



A theoretical investigation into novel germylenes: effects of nitrogen substitution on stability and multiplicity

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Abstract

The effects of substituting nitrogen atoms on the stability of novel singlet (s) and triplet (t) forms of germylenes (**1–20**) are compared and contrasted, at B3LYP/AUG-cc-pVTZ level of theory. Every one of the 40 new divalents scrutinized appears as a minimum on its energy surface, for showing no negative force constant. Also, every singlet (**1_s–20_s**) appears more stable than its corresponding triplet (**1_t–20_t**). The highest stability (ΔE_{s-t}) is achieved by germylene (**11**) where all the three nitrogens are bonded to the central boron atom. The E_{HOMO} slightly decreases when the number of electronegative, σ -acceptor nitrogen atoms increases, and also causes it to be less electron-rich. Germylene **16_s** with low stability ($\Delta E_{s-t} = 17.19$ kcal/mol), bond gap ($\Delta E_{\text{HOMO-LUMO}} = 57.46$ kcal/mol⁻¹), and atomic charge on $-\ddot{\text{G}}\text{e}$ (+0.9012), has high electrophilicity ($\omega = 3.78$ eV) and nucleophilicity ($N = 3.87$ eV). Germylenes **8_s**, **14_s**, and **19_s** with coordinate covalent bond between nitrogen (N(Y)) and germylene center have low ω and high $\Delta E_{\text{HOMO-LUMO}}$. The purpose of the present work was, therefore, to assess the influence of nitrogen substituents on the stability (ΔE_{s-t}), band gaps ($\Delta E_{\text{HOMO-LUMO}}$), N , ω , and heat of hydrogenation (ΔE_{H}). This investigation is aimed to introduce novel germylenes that can be applied as cumulated multi-dentate NH $\ddot{\text{G}}\text{e}$ ligands.

Keywords Germylene · Band gap · Coordinate covalent bond · DFT

Introduction

The divalent germylenes, GeR₂, have gained much attention over the last four decades because of their electron-deficient radicals applied in chemical vapor deposition, semiconductor manufacturing, the photonics, and aerospace industries and other roles [1–3].

NHGe derivatives with the coordination of electronegative and π -electron-donating heteroatoms have high reactivity [3–10]. The NHGe has a weaker $p_{\pi}\text{--}p_{\pi}$ interaction between nitrogen and germylene center than the corresponding NHC because germanium is less electronegative and larger than carbon. This leads to a reduction in the π electron density on the germylene center which makes the NHGe to be a better π

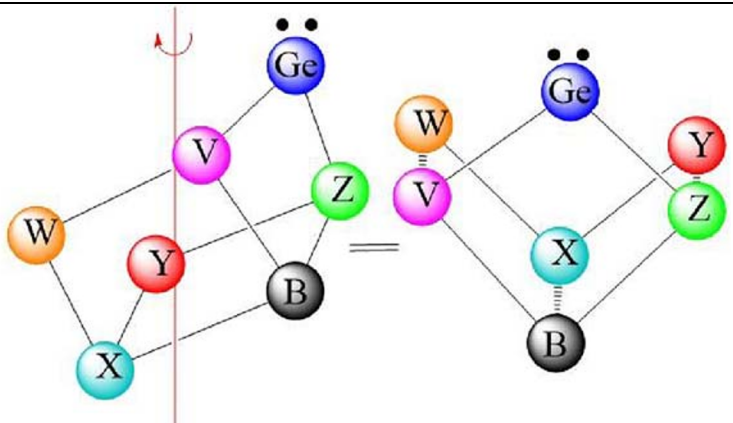
acceptor [11, 12]. In 1982, the first *N*-heterocyclic germylene with four-membered ring was reported by M. Veith [13]. The systematic theoretical studies employing correlated wave functions on R₂Ge have shown a strong tendency for germylenes to have singlet ground states and a substantial electronic effect of different substituents on the ΔE_{s-t} of divalent species [14–17]. The electronegative substituents at germylenes increase the ΔE_{s-t} gap, whereas the electropositive ones reduce it [18].

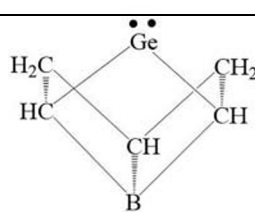
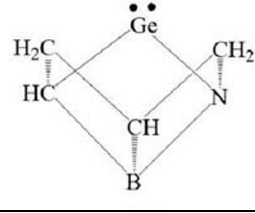
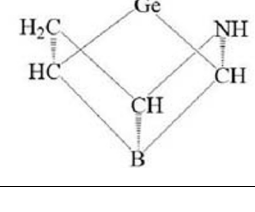
Interestingly, many organogermanium compounds have biological activities that have attracted much attention. In addition, Heremann reported saturated and unsaturated five-membered NHGe compounds, [19] which could be used as the original body to prepare the Ge-film by chemical vapor deposition (VCD) [20]. Therefore, the studies on germylenes and germylene reactions have important theoretical as well as practical significance. The aim of our work is to answer the question that arises whether novel singlet and triplet germylenes are researchable and how nitrogen substitutions may influence their stability, multiplicity (singlet (s) vs. triplet (t)), band gap ($\Delta E_{\text{HOMO-LUMO}}$), nucleophilicity (N), and electrophilicity (ω) at B3LYP/AUG-cc-pVTZ//B3LYP/6–311++G** level of theory. In addition, a number

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Table 1 Optimized bond length (Å), carbenic angle ($\angle Z\dot{G}eV/\text{deg}$), and dihedral angle ($\angle \dot{G}eVBZ/\text{deg}$) for novel singlet (1_s-20_s) and triplet (1_t-20_t) germynes, at B3LYP/6-311++G** level


Structures	Germynes	Symmetry	Bond length (Å)		Gerymne angle (deg)	Dihedral angle (deg)
			Z- $\dot{G}e$	$\dot{G}e$ -V		
	1_s	C_s	2.03	2.03	83.60	-27.72
	1_t	C_s	2.13	2.13	78.48	-15.61
	2_s	C_1	1.96	2.04	76.66	-5.32
	2_t	C_1	1.98	2.35	73.42	-14.10
	3_s	C_1	2.05	2.00	83.78	-33.39
	3_t	C_1	1.99	2.14	80.56	-17.06

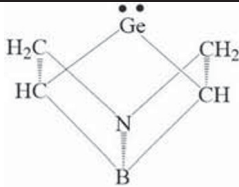
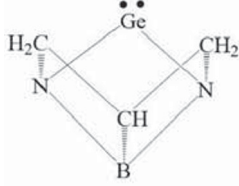
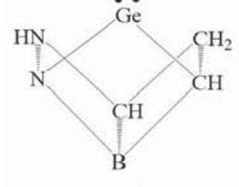
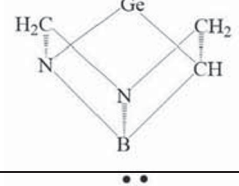
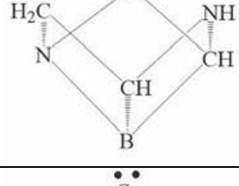
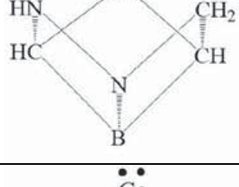
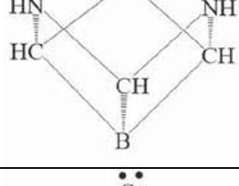
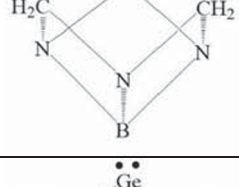

of them show prospects of being employed as multi-dentate NHGe ligands.

Computational methods

Our computational study, due to its excellent performance-to-cost ratio as compared with the correlated wave function theory, is confined to B3LYP calculations [21], while some recent reports have questioned the reliability of the most popular density functional, B3LYP [22]. We used B3LYP with the 6-311++G** basis set that is prevalent in many other papers on

germylenes [11, 23, 24]. Triplet states were calculated using the unrestricted broken spin-symmetry UB3LYP/6-311++G** method implemented in the GAMESS software package [25, 26]. The vibrational frequency computations are applied to characterize the nature of stationary points, as true minima only real frequency values (with a positive sign) or the transition states only one imaginary frequency value (with a negative sign) is accepted respectively [27, 28].

The reactivity parameters are estimated via following the expressions: $N = E_{\text{HOMO}(\text{Nu})} - E_{\text{HOMO}(\text{TCNE})}$; (tetracyanoethylene (TCNE) is preferred as the reference); $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu \approx (E_{\text{HOMO}} + E_{\text{LUMO}})/2$) and η is

	4_s	<i>C₁</i>	2.05	2.05	83.45	-22.29
	4_t	<i>C₁</i>	2.11	2.11	80.43	-13.55
	5_s	<i>C_S</i>	1.98	1.96	78.48	-0.48
	5_t	<i>C_S</i>	2.12	2.12	67.29	-9.95
	6_s	<i>C₁</i>	2.03	2.00	75.96	-4.26
	6_t	<i>C₁</i>	2.14	2.27	69.03	-13.96
	7_s	<i>C₁</i>	2.05	1.98	78.06	-3.15
	7_t	<i>C₁</i>	2.06	2.04	77.12	-14.93
	8_s	<i>C₁</i>	2.04	2.02	76.32	4.17
	8_t	<i>C₁</i>	2.64	1.96	68.83	-21.80
	9_s	<i>C₁</i>	2.03	2.08	82.51	-23.80
	9_t	<i>C₁</i>	2.13	2.03	80.02	-19.72
	10_s	<i>C₁</i>	2.03	2.03	83.35	-35.85
	10_t	<i>C₁</i>	2.02	2.82	67.74	-20.95
	11_s	<i>C₁</i>	1.98	1.98	78.87	0.97
	11_t	<i>C₁</i>	2.16	2.15	67.71	-11.69
	12_s	<i>C₁</i>	2.04	2.01	77.13	-1.47

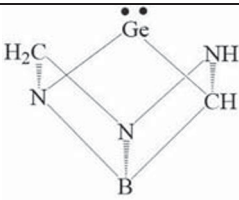
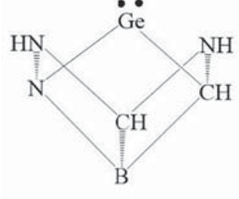
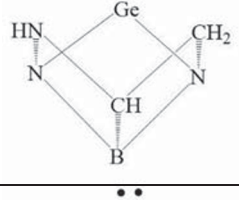
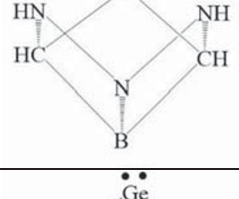
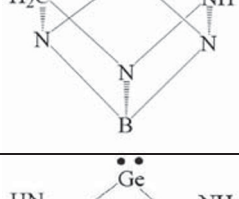
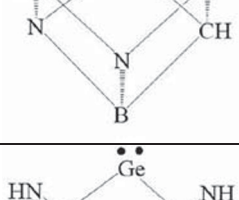
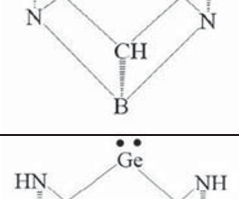
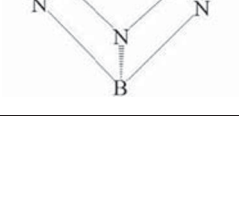
	12_t	<i>C₁</i>	2.08	2.52	69.79	-13.07
	13_s	<i>C₁</i>	2.06	2.00	77.47	0.32
	13_t	<i>C₁</i>	2.51	2.00	71.27	-19.98
	14_s	<i>C₁</i>	2.03	2.09	75.60	4.36
	14_t	<i>C₁</i>	2.50	1.99	69.27	-20.24
	15_s	<i>C₁</i>	1.95	2.04	77.82	3.24
	15_t	<i>C₁</i>	1.99	2.44	67.42	-13.41
	16_s	<i>C₁</i>	2.05	2.05	82.35	-32.11
	16_t	<i>C₁</i>	2.17	2.17	77.42	-22.50
	17_s	<i>C₁</i>	2.04	1.97	77.73	4.50
	17_t	<i>C₁</i>	1.97	2.19	72.11	-10.23
	18_s	<i>C₁</i>	2.06	2.09	76.47	5.22
	18_t	<i>C₁</i>	2.48	2.01	70.65	-18.07
	19_s	<i>C₁</i>	2.05	1.93	77.62	6.25
	19_t	<i>C₁</i>	2.16	2.15	68.83	-13.79
	20_s	<i>C₁</i>	2.06	2.05	76.73	8.12
	20_t	<i>C₁</i>	2.00	2.20	70.62	-14.16

Table 2 Calculated second-order perturbation stabilization energies ($E^{(2)}$), for the intermolecular interactions (donor/acceptor NBO) of singlet (1_s – 20_s) germynes, at the B3LYP/6–311++G** level of theory

Germynes	Donor \rightarrow acceptor	$E^{(2)}$ (kcal/mol $^{-1}$)
1_s	LP $\ddot{G}e \rightarrow \sigma^*_{C(V)-C(W)}$ and $C(Y)-C(Z)$	2.95
2_s	LP $N(Z) \rightarrow LP^*_{\ddot{G}e}$	13.65
3_s	LP $\ddot{G}e \rightarrow \sigma^*_{C(V)-C(W)}$	2.60
	LP $\ddot{G}e \rightarrow \sigma^*_{N(Y)-C(Z)}$	3.20
4_s	LP $\ddot{G}e \rightarrow \sigma^*_{C(V)-C(W)}$ and $C(Y)-C(Z)$	1.96
5_s	LP $N(V) \rightarrow LP^*_{\ddot{G}e}$	4.28
	LP $N(Z) \rightarrow LP^*_{\ddot{G}e}$	1.80
6_s	LP $\ddot{G}e \rightarrow \sigma^*_{N(V)-B}$	1.34
7_s	LP $N(V) \rightarrow LP^*_{\ddot{G}e}$	10.70
8_s	LP $\ddot{G}e \rightarrow \sigma^*_{N(V)-B}$	4.32
9_s	LP $\ddot{G}e \rightarrow \sigma^*_{C(Y)-C(Z)}$	1.59
	LP $\ddot{G}e \rightarrow \sigma^*_{C(V)-N(W)}$	1.09
10_s	LP $\ddot{G}e \rightarrow \sigma^*_{N(Y)-C(Z)}$ and $C(V)-N(W)$	2.48
	LP $N(Z) \rightarrow \sigma^*_{C(Z)-\ddot{G}e}$	2.31
11_s	LP $N(V)$ and $N(Z) \rightarrow LP^*_{\ddot{G}e}$	2.69
12_s	LP $N(V) \rightarrow LP^*_{\ddot{G}e}$	9.65
13_s	LP $N(V) \rightarrow LP^*_{\ddot{G}e}$	6.72
14_s	-	-
15_s	LP $N(V) \rightarrow LP^*_{\ddot{G}e}$	0.60
	LP $N(Z) \rightarrow LP^*_{\ddot{G}e}$	9.15
16_s	LP $\ddot{G}e \rightarrow \sigma^*_{C(V)-N(W)}$ and $N(Y)-C(Z)$	3.03
17_s	LP $N(V) \rightarrow LP^*_{\ddot{G}e}$	7.88
18_s	LP $N(Y) \rightarrow LP^*_{\ddot{G}e}$	47.25
19_s	LP $\ddot{G}e \rightarrow LP^*_{N(V)-B}$	1.29
20_s	LP $N(Z) \rightarrow LP^*_{\ddot{G}e}$	3.01
	LP $N(V) \rightarrow LP^*_{\ddot{G}e}$	1.32
	LP $N(W) \rightarrow LP^*_{\ddot{G}e}$	42.73

chemical hardness ($\eta = E_{LUMO} - E_{HOMO}$) at the same level of theory [29].

To reach more accurate energetic data, single point calculations are accomplished B3LYP/AUG-cc-pVTZ (correlation consistent polarized valence triple zeta) based on the B3LYP/6–311++G** geometries [30].

Results and discussion

We have compared and contrasted novel singlet (s) and triplet (t) germynes (1_s – 20_s vs. 1_t – 20_t) with regard to their geometrical parameters (Table 1); second-order perturbation stabilization energies ($E^{(2)}$) (Table 2); occupancy numbers (Table 3); relative stability ($\Delta E_{s-t} = E_t - E_s$) and ΔE_H (Table 4); the frontier molecular orbital energies (HOMO and LUMO) for singlet germynes along with their band gaps ($\Delta E_{HOMO-LUMO}$) (Table 5) at B3LYP/AUG-cc-pVTZ//B3LYP/6–311++G** level of theory.

The range of bond angle $\angle Z\ddot{G}eV$ for our germynes is from 67.29° to 83.78°. The singlet state of our germynes has longer bond angle ($\angle Z\ddot{G}eV$) than their corresponding triplets. The optimized bond lengths for ($Z-\ddot{G}e$ or $\ddot{G}e-V$) 1_s – 20_s vs. 1_t – 20_t vary in a range of 1.93 to 2.82 Å. The $Z-\ddot{G}e$ or $\ddot{G}e-V$ bond lengths of our singlet germynes, except 18_s , depend on the π -bonds and π -donor interactions (LP $N \rightarrow LP^*_{\ddot{G}e}$) nature of the nitrogen adjacent to gerymlyne center. For instance, the $\ddot{G}e-C$ bond lengths in gerymlyne 6_s with $\ddot{G}e=N$ bond and 2_s with high LP $N(Z) \rightarrow LP^*_{\ddot{G}e}$ interaction ($E^{(2)} = 13.65$ kcal/mol $^{-1}$) are 0.03 Å and 0.08 Å longer than $\ddot{G}e-N$ bond lengths, respectively (Tables 1 and 2).

Germynes 6_s , 8_s , 14_s , and 19_s have coordinate covalent bonds between nitrogen and boron or gerymlyne atoms. They do not show any occupancy number for a lone pair on nitrogen at situation V or Y but display occupancy number for $\pi_{(N(V)-B)}$ or $\sigma_{(\ddot{G}e-N(Y))}$ bonds (Table 3).

Our germynes have singlet ground state, so every triplet gerymlyne (1_t – 20_t) appears at a higher level of energy than its corresponding singlet (1_s – 20_s). For instance, 1_s appears at almost 26.52 kcal/mol $^{-1}$ lower in energy than its corresponding 1_t . Our highest and lowest stable germynes are 11 ($\Delta E_{s-t} = 34.27$ kcal/mol $^{-1}$) and 15 ($\Delta E_{s-t} = 14.87$ kcal/mol $^{-1}$), respectively. The overall stability order of our germynes based on their ΔE_{s-t} values is $11 > 7 > 5 > 4 > 18 > 9 > 20 > 3 > 2 > 1 > 14 > 17 > 12 > 8 > 6 > 19 > 10 > 13 > 16 > 15$. This stability can be related to our imposed structures. Gerymlyne 18_s have high stability ($\Delta E_{s-t} = 32.29$ kcal/mol $^{-1}$), vibrational frequencies ($\nu_{min} = 220.60$ cm $^{-1}$), and dipole moment ($D = 3.71$). Interestingly, gerymlyne 16_s with low stability ($\Delta E_{s-t} = 17.19$ kcal/mol $^{-1}$) has high dipole moment ($D = 3.80$) (Table 4).

The electrostatic potential (ESP) map is related to the electronic density and is considered a fundamental determinant of atomic and molecular properties [31]. Therefore, ESP has largely been used as a molecular descriptor of the chemical reactivity, which takes part in both electrophilic and nucleophilic reactions. For investigation, ESP surfaces are plotted over the optimized electronic structures of our germynes using density functional B3LYP method with 6–311++G** basis set because the computationally or experimentally observed ESP surface directly provides information about the electrophilic (electronegative charge region) and nucleophilic (most positive charge region) regions (Table 3). The ESP map shows that the negative potential sites are on nitrogen atoms. The red and blue regions indicate the lowest and highest electrostatic potential energy values, respectively [31].

Gerymlyne 5_s with two nitrogens adjacent to its gerymlyne center has more positive atomic charges on $-\ddot{G}e-$ (+1.1876) and B (+0.8576) than 2_s , which has one nitrogen ($-\ddot{G}e-$ = +1.0487

Table 3 Calculated occupancy number of LP_{Ge} , $\pi_{(\text{N}-\text{Ge})}$ or $(\text{Ge}-\text{N})$, $\sigma_{(\text{Ge}-\text{B})}$, $LP_{\text{N}(\text{V},\text{W},\text{X},\text{Y},\text{Z})}$ using NBO analysis, and the ESP diagrams for singlet germynes, at the B3LYP/6-311++G** level of theory

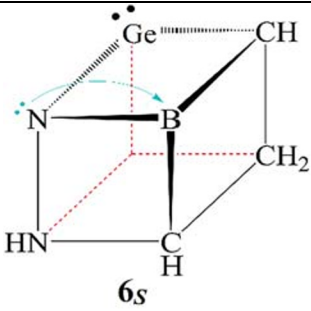
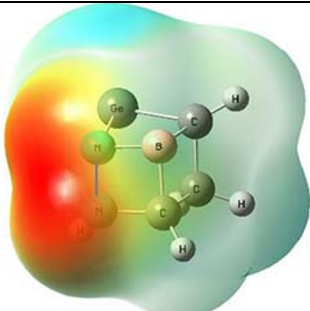
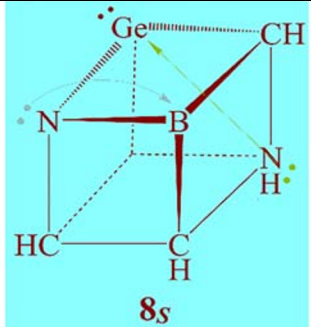
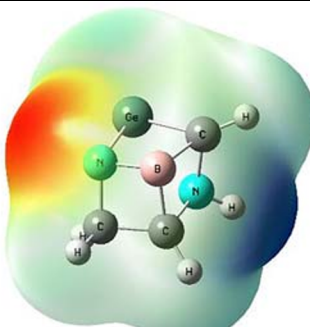
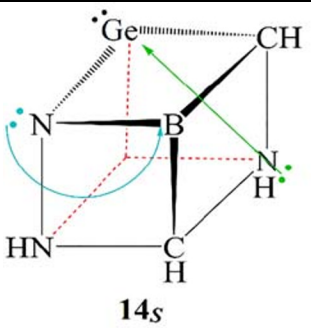
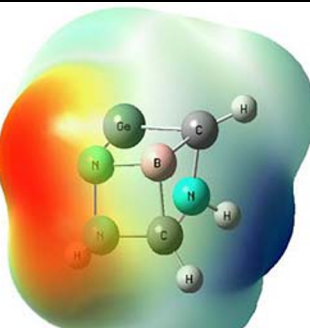
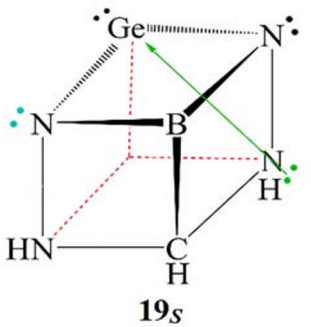
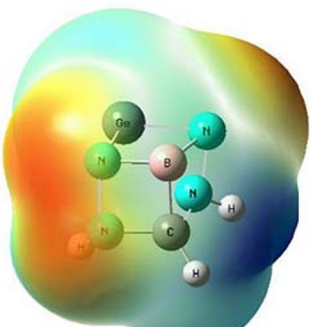
Germynes	ESP	Occupancy number			
		LP_{Ge}	$\sigma_{(\text{Ge}-\text{N}(\text{Y}))}$	$\pi_{(\text{N}(\text{V})-\text{B})}$	$LP_{\text{N}(\text{V},\text{W},\text{X},\text{Y},\text{Z})}$
 <p>6s</p>		1.99	-	1.83	N(V)= N(W)=1.92
 <p>8s</p>		1.98	1.94	1.84	N(V)= N(Y)=
 <p>14s</p>		1.99	1.96	1.86	N(V)= N(W)=1.75 N(Y)=
 <p>19s</p>		1.98	1.94	-	N(V)=1.88 N(W)=1.91 N(Y)= N(Z)=1.96

Table 4 Singlet–triplet energy gaps (ΔE_{s-t} , kcal mol⁻¹), heats of hydrogenation (ΔE_{H_t} , kcal/mol⁻¹), along with dipole moments (D), and the smallest calculated vibrational frequencies (ν_{\min} , cm⁻¹) of our germynes, at B3LYP/AUG-cc-pVTZ level of theory

Germynes	ΔE_{s-t}	D_s^b	ν_{\min}^b	$\Delta E_{H_s}^a$	D_t^b	ν_{\min}^b	$\Delta E_{H_t}^a$
1_s, 1_t	26.52	0.90	169.80	-20.21	2.19	170.86	14.46
2_s, 2_t	27.25	1.75	135.54	-18.19	2.51	96.62	12.98
3_s, 3_t	27.58	0.87	174.87	-18.42	1.57	153.39	10.32
4_s, 4_t	32.95	1.67	160.15	-19.45	0.44	213.83	1.36
5_s, 5_t	33.60	2.18	24.12	-15.01	3.47	110.25	-0.19
6_s, 6_t	23.09	3.24	142.61	-18.30	3.39	78.84	-3.36
7_s, 7_t	33.70	2.11	166.42	-15.79	2.13	214.15	2.44
8_s, 8_t	23.10	2.81	198.79	-11.00	2.65	82.94	13.08
9_s, 9_t	31.19	1.23	90.88	-18.68	1.34	187.92	-4.56
10_s, 10_t	22.32	1.26	180.02	-16.17	2.69	61.89	-0.97
11_s, 11_t	34.27	2.75	117.33	-11.33	1.59	112.99	8.59
12_s, 12_t	24.83	4.06	176.77	-14.47	2.43	83.22	-1.12
13_s, 13_t	19.27	1.90	188.25	-12.20	2.48	93.65	6.00
14_s, 14_t	26.15	3.77	249.14	-6.38	2.99	118.97	-1.97
15_s, 15_t	14.87	2.63	164.31	-11.76	3.05	71.50	6.18
16_s, 16_t	17.19	3.80	95.12	-20.88	1.16	75.09	-1.73
17_s, 17_t	25.11	3.49	204.13	-7.43	2.11	181.39	9.92
18_s, 18_t	32.29	3.71	220.60	-3.87	3.79	11.60	4.18
19_s, 19_t	22.93	3.07	240.58	-4.25	2.42	149.55	0.72
20_s, 20_t	30.69	3.34	232.49	-1.79	1.04	151.94	3.07

^a R₁R₂Ge + H₂ → R₁R₂GeH₂^b At B3LYP/6-311++G****Table 5** NBO charges on -Ge- and B atoms for singlet (**1_s-20_s**) and triplet (**1_t-20_t**) germynes, at B3LYP/6-311++G** level of theory

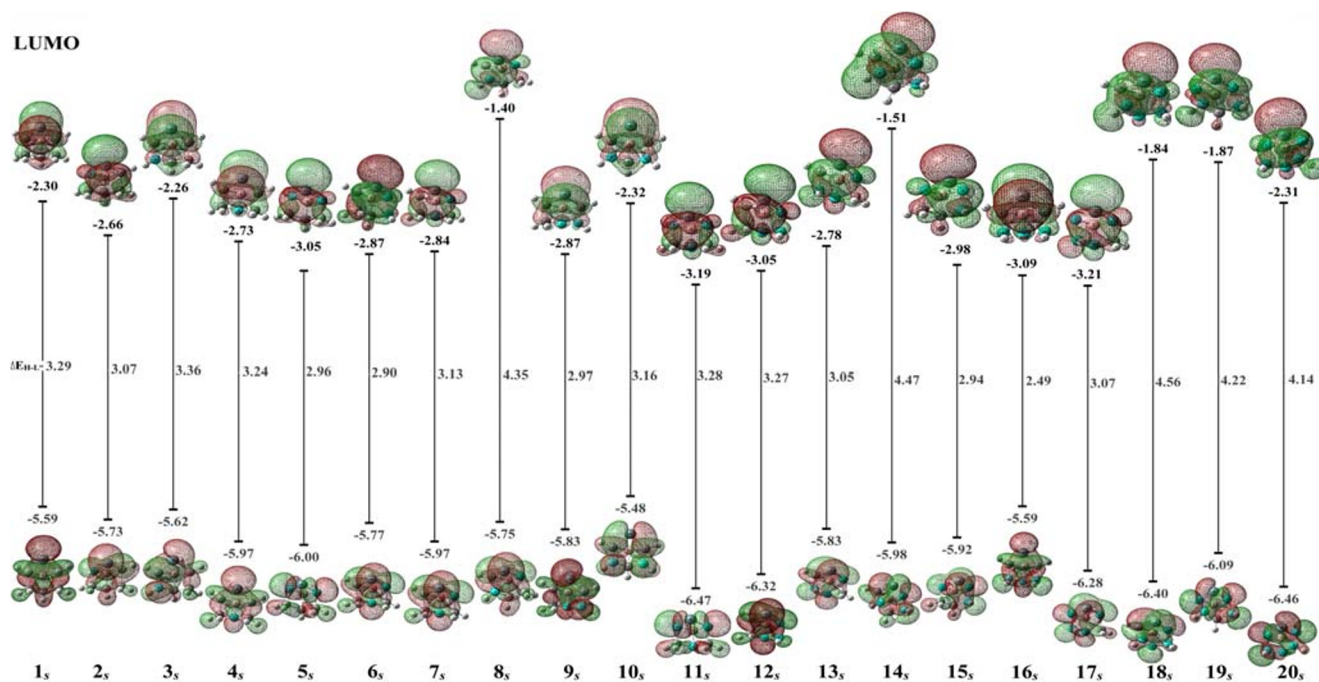
Germynes	Ge	B	Germynes	Ge	B
1_s	0.9100	0.5960	1_t	0.5003	0.6697
2_s	1.0487	0.7724	2_t	0.5626	0.7158
3_s	0.9062	0.4496	3_t	0.5154	0.6524
4_s	0.9521	0.6660	4_t	0.5566	0.7744
5_s	1.1876	0.8576	5_t	0.5255	0.8108
6_s	1.0398	0.7252	6_t	0.4422	0.7801
7_s	1.0326	0.8493	7_t	0.5875	0.8212
8_s	0.9267	0.7525	8_t	0.5013	0.7332
9_s	0.9698	0.5733	9_t	0.4614	0.7417
10_s	0.9064	0.3363	10_t	0.4212	0.6044
11_s	1.1615	0.9043	11_t	0.5491	0.9019
12_s	1.0144	0.8255	12_t	0.4918	0.8823
13_s	0.8916	0.8575	13_t	0.4955	0.8139
14_s	0.8998	0.7188	14_t	0.4791	0.7292
15_s	1.0396	0.8636	15_t	0.5676	0.8645
16_s	0.9012	0.5731	16_t	0.4193	0.7182
17_s	1.0076	0.9181	17_t	0.5600	0.9218
18_s	0.9008	0.8184	18_t	0.4946	0.8154
19_s	1.0372	0.8436	19_t	0.5279	0.8705
20_s	1.0248	0.9170	20_t	0.5821	0.8908

and B = +0.7724). Also, germylene **11_s** with three nitrogens adjacent to its boron has high positive atomic charge on its B (+0.9043) than **1_s** which has no nitrogen (B = +0.5960). The atomic charges of the singlet germylene centers are significantly high positive compared to their corresponding triplets (Figure 1). Germylene **5_s** with the lowest vibrational frequencies (ν_{\min} = 24.12 cm⁻¹) has high positive atomic charge on the B (+0.8576) and -Ge- (1.1876) (Tables 4 and 5).

The crucial factor for stability of germynes is nucleophilicity index, *N*, which was introduced by Domingo et al. [29] The nucleophilicity of our germynes is decreased when their energy of the highest occupied molecular orbital (*E*_{HOMO}) is decreased [32]. For instance, germylene **10_s** has the highest nucleophilicity (3.98 eV) and *E*_{HOMO} (-5.48 eV) (Table 5).

As *E*_{HOMO} slightly decreased, the number of σ -acceptor nitrogen atoms increased, also caused less electron-rich. For example, germylene **19_s** with four nitrogens has lower *E*_{HOMO} (-6.09 kcal/mol⁻¹) than **2_s** (-5.73 kcal/mol⁻¹) which has one nitrogen (Table 6). Germylene **11** with high stability (34.27 kcal/mol⁻¹) and ω (3.56 eV) has the lowest *N* (2.98 eV) (Tables 5, 6, and Figure 1).

Germynes **1_s**, **3_s**, **10_s**, and **16_s** regardless of LP_{Ge} → σ^* interactions have high *N* because they do not have any



HOMO

Fig. 1 Schematic E_{HOMO} , E_{LUMO} (eV), and $\Delta E_{\text{HOMO-LUMO}}$ (kcal/mol⁻¹) for singlet silylenes at the B3LYP/6311++G** level of theory. IsoValue = 0.02 and the density = 0.0004

Table 6 Frontier molecular orbital energies (E_{HOMO} /eV and E_{LUMO} /eV), along with their $\Delta E_{\text{HOMO-LUMO}}$ (kcal/mol⁻¹), nucleophilicity (N), and global electrophilicity (ω) for the singlet (s) germynes (**1_s**–**20_s**), at B3LYP/6-311++G**

Germynes	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{HOMO-LUMO}}$	N (eV)	ω (eV)
1_s	-5.59	-2.30	75.97	3.86	2.36
2_s	-5.73	-2.66	70.69	3.72	2.87
3_s	-5.62	-2.26	77.37	3.83	2.32
4_s	-5.97	-2.73	74.65	3.49	2.92
5_s	-6.00	-3.05	68.18	3.45	3.46
6_s	-5.77	-2.87	66.88	3.68	3.21
7_s	-5.97	-2.84	72.16	3.49	3.09
8_s	-5.75	-1.40	100.32	3.70	1.47
9_s	-5.83	-2.87	68.47	3.62	3.19
10_s	-5.48	-2.32	72.87	3.98	2.40
11_s	-6.47	-3.19	75.60	2.98	3.56
12_s	-6.32	-3.05	75.49	3.13	3.35
13_s	-5.83	-2.78	70.35	3.62	3.03
14_s	-5.98	-1.51	103.03	3.48	1.57
15_s	-5.92	-2.98	67.81	3.53	3.37
16_s	-5.59	-3.09	57.46	3.87	3.78
17_s	-6.28	-3.21	70.91	3.17	3.66
18_s	-6.40	-1.84	105.05	3.05	1.86
19_s	-6.09	-1.87	97.31	3.36	1.88
20_s	-6.46	-2.31	95.57	3.00	2.32

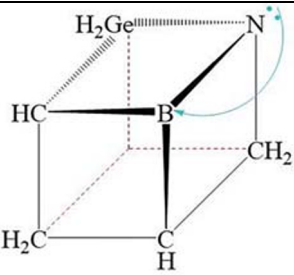
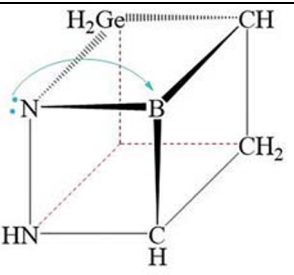
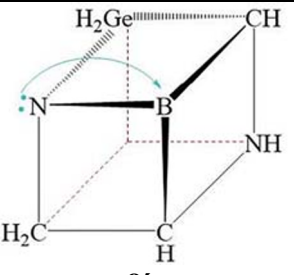
nitrogen adjacent to the germylene center. Germylene **2_s** despite nitrogen adjacent to the germylene center has high N (3.72 eV) for high $\text{LP}_{\text{N}(\text{Z})} \rightarrow \text{LP}_{\text{Ge}}^*$ interaction ($E^{(2)} = 13.65$ kcal/mol⁻¹). Two factors that have an effect on our ω and $\Delta E_{\text{HOMO-LUMO}}$ are σ -bond ($\sigma_{\text{Ge-N}(\text{Y})}$) and $\text{LP}_{\text{N}(\text{W or Y})} \rightarrow \text{LP}_{\text{Ge}}^*$ interactions. Hence, germynes **8_s**, **14_s**, and **19_s** with σ -bond between nitrogen (N(Y)) and germylene center have low ω and high $\Delta E_{\text{HOMO-LUMO}}$. This σ -bond arose from a tendency of nonbonding electrons of nitrogen to empty p orbital of the germylene center. Also, germylene **18_s** with $\text{LP}_{\text{N}(\text{Y})} \rightarrow \text{LP}_{\text{Ge}}^*$ ($E^{(2)} = 47.25$ kcal/mol⁻¹) and **20_s** with $\text{LP}_{\text{N}(\text{W})} \rightarrow \text{LP}_{\text{Ge}}^*$ ($E^{(2)} = 42.73$ kcal/mol⁻¹) interaction have low ω and high $\Delta E_{\text{HOMO-LUMO}}$.

Germylene **20_s** despite $\text{LP}_{\text{N}(\text{W})} \rightarrow \text{LP}_{\text{Ge}}^*$ ($E^{(2)} = 42.73$ kcal/mol⁻¹) interaction has similar ω with **3_s** which do not have any $\text{LP}_{\text{N}(\text{Z})}$ and $\text{LP}_{\text{N}(\text{V})} \rightarrow \text{LP}_{\text{Ge}}^*$ interactions (Tables 2 and 6).

Recently, we have reached novel borastannylenes that have similar structures with our germynes, but they have different properties at geometrical parameters, stability ($\Delta E_{\text{s-t}}$), the heat of hydrogenation (ΔE_{H}), nucleophilicity (N), and electrophilicity (ω). Such various properties have attributed to the effect of our imposed topology and $\text{LP}_{\text{N}(\text{V})}$ interactions [33].

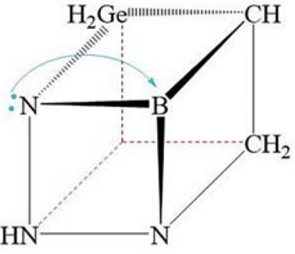
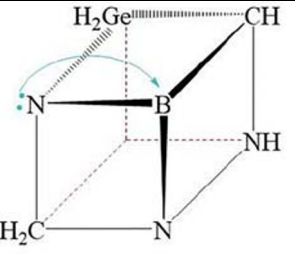
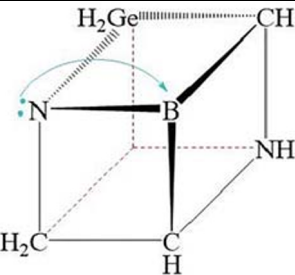
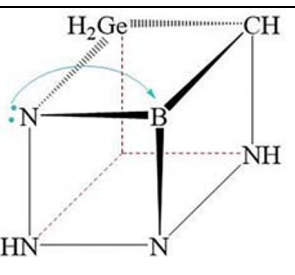
In fact, we have introduced 4,6-diaza-7-boratricyclo[1.1.1.0^{1,7}.0^{7,3}.0^{7,5}]hexa-2-stannylene (**10_s**) with high stability and N that can be applied as accumulated multi-dentate ligands. But, for this purpose, we found that singlet 5-

Table 7 Calculated occupancy number of $LP\pi_{(N-B)}$, and $LP_{N(V, W, X, Y, Z)}$ using NBO analysis for singlet hydrogenated germylenes, at the B3LYP/6-311++G** level of theory

Hydrogenated germylenes	Occupancy number	
	$\pi_{(N-B)}$	$LP_{N(V, W, X, Y, Z)}$
 <p>2'_s</p>	1.86	N(Z)=-
 <p>6'_s</p>	1.88	N(V)=- N(W)=1.93
 <p>8'_s</p>	1.86	N(V)=- N(X)=1.90

aza-7-boratricyclo[1.1.1.0^{1,7}.0^{7,3}.0^{7,5}]hexa-2-germylene (**4_s**) and 1,3-diraaza-7-boratricyclo[1.1.1.0^{1,7}.0^{7,3}.0^{7,5}]hexa-2-germylene (**5_s**) are suitable.

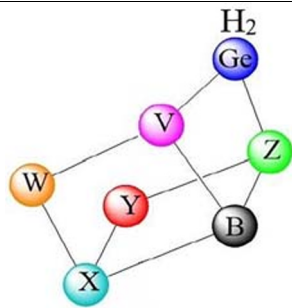
The heats of hydrogenation for our germylene were calculated at B3LYP/AUG-cc-pVTZ level. The calculated heat of hydrogenation [33] is a thermodynamic method to estimate the relative stability of germylenes. For instance, germylene **18_s**, with high stability ($\Delta E_{s-t} = 32.29$ kcal/mol⁻¹) has low heat of hydrogenation ($\Delta E_H = -3.87$ kcal/mol⁻¹). Also, germylene **16_s**, with low stability ($\Delta E_{s-t} = 17.19$ kcal/mol⁻¹) has the highest heat of hydrogenation ($\Delta E_H = -20.88$ kcal/mol⁻¹). Our triplet

 <p>12'_s</p>	1.85	N(V)=- N(W)=1.95 N(X)=1.92
 <p>13'_s</p>	1.84	N(V)=- N(X)=1.93 N(Y)=1.93
 <p>14'_s</p>	1.88	N(V)=- N(W)=1.91 N(Y)=1.91
 <p>18'_s</p>	1.85	N(V)=- N(W)=1.92 N(X)=1.95 N(Y)=1.94

germylenes have higher heats of hydrogenation than their corresponding singlets. For instance, the heat of hydrogenation **2_s** and **2_t** are -18.19 and $+12.98$ kcal/mol⁻¹, respectively (Table 4).

We have employed the NBO analysis to stress the roles of intermolecular orbital interactions through second-order perturbation theory. The NBO analysis provides significant evidence for the nature of our hydrogenated

Table 8 Calculated second-order perturbation stabilization energies ($E^{(2)}$), for the intermolecular interactions (donor/acceptor NBO) of hydrogenated germylenes, at the B3LYP/6-311++G** level of theory



Hydrogenated germylenes	Donor→Acceptor	$E^{(2)}$ (kcal/mol)
4_s	$LP_{N(X)} \rightarrow LP^*_B$	11.64
5_s	$LP_{N(V \text{ and } Z)} \rightarrow LP^*_B$	5.45
7_s	$LP_{N(V)} \rightarrow LP^*_B$	5.69
	$LP_{N(X)} \rightarrow LP^*_B$	4.93
9_s	$LP_{N(X)} \rightarrow LP^*_B$	7.06
11_s	$LP_{N(V \text{ and } Z)} \rightarrow LP^*_B$	4.33
	$LP_{N(X)} \rightarrow LP^*_B$	3.90
15_s	$LP_{N(V)} \rightarrow LP^*_B$	1.68
	$LP_{N(Z)} \rightarrow LP^*_B$	6.30
16_s	$LP_{N(X)} \rightarrow LP^*_B$	2.89
	$LP_{N(V)} \rightarrow LP^*_B$	4.85
17_s	$LP_{N(X)} \rightarrow LP^*_B$	1.58
	$LP_{N(Z)} \rightarrow LP^*_B$	1.80
19_s	$LP_{N(V)} \rightarrow LP^*_B$	1.26
	$LP_{N(Z)} \rightarrow LP^*_B$	2.81
20_s	$LP_{N(V)} \rightarrow LP^*_B$	1.47
	$LP_{N(W)} \rightarrow LP^*_B$	3.17
	$LP_{N(Z)} \rightarrow LP^*_B$	1.89

germylenes. The nonbonding electrons at the nitrogen appear to have a tendency to make a coordinate covalent bond with the empty p orbital of boron atom. This is demonstrated by hydrogenated germylenes **2_s**, **6_s**, **8_s**, **12_s**,

13_s, **14_s**, and **18_s**, for showing $\pi_{(N-B)}$ occupancy number. Interestingly, hydrogenated germylenes with the nitrogen attached to boron have $\pi_{(N-B)}$ or $LP_N \rightarrow LP^*_B$ interactions. For example, hydrogenated germylenes **2_s** with $\pi_{(N-B)}$ and **4_s** with high $LP_{N(X)} \rightarrow LP^*_B$ interactions ($E^{(2)} = 11.64 \text{ kcal/mol}^{-1}$) have one nitrogen attached to boron. Hydrogenated germylene **20_s** has the lowest ΔE_H ($-1.79 \text{ kcal/mol}^{-1}$) for $LP_{N(W)} \rightarrow LP^*_B$ interaction. This interaction has caused to decrease in the stability of **20_s** (Tables 7 and 8).

Conclusions

In this research, we have studied thermodynamical and geometrical parameters for investigation of the effects of nitrogen substitution on the stability, multiplicity, and reactivity of novel singlet and triplet germylenes (**1_s**–**20_s** and **1_t**–**20_t**, respectively), all of which appear as minima on their potential energy surfaces at B3LYP/AUG-cc-pVTZ//B3LYP/6-311G** level of theory. The germylene **11** with the enormous steric strain for their cubic structure has the highest stability ($\Delta E_{s-t} = 34.27 \text{ kcal/mol}^{-1}$). The E_{HOMO} slightly decreases when the number of electronegative, σ -acceptor nitrogen atoms increases, also causes it to be less electron-rich. We have employed the NBO analysis to stress the roles of intermolecular orbital interactions through second-order perturbation theory. The NBO analysis provides significant evidences for the nature of our germylenes. Based on the following arguments, two factors that have the effect on our ω and $\Delta E_{HOMO-LUMO}$ are σ -bond ($\sigma_{(Ge-N(Y))}$) and $LP_{N(W \text{ or } Y)} \rightarrow LP^*_{Ge}$ interactions. Germylenes **8_s**, **14_s**, and **19_s** with σ -bond between nitrogen (N(Y)) and germylene center have low ω and high $\Delta E_{HOMO-LUMO}$. Germylenes **18_s** and **20_s** with $LP_{N(W \text{ or } Y)} \rightarrow LP^*_{Ge}$ interactions have low ω and high $\Delta E_{HOMO-LUMO}$. The nucleophilicity index, N , is a crucial factor for showing the aptitude of our germylenes for coordination to transition metal complexes. So, we introduce germylenes **4_s** and **5_s** with high stability ($\Delta E_{s-t} = 32.95$ and $33.60 \text{ kcal/mol}^{-1}$, respectively) and N (3.49 and 3.45 eV) that can be applied as multi-dentate ligands.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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