

A Theoretical Approach to New Triplet and Quintet (nitrenoethynyl)alkylmethylenes, (nitrenoethynyl)alkylsilylenes, (nitrenoethynyl)alkylgermylenes

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ABSTRACT: Experimentally unreachable reactive intermediates of triplet and quintet (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes, and (nitrenoethynyl)-X-germylenes were compared and contrasted at B3LYP, M06-2X, WB97XD, HF, MP2, MP4, CCSD, and QCISD(T) levels with 6-311++G(d,p) basis set ($X-M-C\equiv C-N$; $M=C, Si, \text{ and } Ge$; $X = H$ (**1**), *Me* (**2**), *Et* (**3**), *Pr* (**4**), *i-Pr* (**5**), and *t-Bu* (**6**)). The effect of small and bulky groups on these acetylene linked reactive intermediates were studied. All triplet (nitrenoethynyl)-X-methylene species were identified as ground states with one local open-shell singlet carbene ($\delta^1\pi^1$) and other local triplet nitrene moiety ($\pi^1\pi^1$) with 47.75-55.70 kcal/mol quintet-triplet energy gap (ΔE_{q-t}). Silylene and germylene substitutions caused the reduction of ΔE_{q-t} . One local closed-shell singlet silylene or germylene moiety ($\delta^2\pi^0$) and one local triplet nitrene moiety ($\pi^1\pi^1$) were connected to make triplet (nitrenoethynyl)silylenes, and (nitrenoethynyl)germylenes. The species of (nitrenoethynyl)silylenes, and (nitrenoethynyl)germylenes could be applied as dipolar intermediates in mechanism identification of chemical reactions. Quintet states were found as ground states with one local triplet divalency moiety ($\pi^1\pi^1$) and also other local triplet nitrene moiety ($\pi^1\pi^1$).

KEYWORDS: Nitrenoethynyl)alkylmethylenes; (Nitrenoethynyl)alkylsilylenes; (Nitrenoethynyl)alkylgermylenes; Triplet; Quintet.

INTRODUCTION

The calculated chemistry has always been one of the most important aspects to have a deep understanding of the performance of chemical reactions. Reactive intermediates and transition states, with their unstable structure, have had an important role in kinetic and

thermodynamic properties of chemical reactions. Intermediates are richer and also more intricate than their carbenes, nitrenes, silylenes, and also germylenes [6-18]. Hence, many researchers have focused on the study of carbenonitrenes, biscarbenes, as well as bisnitrenes.

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The result of some studies presented 20 singlets, 15 triplets, and one quintet for biscarbenes, while only one triplet state and three singlet states were found for carbenes as a diradical species [19, 20].

Linkers, which caused to connect reactive centers, were introduced as one of the most effective agents in structure, stability, multiplicity, and properties of these types of intermediates [10]. Theoretical and also experimental studies were declared ortho-phenylene, para-phenylene, and meta-phenylene as valuable linkers [21-28]. Quintet ground state of meta-phenylene-bis-phenylmethylene, with two carbenic centers was formed by the photolysis of 1,3-bis-(α -diazobenzyl)-benzene [21]. Also, photolysis of 1,3-diazidobenzene at 77°K yielded quintet meta-phenylenedinitrene that was found according to the previous theoretical study [22]. In addition singlet para-benzyne diradicals, singlet para-phenylenebis(chloromethylene), and phenylene-1,4-dinitrene were introduced through photolysis of their relative diazirine by experimental and theoretical chemistry [24, 25, 28]. Photolysis of bis-diazirine in a matrix-isolated in Ar at 10 K underwent elimination of two equivalent N₂ to generate para-phenylene-bis(chloromethylene) [27].

Intermediates with two reactive centers, which connected through p-phenylene linker, were produced in an inert matrix at low temperatures. They were also investigated by different levels of theory [24-28]. In this regards, singlet ground state was found for parent p-phenylenebiscarbene and p-phenylenebisnitrene [24, 28]. Since p-phenylene linker caused the conjugative interaction between the diradical centers, singlet ground states were expected to promote antiferromagnetic couplings [7]. While, quintet ground states were introduced form-phenylene biscarbenes [21, 22]. Hence m-phenylene linker was more considered due to generation of high-spin organic species [23]. In spite of this fact that p-phenylene and o-phenylene reported very similar, o-phenylene linker could show some different behavior due to neighbor reactive centers [10]. Nonetheless, a few studies have been reported on o-phenylene linker [8].

Also besides linkers, various groups on divalency centers could display fundamental effect on their structures and properties [12, 25, 26, 28]. Notwithstanding that CC double bond or CC triple bond linkers could be an appropriate linker for the coupling of

two reactive centers, a few studies were reported in this regard [9, 29-31]. Accordingly, and following our previous study on (nitrenoethynyl)halomethylenes and (nitrenoethynyl)halosilylenes [30, 31], in this study (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes, and (nitrenoethynyl)-X-germylenes were scrutinized at eight theoretical levels (X-M-C \equiv C-N; X = H (**1**), Me (**2**), Et (**3**), Pr (**4**), i-Pr (**5**), and t-Bu (**6**); M=C, Si, and Ge) (Fig. 1). Their theoretical study appeared to be imperative owing to the fact that they were experimentally unreachable.

Computational methods

The singlet (s), triplet (t), and quintet (q) states of (nitrenoethynyl)methylenes, (nitrenoethynyl)silylenes, and (nitrenoethynyl)germylenes were fully optimized at eight ab initio and DFT levels (Fig. 1). All calculations were carried out using the Gaussian 09 program package [32]. The standard 6-311++G(d,p) basis set used for *ab initio* included Hartree-Fock (HF) and the second-order Møller-Plesset (MP2) and also for density functional theory DFT with B3LYP, M06-2X, and WB97XD [33-36]. The MP2/6-311++G(d,p) optimized structures were used as input for single-point calculation at MP4, CCSD(T), and QCISD(T) levels with the same basis set due to improving the level of confidence of predictions [37-40]. All singlet states were computed with spin restricted wave functions, while the triplet and quintet states were computed using the unrestricted formalism. The harmonic vibrational frequencies and Zero Point Energies (ZPE) were computed for all DFT and HF optimized structures which weren't included because of briefness. The Zero Point Energies (ZPE) at the HF and B3LYP were scaled by 0.89 and 0.98, respectively [41, 42].

Minimum structures displayed no imaginary frequency value while transition states showed just one imaginary frequency value. The natural bond orbital (NBO) population analysis was performed at the B3LYP/6-311++G(d,p) level [43]. In addition, HOMO-LUMO calculations were obtained using the above method and basis set.

RESULTS AND DISCUSSION

Following our quest for new carbenonitrenes [30, 31], the steric effects on structure, dipole moment, atomic

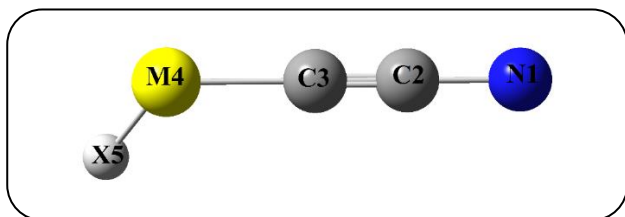


Fig. 1: The input structure for (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes, and (nitrenoethynyl)-X-germylene with initially anticipated singlet(s), triplet(t), and quintet(q) states, ($X-M-C\equiv C-N$; $M=C, Si, Ge$; $X=H$ (1), Me (2), Et (3), Pr (4), i-Pr (5) and t-Bu (6)).

charge, hybridization of atoms, stability, HOMO-LUMO band gap, and chemical reactivity of (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes, and (nitrenoethynyl)-X-germylenes were compared and contrasted at B3LYP, M06-2X, WB97XD, HF, MP2, MP4, CCSD(T), and QCISD(T) levels using 6-311++G(d,p) basis set ($X-M-C\equiv C-N$; $M=C, Si, and Ge$; $X=H$ (1), Me (2), Et (3), Pr (4), i-Pr (5), and t-Bu (6)) (Figs. S1-S2, Tables 1–5, S1-S5).

All using levels of theory to the exclusion of HF/6-311++G(d,p) introduced singlet ground states (were taken as references and set at 0.00 kcal/mol), while triplet and quintets were found at the second and at the least ranking of stability, in turn (Table 1).

Among eight different levels of theory, B3LYP found quite reliable due to insignificant spin contamination than their corresponding levels ($\langle S^2 \rangle = 2.0$ for triplet and $\langle S^2 \rangle = 6.0$ for quintet states) (Table S1) [29, 30, 44-46].

Calculations introduced all singlet (nitrenoethynyl)alkylmethylenes, (nitrenoethynyl)alkylsilylenes, and (nitrenoethynyl)alkylgermylenes as neutral molecules with no carbene/silylene/germylene and nitrene moiety. (Nitrenoethynyl)alkylmethylenes (**1_{Cs}**-**6_{Cs}**) were made of one local open-shell singlet carbene moiety ($\pi^1\pi^1$) and other local open-shell singlet nitrene moiety ($\pi^1\pi^1$) that was completely agree with “c” canonical form (Fig. S1, Tables S2-S4). While their Si and Ge derivatives displayed one local closed-shell singlet silylene or germylene moiety ($\delta^2\pi^0$) and the other local closed-shell singlet nitrene moiety ($\pi^2\pi^0$) (Fig. S1, Table S4).

In addition, the regular population analysis including shapes and energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was also performed at B3LYP/6-

311++G(d,p) (Fig. S2). The C_3-M_4 bond indicated the highest contribution in their relative HOMO orbitals, while C_2-C_3 bond and M_4 atomic orbitals revealed the highest contribution in their relative LUMOs. The HOMO–LUMO energy gap ($\Delta E_{LUMO-HOMO}$) has been a conventional measure of kinetic stability [47].

Narrow HOMO–LUMO gap resulted to low kinetic stability and high chemical reactivity. While (nitrenoethynyl)-X-methylenes displayed larger HOMO–LUMO gap (about 0.244-0.253 eV), (nitrenoethynyl)-X-silylenes and (nitrenoethynyl)-X-germylenes demonstrated lower bandgap (about 0.101-0.103eV and 0.095-0.102eV respectively) (Fig. S2). A smaller bandgap led to lower stability against electronic excitations and also lower hardness but higher chemical reactivity.

Indeed the stable cyanoacetylenes and their Si and Ge derivatives were distinguished for all singlet species ($X-M\equiv C-C\equiv N$; $M=C, Si, and Ge$; $X=H$ (1), Me (2), Et (3), Pr (4), i-Pr (5), and t-Bu (6)) (Fig. S1, Table S2-S4). Hence, we concentrated just on triplet and quintet (nitrenoethynyl)alkylmethylenes, (nitrenoethynyl)alkylsilylenes, and (nitrenoethynyl)alkylgermylenes.

Triplet states

Triplet states of the carbenonitrenes (**1_{Ct}**-**3_{Ct}**, **6_{Ct}**), silylenonitrenes (**1_{Sit}**-**4_{Sit}**, **6_{Sit}**), and germylenonitrenes (**1_{Get}**, **2_{Get}**, **6_{Get}**) were found planar with C_s symmetry (Table 2).

There are no significant changes for geometrical parameters of carbenonitrenes (Tables 2, 3). Replacement of C_4 by silylene and germylene induced a smaller $C_3M_4X_5$ bond angle through their atomic bigger size of Si and Ge. In addition, $C_3Si_4X_5$ bond angle exposed upward trend owing to X_5 growth: **6_{Sit}** (104.3°) > **5_{Sit}** (103.1°) > **4_{Sit}** (102.5°) > **3_{Sit}** = **2_{Sit}** (102.4°) > **1_{Sit}** (96.5°). Also the same trend was observed for $C_3Ge_4X_5$ bond angles: **6_{Get}** (100.1°) > **5_{Get}** (99.3°) > **4_{Get}** (99.0°) > **3_{Get}** (98.9°) > **2_{Get}** (98.2°) > **1_{Get}** (93.6°) (Table 2). Moreover, larger bond length and smaller bond order were realized for C_3-M_4 and M_4-X_5 than their corresponding in carbenonitrenes (Tables 2, 3).

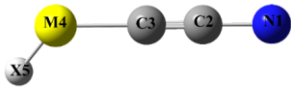
The lowest dipole moment was found for triplet species (Table 1). The highest dipole moment was allocated to the species with the largest X (t-Bu) and the lowest dipole moment was dedicated to the species

Table 1: Relative energies (kcal/mol) and dipole moments (D) for anticipated singlet(s), triplet (t), and quintet (q) states of (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes and (nitrenoethynyl)-X-germylene (X-M-C≡C-N; M=C, Si, Ge; X= H (1), Me (2), Et (3), Pr (4), i-Pr (5) and t-Bu (6)).

Species	Relative energies (Kcal/mol)								Dipole moments(D)
	HF/6-311++G(d,p)	^a MP2/6-311++G(d,p)	^a MP4(SDTQ)/6-311++G(d,p)	^a CCSD/6-311++G(d,p)	^a QCISD(T)/6-311++G(d,p)	B3LYP/6-311++G(d,p)	^a M06-2X/6-311++G(d,p)	^a WB97XD/6-311++G(d,p)	B3LYP/6-311++G(d,p)
1 _{Cs}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.92
1 _{Ct}	69.36	97.32	90.13	79.59	82.16	78.02	85.17	83.97	2.76
1 _{Cq}	74.11	161.73	152.32	133.58	140.27	131.73	139.21	139.21	2.90
2 _{Cs}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.41
2 _{Ct}	70.14	100.96	94.28	82.25	85.54	83.24	84.74	77.18	4.15
2 _{Cq}	76.51	162.52	152.64	133.62	140.06	131.58	139.41	139.41	3.89
3 _{Cs}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.54
3 _{Ct}	70.29	110.84	101.96	91.37	93.31	83.23	92.57	79.29	4.75
3 _{Cq}	76.71	162.68	152.55	133.29	139.65	131.58	139.40	139.40	4.11
4 _{Cs}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.59
4 _{Ct}	69.09	110.75	101.80	91.23	93.13	83.23	92.44	73.58	4.84
4 _{Cq}	77.01	162.59	152.39	133.12	139.43	131.71	139.38	139.38	3.55
5 _{Cs}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.61
5 _{Ct}	70.39	101.74	94.64	82.13	85.20	83.87	92.30	88.23	4.92
5 _{Cq}	77.12	163.38	153.09	133.51	139.94	131.63	138.79	153.01	4.13
6 _{Cs}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.66
6 _{Ct}	71.08	110.98	101.97	91.16	92.92	76.27	83.76	79.61	5.00
6 _{Cq}	7.70	164.00	153.31	133.26	139.55	131.97	138.32	134.34	4.19
1 _{Sis}	31.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.59
1 _{Sit}	0.00	41.36	33.37	12.30	20.43	12.87	12.48	10.60	3.25
1 _{Siq}	19.73	77.26	72.73	51.12	60.61	57.02	53.87	53.43	3.42
2 _{Sis}	27.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.76
2 _{Sit}	0.00	41.88	33.81	12.91	20.85	11.90	12.76	23.70	4.20
2 _{Siq}	21.90	80.06	75.20	53.63	62.29	57.45	55.63	54.61	4.17
3 _{Sis}	27.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.15
3 _{Sit}	0	42.84	34.75	13.44	21.11	12.11	12.93	10.54	4.43
3 _{Siq}	22.02	81.00	76.01	53.98	63.06	57.46	55.76	54.65	4.45
4 _{Sis}	26.83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.40
4 _{Sit}	0.00	43.18	35.01	13.60	22.57	12.25	13.14	10.75	4.57
4 _{Siq}	21.99	80.21	75.09	53.02	62.43	57.00	54.95	54.04	4.61
5 _{Sis}	26.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.35
5 _{Sit}	0.00	43.44	35.41	13.87	22.00	13.08	13.52	11.31	4.55
5 _{Siq}	20.65	80.35	75.23	52.89	62.41	56.83	54.91	53.98	4.49
6 _{Sis}	26.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.50
6 _{Sit}	0.00	43.53	35.54	13.60	21.77	13.27	13.50	11.46	4.63
6 _{Siq}	20.32	80.26	75.09	52.35	61.91	56.60	54.48	53.78	4.58
1 _{Ges}	28.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.44
1 _{Get}	0.00	34.65	26.73	4.77	13.44	6.38	3.51	3.70	2.94
1 _{Geq}	24.00	73.10	67.93	45.25	55.04	55.12	43.49	54.34	3.67
2 _{Ges}	32.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.47
2 _{Get}	0.00	35.37	27.62	5.66	14.27	5.79	3.59	3.39	4.26
2 _{Geq}	25.85	75.89	70.43	47.64	57.35	49.21	41.51	51.18	4.54
3 _{Ges}	31.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.88
3 _{Get}	0.00	36.18	28.43	14.75	14.75	7.20	4.40	4.43	4.44
3 _{Geq}	24.30	75.20	69.62	46.83	56.27	53.60	44.21	53.44	4.81
4 _{Ges}	31.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.02
4 _{Get}	0.00	36.24	28.45	6.22	14.74	7.32	4.62	4.62	4.46
4 _{Geq}	24.21	75.25	69.65	46.69	56.26	46.53	39.67	48.98	4.87
5 _{Ges}	31.64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.17
5 _{Get}	0.00	36.92	29.22	6.57	15.23	7.85	4.55	4.87	4.61
5 _{Geq}	23.82	75.51	69.75	46.42	56.09	52.58	43.51	52.46	5.12
6 _{Ges}	31.72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.45
6 _{Get}	0.00	37.52	29.96	7.06	15.79	8.17	4.75	5.23	4.62
6 _{Geq}	23.18	75.30	69.50	45.98	55.68	51.02	43.11	51.02	5.59

a) ZPE corrections not included.

Table 2: Selected B3LYP/6-311++G(d,p) optimized geometrical parameters of triplet(t), and quintet(q) states of (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes, and (nitrenoethynyl)-X-germylene where bond lengths (Å) and bond angles in degrees (°), and point groups in parenthesis are given (X-M-C≡C-N; M=C, Si, Ge; X= H (1), Me (2), Et (3), Pr (4), i-Pr (5) and t-Bu (6)).



A sample molecule of triplet and quintet (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes and (nitrenoethynyl)-X-germylene

species	Bond Length (Å)				Bond angles(°)			Point Group
	N ₁ C ₂	C ₂ C ₃	C ₃ M ₄	M ₄ X ₅	N ₁ C ₂ C ₃	C ₂ C ₃ M ₄	C ₃ M ₄ X ₅	
1 _{Ct}	1.18	1.35	1.33	1.09	171.749	142.251	130.282	C _s
1 _{Cq}	1.25	1.26	1.47	1.09	174.713	159.736	128.688	C _s
2 _{Ct}	1.18	1.35	1.33	1.47	171.499	144.222	133.554	C _s
2 _{Cq}	1.24	1.27	1.47	1.46	174.522	157.753	128.087	C _i
3 _{Ct}	1.18	1.35	1.35	1.47	172.845	136.173	128.361	C _s
3 _{Cq}	1.24	1.27	1.47	1.47	174.498	157.785	128.112	C _s
4 _{Ct}	1.18	1.35	1.35	1.47	172.831	136.309	128.549	C _i
4 _{Cq}	1.24	1.27	1.47	1.47	174.525	158.329	128.140	C _i
5 _{Ct}	1.18	1.35	1.36	1.47	172.853	135.896	128.538	C _i
5 _{Cq}	1.24	1.27	1.47	1.47	174.625	159.011	128.260	C _i
6 _{Ct}	1.18	1.35	1.33	1.49	171.348	147.124	135.146	C _s
6 _{Cq}	1.24	1.27	1.47	1.48	174.819	160.519	128.730	C _s
1 _{Sit}	1.19	1.32	1.81	1.52	177.688	157.315	96.466	C _s
1 _{Siq}	1.21	1.30	1.88	1.49	177.722	160.455	116.899	C _s
2 _{Sit}	1.19	1.33	1.82	1.91	177.304	152.320	102.433	C _s
2 _{Siq}	1.21	1.30	1.89	1.90	177.983	162.283	116.304	C _s
3 _{Sit}	1.19	1.33	1.81	1.92	177.414	153.235	102.441	C _s
3 _{Siq}	1.21	1.30	1.89	1.92	177.996	162.258	115.062	C _s
4 _{Sit}	1.19	1.33	1.81	1.92	177.396	153.334	102.461	C _s
4 _{Siq}	1.21	1.30	1.89	1.92	177.978	162.013	115.610	C _i
5 _{Sit}	1.19	1.33	1.81	1.94	177.410	153.393	103.143	C _i
5 _{Siq}	1.21	1.30	1.89	1.94	178.031	162.757	114.749	C _i
6 _{Sit}	1.19	1.33	1.80	1.95	177.437	153.041	104.264	C _s
6 _{Siq}	1.21	1.30	1.90	1.97	178.097	163.142	114.211	C _s
1 _{Get}	1.19	1.32	1.93	1.59	177.679	155.689	93.597	C _s
1 _{Geq}	1.21	1.30	1.98	1.56	177.489	153.639	117.416	C _s
2 _{Get}	1.19	1.33	1.94	2.01	177.453	152.038	98.173	C _s
2 _{Geq}	1.21	1.30	1.99	2.02	177.902	154.693	115.872	C _s
3 _{Get}	1.19	1.33	1.93	2.02	177.465	151.828	98.907	C _i
3 _{Geq}	1.21	1.31	2.00	2.06	177.862	154.741	113.928	C _i
4 _{Get}	1.19	1.33	1.93	2.02	177.440	151.505	99.020	C _i
4 _{Geq}	1.21	1.31	2.00	2.05	177.881	154.608	113.887	C _i
5 _{Get}	1.19	1.33	1.93	2.04	177.509	151.984	99.296	C _i
5 _{Geq}	1.21	1.31	2.01	2.11	178.002	156.017	111.545	C _s
6 _{Get}	1.19	1.33	1.92	2.06	177.546	152.733	100.081	C _s
6 _{Geq}	1.21	1.31	2.02	2.19	178.222	157.951	109.085	C _s

Table 3: Bond orders of anticipated triplet (t), and quintet (q) states of (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes and (nitrenoethynyl)-X-germylene at B3LYP/6-311++G(d,p) (X-M-C≡C-N; M=C, Si, Ge; X= H (1), Me (2), Et (3), Pr (4), i-Pr (5) and t-Bu (6)).

Species	Bond orders				Species	Bond orders			
	N ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	M ₄ -X ₅		N ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	M ₄ -X ₅
1 _{Ct}	2.53	1.38	1.90	0.91	4 _{Sit}	2.36	1.56	0.99	0.75
1 _{Cq}	1.84	2.00	1.05	0.93	4 _{Siq}	2.15	1.74	0.74	0.74
2 _{Ct}	2.52	1.39	1.83	1.10	5 _{Sit}	2.37	1.56	1.00	0.70
2 _{Cq}	1.91	1.93	1.03	1.11	5 _{Siq}	2.15	1.74	0.73	0.69
3 _{Ct}	2.47	1.42	1.54	1.12	6 _{Sit}	2.37	1.55	1.00	0.65
3 _{Cq}	1.91	1.93	1.04	1.09	6 _{Siq}	2.15	1.74	0.72	0.64
4 _{Ct}	2.47	1.42	1.55	1.12	1 _{Get}	2.34	1.58	0.93	0.86
4 _{Cq}	1.91	1.93	1.04	1.09	1 _{Geq}	2.20	1.70	0.72	0.79
5 _{Ct}	2.47	1.42	1.54	1.08	2 _{Get}	2.34	1.57	0.90	0.79
5 _{Cq}	1.90	1.94	1.04	1.06	2 _{Geq}	2.19	1.70	0.71	0.73
6 _{Ct}	2.47	1.42	1.54	1.05	3 _{Get}	2.35	1.57	0.91	0.76
6 _{Cq}	1.88	1.95	1.04	1.03	3 _{Geq}	2.19	1.70	0.70	0.67
1 _{Sit}	2.35	1.57	1.00	0.85	4 _{Get}	2.35	1.57	0.91	0.76
1 _{Siq}	2.15	1.74	0.75	0.83	4 _{Geq}	2.20	1.70	0.70	0.67
2 _{Sit}	2.36	1.56	0.98	0.78	5 _{Get}	2.35	1.57	0.92	0.71
2 _{Siq}	2.15	1.74	0.74	0.78	5 _{Geq}	2.19	1.70	0.69	0.59
3 _{Sit}	2.36	1.56	0.99	0.75	6 _{Get}	2.35	1.57	0.92	0.66
3 _{Siq}	2.15	1.74	0.74	0.74	6 _{Geq}	2.19	1.70	0.69	0.48

with the smallest X (H) for all triplet carbenonitrenes, silylenonitrene, and germylenonitrenes.

The NBO atomic charges exhibited no substantial varieties of N₁, and C₂ atomic charges through variation of X and M (X= H (1), Me (2), Et (3), Pr (4), i-Pr (5), t-Bu (6); M= C, Si, Ge) (Table 4). The NBO calculation also offered a more positive charge for Si₄ (0.78-1.05) and then Ge₄ (0.73-0.97) than their corresponding C₄ (0-0.18). While 6_{Ct}, 6_{Sit}, and 6_{Get} species showed more positive charge on C₄, Si₄, and Ge₄, the species of 1_{Ct}, 1_{Sit}, and 1_{Get} displayed the least positive charge. As well, negative charges on X₅ were observed especially in 2_{Ct}, 2_{Sit}, and 2_{Get} species. The 1_{Ct} was reported as lone species with a positive charge on X₅.

Therefore silylenonitrenes and germylenonitrenes with Si₄ or Ge₄ as an electrophilic center and N₁ as a nucleophilic center could apply as important intermediates in some chemical reactions. While, the carbenonitrenes showed no important nucleophilic or electrophilic centers.

Regarding hybridization data, N₁C₂ triple bond, C₂C₃ single bond, and C₃C₄ double bond along with one singly occupied p orbital on C₃ and also the other singly occupied p orbital on C₄ were detected for 1_{Ct}- 6_{Ct} species, which was according to “c” canonical form (Fig. 2, Table 5). This canonical form was in a good harmony with their geometrical parameters and bond orders (Table 2). Accordingly, one local open-shell

Table 4: The NBO atomic charge analyses for triplet(*t*) and quintet(*q*) states of (nitrenoethynyl)-*X*-methylenes, (nitrenoethynyl)-*X*-silylenes and (nitrenoethynyl)-*X*-germylene at B3LYP/6-311++G(*d,p*) (*X*-M-C≡C-N; M=C, Si, Ge; X= H (1), Me (2), Et (3), Pr (4), *i*-Pr (5), and *t*-Bu (6)).

Species	Atomic charge				
	N ₁	C ₂	C ₃	M ₄	X ₅
1 _{Ct}	-0.22	0.17	-0.10	0.00	0.16
1 _{Cq}	-0.15	0.02	0.00	0.00	0.13
2 _{Ct}	-0.24	0.16	-0.11	0.18	-0.69
2 _{Cq}	-0.17	0.01	0.03	0.17	-0.72
3 _{Ct}	-0.23	0.18	-0.14	0.16	-0.51
3 _{Cq}	-0.17	0.01	0.03	0.17	-0.52
4 _{Ct}	-0.23	0.18	-0.13	0.15	-0.51
4 _{Cq}	-0.18	0.01	0.03	0.16	-0.53
5 _{Ct}	-0.23	0.18	-0.14	0.17	-0.32
5 _{Cq}	-0.18	0.01	0.03	0.17	-0.34
6 _{Ct}	-0.24	0.19	-0.15	0.18	-0.15
6 _{Cq}	-0.18	0.01	0.03	0.17	-0.17
1 _{Sit}	-0.20	0.09	-0.45	0.78	-0.22
1 _{Siq}	-0.18	0.04	-0.32	0.64	-0.17
2 _{Sit}	-0.22	0.10	-0.47	0.99	-1.11
2 _{Siq}	-0.20	0.03	-0.32	0.85	-1.06
3 _{Sit}	-0.22	0.10	-0.48	1.00	-0.88
3 _{Siq}	-0.20	0.03	-0.32	0.83	-0.82
4 _{Sit}	-0.22	0.10	-0.48	1.00	-0.88
4 _{Siq}	-0.20	0.03	-0.32	0.84	-0.82
5 _{Sit}	-0.22	0.10	-0.50	1.02	-0.65
5 _{Siq}	-0.20	0.03	-0.33	0.83	-0.60
6 _{Sit}	-0.22	0.11	-0.51	1.05	-0.46
6 _{Siq}	-0.20	0.02	-0.33	0.84	-0.40
1 _{Get}	-0.20	0.07	-0.38	0.73	-0.22
1 _{Geq}	-0.19	0.03	-0.28	0.56	-0.12
2 _{Get}	-0.22	0.07	-0.40	0.93	-1.06
2 _{Geq}	-0.21	0.02	-0.28	0.73	-0.94
3 _{Get}	-0.22	0.07	-0.41	0.93	-0.82
3 _{Geq}	-0.21	0.02	-0.29	0.70	-0.68
4 _{Get}	-0.22	0.07	-0.41	0.94	-0.82
4 _{Geq}	-0.22	0.02	-0.29	0.71	-0.69
5 _{Get}	-0.22	0.08	-0.43	0.95	-0.59
5 _{Geq}	-0.22	0.01	-0.30	0.67	-0.43
6 _{Get}	-0.22	0.08	-0.43	0.97	-0.40
6 _{Geq}	-0.23	0.01	-0.31	0.64	-0.18

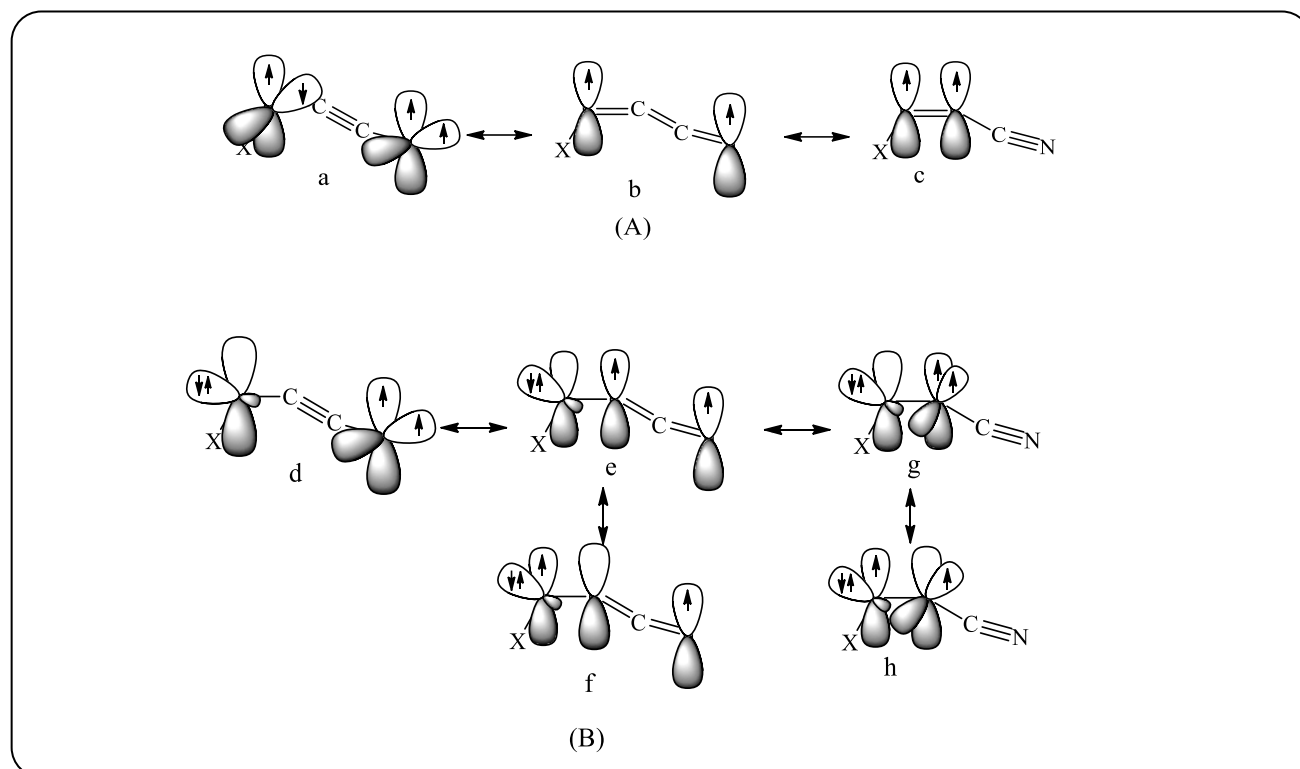


Fig. 2: The significant canonical forms for the anticipated triplet states (*t*) of (nitrenoethynyl)-*X*-methylenes, (nitrenoethynyl)-*X*-silylenes, and (nitrenoethynyl)-*X*-germylenes (*a-h*): (A) for open shell singlet carbenic center and triplet nitrene center; (B) for closed-shell singlet *M* center and triplet nitrene center ($X-M-C\equiv C-N$; $M=C, Si, Ge$; $X=H$ (1), *Me* (2), *Et* (3), *Pr* (4), *i-Pr* (5), and *t-Bu* (6)).

singlet carbene center ($\delta^1\pi^1$) connected to the other local triplet nitrene moiety ($\pi^1\pi^1$) through acetylene linker to produce **1c_t**-**6c_t** species (Fig. 2a).

While both silylenonitrenes and germylenonitrenes were made of one local closed-shell singlet silylene or germylene moiety ($\delta^2\pi^0$) and other local triplet nitrene center ($\pi^1\pi^1$). Hence, N_1C_2 triple bond, C_2C_3 , and C_3M_4 single bonds with two singly occupied p orbitals on C_3 , as well as one unoccupied p orbital and one fully occupied orbital on M_4 , which showed “g” canonical form ($M=Si, Ge$) (Fig. 2).

These findings could be helpful to better comprehension of their relative stabilities. The singlet carbenonitrenes (**1c_s**-**6c_s**) with all octet atoms in their structures were introduced as ground states. Their corresponding triplets of **1c_t**-**6c_t** with two radically subunits in their structures set in the second stable level (Figs. 2, S1, Table 1).

The singlet-triplet energy gap (ΔE_{s-t}) were reduced by switching of divalency center to silylene and germylene due to their singlet instability and also triplet stability

(Table 1). The stability of triplet silylenonitrenes and germylenonitrenes were owing to the most favorable electronic states of silylenes and germylenes (closed-shell singlet silylene or germylene ($\delta^2\pi^0$)). Also, singlet silylenonitrenes and germylenonitrenes with their closed-shell singlet silylene or germylene ($\delta^2\pi^0$) were unable to create a perfect C_3M_4 triple bond that resulted in instability at **1_{Sis}**-**6_{Sis}** and **1_{Ges}**-**6_{Ges}** in contrast to their corresponding **1c_s**-**6c_s** (Fig. S1, Table 1).

Quintet states

The species of **2c_q**, **4c_q**, **5c_q**, **4_{Siq}**, **5_{Siq}**, **3_{Geq}**, **4_{Geq}** were optimized with C_1 symmetry, whereas all other species showed C_s symmetry (Table 2). The bond length of C_4-X_5 enlarged through bigger *X*: **1c_q** (1.09 Å) < **2c_q** (1.46 Å) < **3c_q** = **3_{cq}** = **4c_q** (1.47 Å) < **6c_q** (1.48 Å) (Table 2). Smaller bond angles of $C_2C_3C_4$, and $C_3C_4X_5$ would be found if H was swapped with alkyl group (**2c_q**-**6c_q**) due to longer C_4-X_5 bond length (Table 2). And also with the increasing steric hindrance of alkyl group (from *Me* to *t-Bu*) these angles became bigger expectedly.

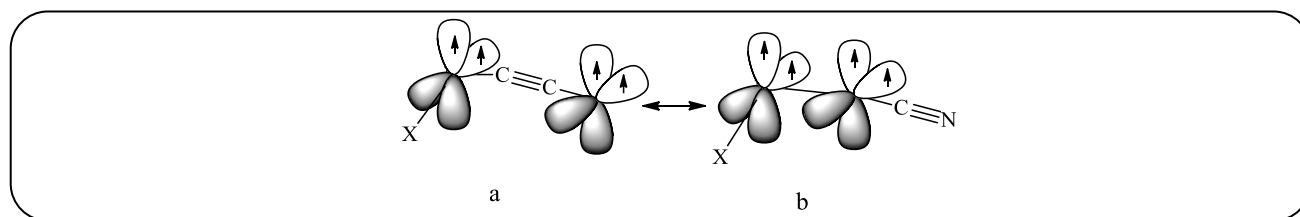


Fig. 3: The significant canonical forms for the anticipated quintet states (*q*) of (nitrenoethynyl)-*X*-methylenes, (nitrenoethynyl)-*X*-silylenes, and (nitrenoethynyl)-*X*-germylenes (*a-c*) (*X-M-C≡C-N*; *M=C, Si, Ge*; *X= H (1), Me (2), Et (3), Pr (4), i-Pr (5), and t-Bu (6)*).

Carbon substitution with silicon and germanium caused longer bond length and also smaller bond order of $\text{Si}_4\text{-X}_5$ and $\text{Ge}_4\text{-X}_5$ in turn (Tables 2, 3). Hence, smaller bond angles of $\text{C}_3\text{Si}_4\text{X}_5$ ($114.2\text{-}116.9^\circ$) and $\text{C}_3\text{Ge}_4\text{X}_5$ ($109.1\text{-}117.4^\circ$) were found. The species of $\mathbf{1}_{\text{Siq}}$ and $\mathbf{1}_{\text{Geq}}$ displayed the largest bond angle of $\text{C}_3\text{M}_4\text{X}_5$ (116.9° , 117.4°), while $\mathbf{6}_{\text{Siq}}$ and $\mathbf{6}_{\text{Geq}}$ species showed the smallest bond angle of $\text{C}_3\text{M}_4\text{X}_5$ (114.2° , 109.1°). Similarly, smaller bond angles of $\text{C}_2\text{C}_3\text{Si}_4$, and $\text{C}_2\text{C}_3\text{Ge}_4$ were found through alkyl substitutions (Table 2).

The optimized dipole moment of quintet species were located between singlet and triplet states. The species of $\mathbf{6}_{\text{Mq}}$, and then $\mathbf{5}_{\text{Mq}}$ showed the highest dipole moments among quintet states ($\text{M}=\text{C, Si, Ge}$) (Table 1).

The NBO calculations showed no important variations of the atomic charge due to *X* changing (Table 4). So that just the species of $\mathbf{1}_{\text{Cq}}$ was found a little different from $\mathbf{2}_{\text{Cq-6Cq}}$. The species of $\mathbf{2}_{\text{Cq-6Cq}}$ showed atomic charges of $-0.17\text{-}0.18$, 0.01 , 0.03 , and $0.17\text{-}0.16$ for N_1 , C_2 , C_3 , and C_4 respectively, while the species of $\mathbf{1}_{\text{Cq}}$ showed -0.15 , 0.02 , 0.00 , and 0.00 atomic charges on N_1 , C_2 , C_3 , and C_4 . The same trend was also observed for silylenonitrenes and germylenonitrenes. The species of $\mathbf{1}_{\text{Ges-6Ges}}$ (-0.19 to -0.23) as well as $\mathbf{1}_{\text{Sis-6Sis}}$ (-0.18 to -0.20) enjoyed with more electron density on N_1 than their relative $\mathbf{1}_{\text{Cs-6Cs}}$ (-0.19 to -0.23). They also benefited from a more positive charge on Si_4 ($0.64\text{-}0.85$) and Ge_4 ($0.56\text{-}0.73$) than their corresponding C_4 ($0.0\text{-}0.17$). Due to the smaller bond order of $\text{Ge}_4\text{-X}_5$, more positive charges were found for Si_4 than Ge_4 (Tables 3, 4). The species of $\mathbf{1}_{\text{Cq}}$, $\mathbf{1}_{\text{Siq}}$, and $\mathbf{1}_{\text{Geq}}$ indicated the lowest positive charge on C_4 , Si_4 , and Ge_4 respectively, while $\mathbf{2}_{\text{Siq}}$ and $\mathbf{2}_{\text{Geq}}$ displayed the highest positive charge of M_4 (0.85 , 0.73) ($\text{M}=\text{Si, and Ge}$).

Accordingly, as seen in singlet and triplet states, $\mathbf{2}_{\text{Siq-6Siq}}$ and $\mathbf{2}_{\text{Geq-6Geq}}$ species could be an effective electrophilic center through their Si_4 , Ge_4 moiety or

as an effective nucleophilic center through their N_1 moiety in the chemical reactions.

Furthermore, N_1C_2 triple bond as well as C_2C_3 , C_3M_4 , and M_4X_5 single bonds along with two singly occupied p orbitals on C_3 and two singly occupied p orbitals on M_4 (with the same spin) were distinguished for $\mathbf{2}_{\text{Cq-6Cq}}$, $\mathbf{1}_{\text{Siq-6Siq}}$, and $\mathbf{1}_{\text{Geq-6Geq}}$ species ($\text{M}=\text{C, Si, Ge}$) (Fig. 3b, Table 5).

While N_1C_2 , C_3C_4 , and C_4H_5 single bonds besides C_2C_3 triple bond along with two singly occupied p orbitals on N_1 and two other singly occupied p orbitals on C_4 were found for the species of $\mathbf{1}_{\text{Cq}}$ (Fig. 3a, Table 5).

All sigma bonds were created by sp orbitals overlapping of N_1 , C_2 , C_3 , and M_4 atoms, in which one local triplet M_4 moiety ($\pi^1\pi^1$) through acetylene linker was joined to the other local triplet N_1 moiety ($\pi^1\pi^1$) that was completely agreed with ‘‘a’’ canonical form (Fig. 3, Tables 5, S5).

Finally, quintet minima with two sextet moieties (two diradical centers) were introduced unstable than their corresponding triplet states.

The highest quintet-triplet energy gap found for $\mathbf{1}_{\text{C-6C}}$ ($47.75\text{-}55.70$ kcal/mol), while $\mathbf{1}_{\text{Si-6Si}}$ and $\mathbf{1}_{\text{Ge-6Ge}}$ displayed smaller quintet-triplet energy gap due to their triplet stability (Table 1). Triplet silylenonitrenes and germylenonitrenes with their closed-shell singlet silylene or germylene ($\delta^2\pi^0$) observed as the most favorable electronic state of silylenes and germylenes (Fig. 2, Table 1).

CONCLUSIONS

The steric effect of eighteen acetylene linked reactive intermediates were studied through B3LYP, M06-2X, WB97XD HF, MP2, MP4, CCSD, and QCISD(T) at 6-311++G(d,p) basis set ($\text{X-M-C}\equiv\text{C-N}$; $\text{M}=\text{C, Si, and Ge}$; $\text{X}=\text{H (1), Me (2), Et (3), Pr (4), i-Pr (5), t-Bu (6)}$). The relative energies, geometrical

Table 5: The NBO hybridizations for triplet(t) and quintet(q) states of (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes and (nitrenoethynyl)-X-germylene at B3LYP/6-311++G(d,p) (X-M-C≡C-N; M=C, Si, Ge; X= H (1), Me (2), Et (3), Pr (4), i-Pr (5) and t-Bu (6)).^a

Species	Hybridization for π bonds						Hybridization for lone pairs ^b					
	$\pi_{(1)} \text{N1-C2}$		$\pi_{(2)} \text{N1-C2}$		$\pi_{(1)} \text{C3-M4}$							
	N ₁	C ₂	N ₁	C ₂	C ₃	M ₄	Lp* _{1C3}	Lp* _{1M4}				
1 _{Ct}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{7.66}	p ^{99.99} d ^{0.11}	p ^{1.00}	p ^{1.00}	s ^{4.24} p ^{22.56}	s ^{5.80} p ^{16.16} d				
2 _{Ct}	p ^{1.00}	p ^{1.00}	p ^{99.84} d ^{6.66}	p ^{99.99} d ^{0.11}	p ^{1.00}	p ^{1.00}	s ^{3.76} p ^{25.53}	s ^{5.19} p ^{18.21}				
3 _{Ct}	p ^{1.00}	p ^{99.99} d ^{0.24}	p ^{1.00}	p ^{1.00}	s ^{9.04} p ^{10.04}	s ^{13.37} p ^{6.46}	p ^{1.00}	p ^{1.00}				
4 _{Ct}	p ^{1.00}	p ^{99.99} d ^{0.24}	p ^{1.00}	p ^{1.00}	s ^{8.98} p ^{10.12}	s ^{13.23} p ^{6.55}	p ^{1.00}	p ^{1.00}				
5 _{Ct}	p ^{1.00}	p ^{99.99} d ^{0.25}	p ^{1.00}	p ^{1.00}	s ^{8.69} p ^{10.48}	s ^{13.52} p ^{6.38}	p ^{99.99} d ^{7.94}	p ^{99.99} d ^{3.55}				
6 _{Ct}	p ^{1.00}	p ^{99.99} d ^{0.26}	p ^{1.00}	p ^{1.00}	s ^{8.05} p ^{11.40}	s ^{13.92} p ^{6.17}	p ^{1.00}	p ^{1.00}				
	$\pi_{(1)} \text{N1-C2}$		$\pi_{(2)} \text{N1-C2}$									
	N ₁	C ₂	N ₁	C ₂	Lp* _{1C3}	Lp* _{2C3}	Lp* _{1M4}					
1 _{Sit}	p ^{1.00}	p ^{99.99} d ^{1.14}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.20}	p ^{1.00}	p ^{1.00}					
2 _{Sit}	p ^{1.00}	p ^{99.99} d ^{1.25}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.43}	p ^{1.00}	p ^{1.00}					
3 _{Sit}	p ^{1.00}	p ^{99.99} d ^{0.96}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.46}	p ^{1.00}	p ^{1.00}					
4 _{Sit}	p ^{1.00}	p ^{99.99} d ^{1.24}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.45}	p ^{1.00}	p ^{1.00}					
5 _{Sit}	p ^{1.00}	p ^{99.99} d ^{0.99}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.60}	p ^{1.00}	p ^{99.99} d ^{3.37}					
6 _{Sit}	p ^{1.00}	p ^{99.99} d ^{1.49}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.77}	p ^{1.00}	p ^{1.00}					
1 _{Get}	p ^{1.00}	p ^{99.99} d ^{0.65}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.11}	p ^{1.00}	p ^{1.00}					
2 _{Get}	p ^{1.00}	p ^{99.99} d ^{0.62}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.18}	p ^{1.00}	p ^{1.00}					
3 _{Get}	p ^{1.00}	p ^{99.99} d ^{0.67}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.21}	p ^{1.00}	s ^{1.09} p ^{89.46} d ^{1.55}					
4 _{Get}	p ^{1.00}	p ^{99.99} d ^{0.65}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.21}	p ^{1.00}	p ^{99.99} d ^{2.16}					
5 _{Get}	p ^{1.00}	p ^{99.99} d ^{0.71}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.22}	p ^{1.00}	p ^{1.00} d ^{0.01}					
6 _{Get}	p ^{1.00}	p ^{99.99} d ^{0.76}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.24}	p ^{1.00}	p ^{1.00}					
	Hybridization for π bonds						Hybridization for lone pairs ^b					
	$\pi_{(1)} \text{N1-C2}$		$\pi_{(1)} \text{C2-C3}$		$\pi_{(2)} \text{C2-C3}$							
	N ₁	C ₂	C ₂	C ₃	C ₂	C ₃	Lp* _{1N1}	Lp* _{2N1}	Lp* _{1C3}	Lp* _{2C3}	Lp* _{1M4}	Lp* _{2M4}
1 _{Cq}	-	-	p ^{1.00}	p ^{1.00}	p ^{99.99}	p ^{99.99} d ^{0.23}	p ^{1.00}	p ^{1.00}	-		p ^{1.00}	s ^{6.49} p ^{14.33}
2 _{Cq}	p ^{99.99} d ^{9.23}	p ^{99.99} d ^{0.17}	-	-	-	-	-	-	p ^{1.00}	s ^{1.07} p ^{92.31} d ^{0.10}	p ^{1.00}	s ^{6.79} p ^{13.68}
3 _{Cq}	p ^{99.99} d ^{9.1}	p ^{99.99} d ^{0.17}	-	-	-	-	-	-	p ^{1.00}	p ^{94.88} d ^{0.1}	p ^{1.00}	s ^{6.789} p ^{13.7}

Table 5: The NBO hybridizations for triplet(t) and quintet(q) states of (nitrenoethynyl)-X-methylenes, (nitrenoethynyl)-X-silylenes and (nitrenoethynyl)-X-germylene at B3LYP/6-311++G(d,p) (X-M-C≡C-N; M=C, Si, Ge; X= H (1), Me (2), Et (3), Pr (4), i-Pr (5) and t-Bu (6)).^a

4 _{Cq}	p ^{99.99} d ^{9.1} ₂	p ^{99.99} d ^{0.17}	-	-	-	-	-	-	p ^{1.00}	p ^{99.99} d ^{0.1} ₀	p ^{99.99} d ^{2.29}	s ^{6.51} p ^{14.32}
5 _{Cq}	p ^{99.99} d ^{9.0} ₇	p ^{99.99} d ^{0.18}	-	-	-	-	-	-	p ^{1.00}	p ^{99.99} d ^{0.1} ₁	s ^{1.69} p ^{58.13} d ^{0.20}	s ^{5.01} p ^{18.89}
6 _{Cq}	p ^{99.99} d ^{9.0} ₂	p ^{99.99} d ^{0.19}	-	-	-	-	-	-	p ^{1.00}	p ^{99.99} d ^{0.1} ₂	s ^{6.66} p ^{13.96}	p ^{1.00}
	$\pi_{(1)} N1-C2$		$\pi_{(2)} N1-C2$									
	N ₁	C ₂	N ₁	C ₂	Lp* _{1C3}	Lp* _{2C3}	Lp* _{1M4}	Lp* _{2M4}				
1 _{Siq}	p ^{1.00}	p ^{99.99} d ^{1.15}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.18}	p ^{1.00}	s ^{5.15} p ^{18.05} d ^{0.37}	p ^{1.00}				
2 _{Siq}	p ^{1.00}	p ^{99.99} d ^{1.64}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.22}	p ^{1.00}	s ^{3.72} p ^{25.48} d ^{0.40}	p ^{1.00}				
3 _{Siq}	p ^{1.00}	p ^{99.99} d ^{1.55}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.21}	p ^{1.00}	s ^{3.10} p ^{30.91} d ^{0.34}	p ^{1.00}				
4 _{Siq}	p ^{1.00}	p ^{99.99} d ^{1.55}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.21}	p ^{1.00}	s ^{3.09} p ^{31.05} d ^{0.33}	p ^{1.00}				
5 _{Siq}	p ^{1.00}	p ^{99.99} d ^{1.65}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.22}	p ^{1.00}	s ^{2.67} p ^{36.14} d ^{0.32}	s ^{1.74} p ^{54.98} d ^{1.56}				
6 _{Siq}	p ^{1.00}	p ^{99.99} d ^{1.62}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.23}	p ^{1.00}	s ^{4.03} p ^{23.70} d ^{0.13}	p ^{1.00}				
1 _{Geq}	p ^{1.00}	p ^{1.00}	s ⁰ p ^{1.00}	p ^{99.99} d ^{0.60}	s ^{1.34} p ^{73.53} d ^{0.12}	p ^{1.00}	s ^{3.62} p ^{26.30} d ^{0.29}	p ^{1.00}				
2 _{Geq}	p ^{1.00}	p ^{99.99} d ^{0.80}	p ^{1.00}	p ^{1.00}	s ^{1.16} p ^{85.35} d ^{0.13}	p ^{1.00}	s ^{2.08} p ^{46.79} d ^{0.26}	p ^{1.00}				
3 _{Geq}	p ^{1.00}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.93}	s ^{1.14} p ^{86.58} d ^{0.13}	p ^{1.00}	s ^{1.82} p ^{53.78} d ^{0.23}	s ^{1.74} p ^{55.18} d ^{1.26}				
4 _{Geq}	p ^{1.00}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.94}	s ^{1.14} p ^{86.30} d ^{0.13}	p ^{1.00}	s ^{1.75} p ^{56.01} d ^{0.21}	s ^{1.08} p ^{89.39} d ^{2.13}				
5 _{Geq}	p ^{1.00}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.81}	s ^{1.03} p ^{96.32} d ^{0.14}	p ^{1.00}	s ^{2.99} p ^{32.41}	p ^{1.00}				
6 _{Geq}	p ^{1.00}	p ^{1.00}	p ^{1.00}	p ^{99.99} d ^{0.95}	s ^{0.88} p ^{99.99} d ^{0.16}	p ^{1.00}	s ^{2.66} p ^{36.54}	p ^{1.00}				

a) Lower participation (<0.1) of d orbitals were negligible and were removed from the table.

b) Anti-bonding molecular orbital.

parameters, dipole moments, NBO atomic charges, and hybridization data were compared and contrasted. No carbene/silylene/germylene and nitrene moiety found for singlet carbenonitrenes, silylenonitrenes, and germylenonitrenes. Triplet carbenonitrenes displayed one local open-shell singlet carbene ($\delta^1\pi^1$) and other local triplet nitrenes ($\pi^1\pi^1$). Triplet silylenonitrenes and germylenonitrenes were identified as locally closed-shell singlet silylene or germylene ($\delta^2\pi^0$) coupled with local triplet nitrene ($\pi^1\pi^1$). The high-spin quintet minima with one local triplet divalency moiety ($\pi^1\pi^1$) and other local triplet nitrene moiety ($\pi^1\pi^1$) emerged 42.85-55.70 kcal/mol higher in energy than their corresponding triplets. Finally, silylenonitrenes and germylenonitrenes with their electrophilic centers (Si₄, Ge₄) and also nucleophilic centers (N₁) could play an important role as an intermediate in mechanism identification of chemical reactions. While no important nucleophilic or electrophilic centers were found for carbenonitrenes.

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REFERENCES

- [1] Kassae M.Z., Musavi S.M., JalaliManesh N., Ghambarian M., A Theoretical Study on Phosphasilylenes CPSi-X (X=H, CN, NH₂ and OMe), *Journal of Molecular Structure: THEOCHEM*, **761**: 7-16 (2006).
- [2] Kassae M.Z., Musavi S.M., Momeni M.R., Shakib F.A., Ghambarian M., How Steric Effects Favor Thiepins over Their Benzene Sulfide Tautomers at Theoretical Levels, *Journal of Molecular Structure: THEOCHEM*, **861**: 117-121 (2008).
- [3] Mohajeri S., Noei M., Molaei N., Cyanogen, Methylacetylene, Hydroquinone, Ethylacetylene, Aniline, Pyrrole, and Ethanol Detection by Using BNNT: DFT Studies, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)* **36**, 89-98 (2017).

- [4] Jafari H., Mohsenifar F., Sayin K., [Effect of Alkyl Chain Length on Adsorption Behavior and Corrosion Inhibition of Imidazoline Inhibitors](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **37**(5): 85-103 (2018).
- [5] Kassae M.Z., Musavi S.M., Ghambarian M., [From Halo-Azasilylenes to Halo-Phosphasilylenes \(X-CNSi vs. X-CPSi\) at ab Initio and DFT Levels](#), *Journal of Organometallic Chemistry* **691**, 2666-2678 (2006).
- [6] Borden W.T., "Diradicals", John Wiley & Sons, Inc., (1982).
- [7] Zuev P., Sheridan R., [Organic Polycarbenes: Generation, Characterization, and Chemistry](#), *Tetrahedron*, **51**: 11337-11376 (1995).
- [8] Nicolaides A., et al. [Of Ortho-Conjugatively Linked Reactive Intermediates: The Cases of Ortho-Phenylene-\(Bis\)Nitrene, -Carbenonitrene, and -\(Bis\)Carbene](#), *Journal of the American Chemical Society* **121**, 10563-10572 (1999).
- [9] Inagaki S., Iwase K., Goto N., [Cross vs. Linear Conjugation as Four p-Orbitals. Substituted Vinylcarbenes and Biscarbenes as Four- \$\pi\$ -Electron Systems](#), *The Journal of Organic Chemistry* **51**, 362-366 (1986).
- [10] Enyo T., Arai N., Nakane N., Nicolaides A., Tomioka H., [o-Phenylene Halocarbenonitrenes and o-Phenylene Chlorocarbenocarbene: A Combined Experimental and Computational Approach](#), *The Journal of Organic Chemistry*, **70**: 7744-7754 (2005).
- [11] Flock M., Pierloot K., Nguyen M.T., Vanquickenborne L.G., [p-Phenylbisphosphinidene and Its Carbene and Nitrene Analogues: An Ab Initio Study](#), *The Journal of Physical Chemistry A* **104**: 4022-4029 (2000).
- [12] Nicolaides A., Enyo T., Miura D., Tomioka H., [p-Phenylencarbenonitrene and its Halogen Derivatives: How Does Resonance Interaction between a Nitrene and a Carbene Center Affect the Overall Electronic Configuration?](#) *Journal of the American Chemical Society*, **123**: 2628-2636 (2001).
- [13] Ling C., Minato M., Lahti P.M., Van Willigen H., [Models for Intramolecular Exchange in Organic \$\pi\$ -Conjugated Open-Shell Systems. a Comparison of 1,1-Ethenediyl and Carbonyl Linked Bis\(arylnitrenes\)](#), *Journal of the American Chemical Society* **114**, 9959-9969 (1992).
- [14] Enyo T., Nicolaides A., Tomioka H., [Halogen Derivatives of m-Phenylene\(carbeno\)nitrene: A Switch in Ground-State Multiplicity](#), *The Journal of Organic Chemistry* **67**, 5578-5587 (2002).
- [15] Kundu S., Samuel P.P., Luebben A., Andrada D.M., Frenking G., Dittrich B., Roesky H.W., [Carbene Stabilized Interconnected Bis-germylene and Its Silicon Analogue with Small Methyl Substituents](#), *Dalton Transactions* (2017).
- [16] Seow C., Xi H.-W., Li Y., So, C.-W., [Synthesis of a Germylidenide Anion from the C-C Bond Activation of a Bis\(germylene\)](#), *Organometallics* **35**, 1060-1063 (2016).
- [17] Zhou Y.-P., Raoufmoghaddam S., Szilvási T., Driess M., [A Bis\(silylene\)-Substituted ortho-Carborane as a Superior Ligand in the Nickel-Catalyzed Amination of Arenes](#), *Angewandte Chemie International Edition* **55**, 12868-12872 (2016).
- [18] Koch A., Kriek S., Görls H., Westerhausen M., [Alkaline Earth Metal-Carbene Complexes with the Versatile Tridentate 2,6-Bis\(3-mesitylimidazol-2-ylidene\)pyridine Ligand](#), *Organometallics* **36**, 994-1000 (2017).
- [19] Borden W.T., Davidson, E.R., [Theoretical Studies of Diradicals Containing Four \$\pi\$ Electrons](#), *Accounts of Chemical Research* **14**: 69-76 (1981).
- [20] Dougherty D.A., [Spin Control in Organic Molecules](#), *Accounts of Chemical Research* **24**: 88-94 (1991).
- [21] Itoh K., [Electron Spin Resonance of an Aromatic Hydrocarbon in Its Quintet Ground State](#), *Chemical Physics Letters* **1**, 235-238 (1967).
- [22] Wasserman E., Murray R.W., Yager W.A., Trozzolo A.M., Smolinsky G., [Quintet Ground States of m-dicarbene and m-dinitrene Compounds](#), *Journal of the American Chemical Society*, **89**: 5076-5078 (1967).
- [23] Iwamura H., [High-spin Organic Molecules and Spin Alignment in Organic Molecular Assemblies](#), in "Advances in Physical Organic Chemistry", 26. (ed. Bethell D.): 179-253, Academic Press, (1991).
- [24] Subhan W., Rempala P., Sheridan R.S., [p-Phenylenebismethylene: Characterization, Calculation, and Conversion to a Conjugated Bis-Carbonyloxide](#), *Journal of the American Chemical Society* **120**, 11528-11529 (1998).
- [25] Zuev P., Sheridan R.S., [p-Phenylenebis\(chloromethylene\): Resonance Interaction of Two Singlet Carbenes](#), *Journal of the American Chemical Society* **115**, 3788-3789 (1993).

- [26] Zuev P.S., Sheridan R.S., [Substituent Switching of Biscarbene Electronic Configurations: p-Phenylenebis\(fluoromethylene\)](#), *Journal of the American Chemical Society* **116**, 9381-9382 (1994).
- [27] Tomioka H., Komatsu K., Nakayama T., Shimizu M., [Photolysis of p-phenylenebis \(chlorodiazirine\), Studied by Matrix Isolation Spectroscopy. Generation, Detection and Characterization of P-Phenylenebis \(chloromethylene\)](#), *Chemistry Letters*, **22**: 1291-1294 (1993).
- [28] Nicolaides A., Tomioka H., Murata S., [Direct Observation And Characterization of p-Phenylenebisnitrene. a Labile Quinoidal Diradical](#), *Journal of the American Chemical Society* **120**, 11530-11531 (1998).
- [29] Kassae M.Z., Musavi S.M., Jalalimanesh N., [A New Generation of Intermediates at Ab Initio and DFT Levels: Allylic Carbenonitrenes, C=\(X\)C-NX=H, CH₃, COOH, F, OH, OCH₃, CF₃, CN, and NH₂](#), *Journal of Theoretical and Computational Chemistry* **07**, 367-379 (2008).
- [30] Kassae M.Z., Soleimani-Amiri S., Majdi M., Mousavi S.M., [Novel Quintet and Triplet \(nitrenoethynyl\)Halomethylenes at Theoretical Levels](#), *Struct. Chem.*, **21**, 229-235 (2010).
- [31] Soleimani Amiri, S., Kassae, M.Z., [Theoretical Study of Singlet, Triplet, and the Quintet States, of \(Nitrenoethynyl\) Halosilylene](#). *Nashrieh Shimi va Mohandesi Shimi Iran (NSMSI)* **35**(4): 87-94 (2016). [Full Article in Persian]
- [32] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Petersson G.A., Nakatsuji H., Li X., Caricato M., Marenich A., Bloino J., Janesko B.G., Gomperts R., Mennucci B., Hratchian H.P., Ortiz J.V., Izmaylov A.F., Sonnenberg J.L., Williams-Young D., Ding F., Lipparini F., Egidi F., Goings J., Peng B., Petrone A., Henderson T., Ranasinghe D., Zakrzewski V.G., Gao J., Rega N., Zheng G., Liang W., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Throssell K., Montgomery J.A., Jr., Peralta J. E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Keith T., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., M. Cossi, Millam J.M., Klene M., Adamo C., Cammi R., Ochterski J.W., Martin R.L., Morokuma K., Farkas O., Foresman J.B., Fox D.J., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2016.
- [33] Frisch M.J., Head-Gordon M., Pople J.A., [Semi-Direct Algorithms for the MP2 Energy and Gradient](#), *Chemical Physics Letters* **166**, 281-289 (1990).
- [34] Becke A.D., [Density-Functional Thermochemistry. IV. A New Dynamical Correlation Functional and Implications for Exact-Exchange Mixing](#), *The Journal of Chemical Physics*, **104**: 1040-1046 (1996).
- [35] Adamo C., Barone V., [Toward Reliable Adiabatic Connection Models Free from Adjustable Parameters](#), *Chemical Physics Letters* **274**, 242-250 (1997).
- [36] Krishnan R., Binkley J.S., Seeger R., Pople J.A., [Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions](#), *The Journal of Chemical Physics* **72**, 650-654 (1980).
- [37] Krishnan R., Pople J.A., [Approximate Fourth-Order Perturbation Theory of the Electron Correlation Energy](#), *International Journal of Quantum Chemistry* **14**, 91-100 (1978).
- [38] Krishnan R., Frisch M.J., Pople J.A., [Contribution of Triple Substitutions to the Electron Correlation Energy in Fourth Order Perturbation Theory](#), *The Journal of Chemical Physics*, **72**: 4244-4245 (1980).
- [39] Pople J.A., Head-Gordon M., Raghavachari K., [Quadratic Configuration Interaction. a General Technique for Determining Electron Correlation Energies](#), *The Journal of Chemical Physics*, **87**: 5968-5975 (1987).
- [40] Scuseria G.E., Schaefer H.F., [Is Coupled Cluster Singles and Doubles \(CCSD\) More Computationally Intensive than Quadratic Configuration Interaction \(QCISD\)?](#) *The Journal of Chemical Physics*, **90**: 3700-3703 (1989).
- [41] Hout R.F., Levi B.A., Hehre W.J., [Effect of Electron Correlation on Theoretical Vibrational Frequencies](#), *Journal of Computational Chemistry*. **3**: 234-250 (1982).
- [42] Francl M.M., Pietro W.J., Hehre W.J., Binkley J.S., Gordon M.S., DeFrees D.J., Pople J.A., [Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-Type Basis Set for Second-Row Elements](#), *The Journal of Chemical Physics*, **77**: 3654-3665 (1982).
- [43] Carpenter J.E., Weinhold F., [Analysis of the Geometry of the Hydroxymethyl Radical by the "Different Hybrids for Different Spins" Natural Bond Orbital Procedure](#), *Journal of Molecular Structure: THEOCHEM*, **169**: 41-62 (1988).

- [44] Barrientos C., Redondo P., Largo A., [Reaction of \$C_3H_2^+\$ with Atomic Nitrogen: A Theoretical Study](#), *The Journal of Physical Chemistry A*, **104**: 11541-11548 (2000).
- [45] Barrientos C., Cimas A., Largo A., [Structure and Stability of \$AlC_2N\$ Isomers: A Comparative Ab Initio and DFT Study](#), *The Journal of Physical Chemistry A* **105**, 6724-6728 (2001).
- [46] Apeloig Y., Pauncz R., Karni M., West R., Steiner W., Chapman D., [Why is Methylene a Ground State Triplet While Silylene Is a Ground State Singlet?](#) *Organometallics*, **22**: 3250-3256 (2003).
- [47] Tang C., Zhu W., Deng K., [The Evolutions of the Structure Stability, Vibrational Frequency, Frontier Orbital, and Electronegativity of the Unconventional Exohedral Fullerenes \$C_{64}X_4\$ \(X=H, F, Cl, Br, and D\): A Density Functional Study](#), *Journal of Molecular Structure: THEOCHEM*, **909**: 43-48 (2009).