental electronic reorganization upon singlet–triplet excitation.

Analysis of lone pair hybridization

The silicon lone pair in singlet silylenes shows low sp hybridization indices, indicating a predominantly p -type character. This finding is consistent with the presence of a stereochemically active lone pair oriented perpendicular to the Si-X plane. The gradual increase in p -character from halogen- to alkyl-

and aryl-substituted systems reflects increasing electron donation toward the silicon center and enhanced lone-pair delocalization.

As expected, no corresponding lone pair is defined for triplet silylenes, further emphasizing the distinct electronic nature of the two spin states.

Table 7. NBO-derived silicon hybridization and $\sigma(\text{Si-X})_1 \rightarrow \sigma^*(\text{Si-X})_2$ stabilization energies in singlet and triplet silylenes

Molecules	Si hybridization in Si-X		Si hybridization (LP)	$\sigma(\text{Si-X})_1 \rightarrow \sigma^*(\text{Si-X})_2$ Stabilization energy (kcal/mol)	
	Singlet state	Triplet state		Singlet state	Triplet state
SiH ₂	$sp^{7.37}d^{0.1}$	$sp^{1.08}d^{0.02}$	$sp^{0.29}$	1.02	5.65
SiF ₂	$sp^{9.12}d^{0.23}$	$sp^{1.03}d^{0.02}$	$sp^{0.17}$	3.01	3.75
SiCl ₂	$sp^{10.94}d^{0.32}$	$sp^{1.04}d^{0.03}$	$sp^{0.14}$	1.59	4.27
SiBr ₂	$sp^{12.54}d^{0.24}$	$sp^{1.03}d^{0.02}$	$sp^{0.13}$	1.11	4.50
SiMe ₂	$sp^{6.75}d^{0.1}$	$sp^{1.03}d^{0.02}$	$sp^{0.31}$	1.68	6.24
SiEt ₂	$sp^{6.9}d^{0.1}$	$sp^{1.01}d^{0.02}$	$sp^{0.32}$	1.72	6.92
Si(<i>i</i> pr) ₂	$sp^{7.07}d^{0.11}$	$sp^{1.01}d^{0.02}$	$sp^{0.31}$	1.83	7.89
Si(<i>t</i> Bu) ₂	$sp^{6.88}d^{0.11}$	$sp^{0.02}$	$sp^{0.32}$	3.28	9.28
SiPh ₂	$sp^{6.07}d^{0.11}$	$sp^{1.02}d^{0.02}$	$sp^{0.36}$	2.57	5.62

Analysis of $\sigma(\text{Si-X})_1 \rightarrow \sigma^*(\text{Si-X})_2$ stabilization energies

The $\sigma(\text{Si-X})_1 \rightarrow \sigma^*(\text{Si-X})_2$ stabilization energies are consistently larger in the triplet state compared to the singlet state, indicating stronger hyperconjugative interactions in the open-shell configuration. These interactions increase notably with bulkier alkyl substituents, reflecting enhanced σ -donation and greater orbital overlap. The comparatively lower stabilization energies in singlet silylenes suggest that the localized lone pair reduces the extent of σ - σ^* delocalization. NBO analysis reveals that singlet silylenes are characterized by bent geometries, strongly polarized Si-X bonds, and a localized p -type lone pair, whereas triplet silylenes exhibit near-linear bonding with enhanced σ - σ^* delocalization. The observed trends in hybridization and stabilization energies provide a clear orbital-level explanation for the structural, energetic, and spectroscopic differences between singlet and

triplet silylenes, reinforcing the substituent-controlled nature of their electronic behavior

Conclusion

A comprehensive DFT investigation of substituted silylenes has revealed that their electronic structure, stability, and reactivity are strongly governed by both substituent effects and spin state. All studied systems exhibit a clear energetic preference for the singlet state, with singlet-triplet gaps significantly modulated by the electronic and steric nature of the substituents. Singlet silylenes display bent geometries, localized silicon-centered lone pairs, strong charge polarization, and pronounced ambiphilic character, as evidenced by MEP, NBO, and ²⁹Si NMR analyses. In contrast, triplet silylenes are characterized by more linear bonding, enhanced σ - σ^* delocalization, reduced polarity, and narrower spectroscopic signatures. The strong correlations observed among structural parameters, frontier orbital energies,

global reactivity indices, and electrostatic potential distributions provide a unified picture of substituent-controlled singlet-triplet behavior. These findings not only deepen the fundamental understanding of divalent silicon chemistry but also offer practical spectroscopic and electronic descriptors for differentiating silylene spin states, thereby facilitating their rational design and experimental characterization.

ORCID

Mehdi Nabati

<https://orcid.org/0000-0002-3353-0628>

Reference

- [1] Panayides, J.L., Riley, D.L., Hasenmaile, F., Van Otterlo, W.A. **The role of silicon in drug discovery: A review.** *RSC Medicinal Chemistry*, **2024**, 15(10), 3286-3344.
- [2] Tamao, K. **Discovery and synthetic applications of novel silicon-carbon bond cleavage reactions based on the coordination number change of organosilicon compounds.** *Proceedings of the Japan Academy, Series B*, **2008**, 84(5), 123-133.
- [3] Soltani, S., Sardari, S., Soror, S.A. **Computer simulation of a novel pharmaceutical silicon nanocarrier.** *Nanotechnology, Science and Applications*, **2010**, 149-157.
- [4] Hübler, K., Hunt, P.A., Maddock, S.M., Rickard, C.E., Roper, W.R., Salter, D.M., Wright, L.J. **Examination of metal-silicon bonding through structural and theoretical studies of an isostructural set of Five-coordinate silyl complexes, Os (SiR₃) Cl (CO)(PPh₃)₂ (R= F, Cl, OH, Me).** *Organometallics*, **1997**, 16(23), 5076-5083.
- [5] Mao, J., Chen, M., Zhong, Y., Song, R.J. **Recent developments in difunctionalization of unsaturated hydrocarbons with organosilicon reagents.** *Organic & Biomolecular Chemistry*, **2025**, 23(1), 59-77.
- [6] Qiao, Z., Cao, F., Chen, M., Zhong, Q., Liu, J., Li, G., Mo, Z. **Isolation and reactivity of a silylene-stabilized borasilylidene.** *Journal of the American Chemical Society*, **2025**, 147(49), 44708-44713.
- [7] Creary, X. **3-Trimethylsilylcyclobutylidene. The γ -effect of silicon on carbenes.** *Journal of the American Chemical Society*, **2013**, 135(17), 6570-6578.
- [8] Heinemann, C., Müller, T., Apeloig, Y., Schwarz, H. **On the question of stability, conjugation, and "aromaticity" in imidazol-2-ylidenes and their silicon analogs.** *Journal of the American Chemical Society*, **1996**, 118(8), 2023-2038.
- [9] Mizuhata, Y., Sasamori, T., Tokitoh, N.J. **Stable heavier carbene analogues.** *Chemical Reviews*, **2009**, 109(8), 3479-3511.
- [10] Jagannathan, J.R., Fettingner, J.C., Shaw, J.T., Franz, A.K. **Enantioselective Si-H insertion reactions of diarylcarbenes for the synthesis of silicon-stereogenic silanes.** *Journal of the American Chemical Society*, **2020**, 142(27), 11674-11679.
- [11] Roy, S., Dittrich, B., Mondal, T., Koley, D., Stückl, A.C., Schwederski, B., Linser, R., Roesky, H.W. **Carbene supported dimer of heavier ketenimine analogue with p and si atoms.** *Journal of the American Chemical Society*, **2015**, 137(19), 6180-6183.
- [12] Sun, J., Ou, C., Wang, C., Uchiyama, M., Deng, L. **Silane-functionalized n-heterocyclic carbene-cobalt complexes containing a five-coordinate silicon with a covalent Co-Si bond.** *Organometallics*, **2015**, 34(8), 1546-1551.
- [13] Mohapatra, C., Samuel, P.P., Li, B., Niepötter, B., Schürmann, C.J., Herbst-Irmer, R., Roesky, H.W. **Insertion of cyclic alkyl (amino) carbene into the Si-H bonds of hydrochlorosilanes.** *Inorganic Chemistry*, **2016**, 55(5), 1953-1955.
- [14] Bag, P., Ahmad, S.U., Inoue, S. **Synthesis and reactivity of functionalized silicon (II) compounds: iminosilylene, phosphinosilylene, hydrosilylene, and related compounds.** *Bulletin of the Chemical Society of Japan*, **2017**, 90(3), 255-271.
- [15] Mondal, K.C., Roy, S., Dittrich, B., Andrada, D.M., Frenking, G., Roesky, H.W. **A triatomic silicon (0) cluster stabilized by a cyclic alkyl (amino) carbene.** *Angewandte Chemie International Edition*, **2016**, 55(9), 3158-3161.
- [16] Hayakawa, N., Sadamori, K., Mizutani, S., Agou, T., Sugahara, T., Sasamori, T., Matsuo, T. **Synthesis and characterization of N-heterocyclic carbene-coordinated silicon compounds bearing a fused-ring bulky end group.** *Inorganics*, **2018**, 6(1), 30.
- [17] Mai, V.H., Korobkov, I., Nikonov, G.I. **Half-sandwich silane σ -complexes of ruthenium supported by NHC carbene.** *Organometallics*, **2016**, 35(7), 936-942.
- [18] Schneider, H., Schmidt, D., Radius, U. **A Facile route to backbone-tethered N-heterocyclic carbene (NHC) ligands via nhc to anhc rearrangement in NHC silicon halide adducts.** *Chemistry-A European Journal*, **2015**, 21(7), 2793-2797.
- [19] Hendi, Z., Pandey, M.K., Kushvaha, S.K., Roesky, H.W. **Recent progress in transition metal complexes featuring silylene as ligands.** *Chemical Communications*, **2024**, 60(71), 9483-9512.
- [20] Nabati, M., Pournamdari, E., Bodaghi-Namileh, V., Dashti-Rahmatabadi, Y., Sarshar, S. **Substitution of**

Carbonyl Group of Ellagic Acid with Silanediol Group for Better Inhibition of VEGFR-2 Kinase Enzyme, *Advanced Journal of Chemistry, Section B: Natural Products and Medical Chemistry*, **2020**, 2(2), 64-72.

[21] Nabati, M., Bodaghi-Namileh, V. Design of novel tazarotene derivatives as potential antipsoriatic drugs: physicochemical properties study and molecular docking analysis of their binding to retinoic acid receptor family (RAR- α , RAR- β and RAR- γ), *Journal of Medicinal and Chemical Sciences*, **2020**, 3(2), 162-175.

[22] Haaf, M., Schmedake, T.A., West, R. Stable silylenes. *Accounts of Chemical Research*, **2000**, 33(10), 704-714.

[23] Nabati, M., Sabahnou, H., Bodaghi-Namileh, V. Molecular structure determination and stability parameters study of ^{99m}Tc -MDP (technetium ^{99m} methylene diphosphonate) cold kit and analysis of its binding to osteocalcin receptor as a bone scan agent, *Chemical Methodologies*, **2020**, 4(3), 297-310.

[24] Nabati, M., Bodaghi-Namileh, V. Evaluation of Medicinal Effects of Isoxazole Ring Isosteres on Zonisamide for Autism Treatment by Binding to Potassium Voltage-Gated Channel Subfamily D Member 2 (Kv 4.2), *Advanced Journal of Chemistry, Section A*, **2020**, 3(4), 462-472.

[25] M. J. ea Frisch, G. W. Trucks, H. Bernhard Schlegel, G. E. Scuseria, M. An Robb, J. R. Cheeseman,

G. Scalmani, V. P. G. A. Barone, *Et al.*, Gaussian 16, Inc., Wallingford CT, **2016**.

[26] GaussView, V. 6.0, RD, Dennington II, TA Keith, J. Millam, Gaussian. Inc., Wallingford, CT. **2016**.

[27] Shavitt, I. Geometry and singlet-triplet energy gap in methylene: A critical review of experimental and theoretical determinations. *Tetrahedron*, **1985**, 41(8), 1531-1542.

[28] Hajipour, M., Ghiasi, R., Baniyaghoob, S. Insights into fluorine substituent effect on the electronic, optical and spectroscopic properties of borazanaphthalene. *Results in Chemistry*, **2025**, 15, 102326.

[29] Ghiasi, R., Amini, E. Substituent and solvent effects on geometric and electronic structure of $\text{C5H5Ir}(\text{PH}_3)_3$ iridabenzene: A theoretical insight. *Journal of Structural Chemistry*, **2015**, 56(8), 1483-1494.

[30] Ghiasi, R., Pasdar, H., Fereidoni, S. Solvent and substitution effects on the structure and properties of a half-sandwich complex of vanadium with a terminal borylene ligand: Theoretical study. *Russian Journal of Inorganic Chemistry*, **2016**, 61(3), 327-333.

[31] Soleimani-Amiri, S., Khanmohammadi, A., Vessally, E., Makasana, J., Ballal, S., Panigrahi, R., Joshi, K.K. Metal-porphyrin functionalized carbon nanocones as promising COCl_2 sensors: a DFT and NBO perspective. *Computational and Theoretical Chemistry*, **2025**, 115457.

Graphical Abstract

