



Novel triplet germylenes in focus: normal vs. abnormal triplet exocyclic tetrazol-5-vinylidene germylenes at DFT

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Abstract

Substituent effects on stability (assumed as the singlet and triplet energy gaps, ΔE_{S-T}) of novel 1,4-disubstituted-tetrazole-5-vinylidene germylenes (normal, 1_R) and their corresponding 1,3-disubstituted-tetrazole-5-vinylidene germylenes (abnormal, 2_R) are computed and compared, at B3LYP/6-311++G** and M06/6-311++G**, where $R = H, CN, CF_3, F, SH, C_6H_6, OMe,$ and OH . Interestingly, every triplet vinylidene germylene shows more stability than its corresponding singlet. Also, every triplet abnormal isomer (2_R) emerges to be more stable than its corresponding normal (1_R). All abnormal 2_R isomers show broader band gaps ($\Delta E_{HOMO-LUMO}$) and higher nucleophilicity (N), but less electrophilicity (ω) than their corresponding normal 1_R isomers. The NICS (nuclear-independent chemical shift) results indicate that every 1_R (except singlet 2_{Ph}) emerges more aromatic than its corresponding 2_R . Our Hammett studies indicate that 1_R is more sensitive to the electronic effects of substituents, R , than 2_R . Electron-donating species increase N in both 1_R and 2_R , while electron-withdrawing groups increase stability.

Keywords Tetrazole-vinylidene germylene · Band gap · Singlet-triplet energy gap · Triplet state · Electronic effect

Introduction

N-heterocyclic carbenes (NHCs) are used as organocatalysts to bind every transition metal and form strong metal complexes in the fields of organic and inorganic chemistry [1–5]. Studies on NHCs date back to the research of Wanzlick in the 1960s [6]. In 1991, the first stable NHC was reported by Arduengo and coworkers [7, 8]. They synthesized and characterized colorless crystals of 1,3-di-*l*-adamantylimidazol-2-ylidene. The synthesis of NHC consisting of pendant alkenes was reported by Furstner and coworkers [9]. Recently, Bertrand reported a novel procedure to the synthesis of the stable six-membered NHC [10–12]. After these successful researches and some similar works, many N-heterocyclic

carbenes, silylenes (NHSi), and germylenes (NHGe) were reported [13–15]. NHGes are very versatile ligands and the heavier homologs of the NHCs. Meller and Gräbe reported the first NHGe from some imidazoles, in 1985 [16]; after the discovery of Arduengo et al.'s NHC in 1991 [7], the first post-Arduengo NHGe being reported in 1992 [17]; then in 1994, Heinemann et al.'s [18] study on the stability of Arduengo-type NHGe and NHSi and compare them with the NHC. Since germanium is less electronegative and larger than carbon, the corresponding NHGe has a weaker N-Ge $p\pi-p\pi$ interaction than NHC. This leads to a reduction in the π -electron density on germanium which makes the NHGe to be a better π acceptor [19]. After several years, theoretical researchers found that triplet N-heterocyclic silylenes and germylenes could also be stable [10–27]. In fact, due to the importance of triplet ground-state silylenes and germylenes in chemical semiconductor manufacturing, vapor deposition, and the aerospace and photonics industries, the preparation and theoretical calculation of these isomers have become one of the most important topics in modern organosilicon and germanium chemistry [25].

In 2011, Momeni et al. researched on triplet NH-vinylidene silylenes with $(NRCH_2-CH_2NR)Si=Si$ and $(NRCHCHNR)Si=Si$ structures [28]. In our continued quest for novel divalent NH-vinylidene germylene species [29–38],

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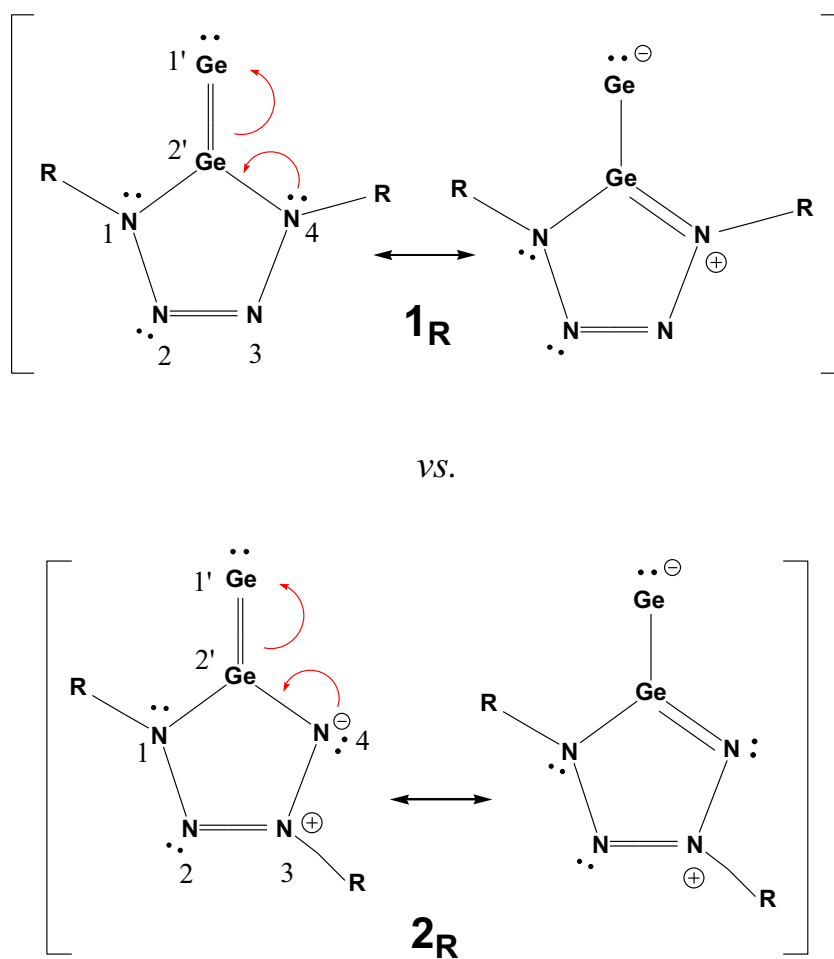
the question immediately arises whether normal and abnormal tetrazol-5-vinylidene germylenes are researchable and how H, CN, CF₃, F, SH, C₆H₆, OMe, and OH groups with different electronic effects may influence their stability, multiplicity (singlet (s) vs. triplet (t)), band gap ($\Delta E_{\text{HOMO-LUMO}}$), aromaticity (NICS), nucleophilicity (N), electrophilicity (ω), and geometrical parameters (Scheme 1). Clearly, it will be shown that appropriate substitutions with different electronic effects in normal and abnormal forms of tetrazol-5-vinylidene germylenes decrease the $\Delta E_{\text{S-T}}$ value of NH-vinylidene germylene enough to bring the resulting novel triplet germylene, which are more stable than the results of other workers.

Computational methods

All geometry optimizations are carried out without any symmetry constraints by means of hybrid functional B3LYP [39–43] and the standardized 6-311++G** basis set, by using GAMMES package of programs [44].

Our computational study is confined to B3LYP calculations due to its excellent performance-to-cost ratio as compared with the correlated wave function theory [45–48]. While recently, some reports appeared to develop the controversies on the reliability of most of the popular density functional, B3LYP, [15] in parallel to many other papers on germylenes, in this work, B3LYP with the 6-311++G** basis set is employed as the method of choice [22, 25, 49–53]. To obtain more accurate energetic data, the M06 calculation is performed as a different density functional [41]. Singlet states are considered with spin-restricted wave function and triplet states are studied by using the unrestricted formalisms [54, 55]. The spin-restricted and spin-unrestricted (with broken symmetry) calculations give the identical values of the singlet ground-state energy (Table S1). Thus, the restricted wave functions were employed to investigate the possible pathways of the singlet germylenes [56]. After spin annihilation, an ideal value (2.001) is indicated for the S^2 expectation values of these divalents, so that their geometries are reliable for our study. The frequency calculations are applied to characterize the structures as minima (the number of imaginary

Scheme 1 Scrutinized normal and abnormal tetrazol-5-vinylidene germylenes where $R = \text{H, CN, CF}_3, \text{F, SH, C}_6\text{H}_6, \text{OMe, and OH}$



frequencies (NIMAG = 0) or transition states (NIMAG = 1) [57]. The global electrophilicity (ω) has been computed as $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu \approx (E_{\text{HOMO}} + E_{\text{LUMO}})/2$) and η is the chemical hardness ($\eta = E_{\text{LUMO}} - E_{\text{HOMO}}$) [58]. The nucleophilicity index N [59] has been considered as $N = E_{\text{HOMO}}(\text{Nu}) - E_{\text{HOMO}}(\text{TCNE})$, where tetracyanoethylene (TCNE) is utilized as the reference.

Results and discussion

Band gap ($\Delta E_{\text{HOMO-LUMO}}$), electrophilicity (ω), and nucleophilicity (N) of normal (1_R) vs. abnormal (2_R) vinylidene germylenes

The excellent σ -donor capacities of NH-silylenes and germylenes make them very useful ligands for research on the variety of organometallic catalysts [60, 61]. Here, we have considered $\Delta E_{\text{HOMO-LUMO}}$, N , and ω indices for our singlet and triplet germylenes, at B3LYP/6-311++G**₂. Abnormal singlet and triplet germylenes (2_R) have higher $\Delta E_{\text{HOMO-LUMO}}$ and nucleophilicity but lower electrophilicity than the corresponding normal (1_R) isomers (Table 1). For instance, the singlet abnormal 2_{OH} ($N = 4.69$ eV) appears more nucleophile than its corresponding singlet normal 1_{OH} ($N = 4.45$ eV).

Such differences may be explained in terms of the difference between the occupancy of their vacant $\pi^*_{\text{Ge(2')-Ge(1')}}$ orbitals (Scheme 1).

The electron donation of the N(4) atom with negative charge is much more efficient in the abnormal than the corresponding normal isomers. The computed NBO results indicate that the donation of $\text{LP}_{\text{N(4)}} (\pi^*_{\text{Ge(2')-Ge(1')}})$ in the abnormal germylenes is approximately twice of that on the normal (Table 1, Scheme 1).

E. Kühn et al. also have reported that variation of substitution pattern in normal and abnormal isomers effects on σ -donor capacities of the species. It is found that the abnormal tetrazolyidene with 1,3-substitutions is considered a better electron donor than its corresponding normal isomer [30, 62].

This is also a good reason why in going from normal to abnormal, N increases as a function of π -donor or π -acceptor abilities of the employed substituents. Between normal and abnormal, 2_{Ph} and 1_{CN} are the most and the least nucleophilic groups (Table 2). Hence, the trend of N values in singlets 1 and 2 is $1_{\text{CN}} < 1_{\text{F}} < 1_{\text{CF}_3} < 1_{\text{SH}} < 1_{\text{OH}} < 1_{\text{Ph}} < 1_{\text{OMe}} < 1_{\text{H}}$; and $2_{\text{CN}} < 2_{\text{F}} < 2_{\text{CF}_3} < 2_{\text{OH}} < 2_{\text{SH}} < 2_{\text{OMe}} < 2_{\text{Ph}} < 2_{\text{H}}$. In triplets, the trend is $1_{\text{CN}} < 1_{\text{CF}_3} < 1_{\text{F}} < 1_{\text{SH}} < 1_{\text{OH}} < 1_{\text{OMe}} < 1_{\text{H}} < 1_{\text{Ph}}$ and $2_{\text{CN}} < 2_{\text{F}} < 2_{\text{CF}_3} < 2_{\text{OH}} < 2_{\text{SH}} < 2_{\text{OMe}} < 2_{\text{H}} < 2_{\text{Ph}}$. Plotting nucleophilicity as a function of σ_m gives negative ρ of -5.07 and -4.46 with a correlation factor of $R^2 = 0.90$ and 0.88 , for

(1_R) and (2_R), respectively (Fig. 1). This indicates that N is highly sensitive to the electronic effects of substituents and that electron-donating groups enhance N . In contrast, plotting $\Delta E_{\text{S-T}}$ as a function of σ_p gives positive ρ of 12.94 and 14.97 with R^2 of 0.9 and 0.6 , for (1_R) and (2_R), respectively (Fig. 2). Hence, stability of our germylenes appears to increase as a function of electron-withdrawing effects of R . These data indicate that both (1_R) and (2_R) show high stability in nucleophilicity (Table 2). Here, 1_R demonstrates a higher sensitivity toward electronic effects of R than 2_R .

Abnormal vinylidene germylenes due to their nucleophilicity and 1,3-substitution patterns are stronger σ -electron donors than their corresponding normal congeners [62]. In this case, the N(4) α -nitrogen atom nearby the Ge(2') is able to transport a higher electron density on germanium than corresponding normal isomers (Table 1, Scheme 1). Consequently, Ge(2')-Ge(1') bond length decreases and N(1)-Ge(2')-N(4) bond angle increases in abnormal isomers more than the corresponding normals (Table 3).

As to the electronic effects of various types of substituents, Ge(2')-Ge(1') bond lengths analyses do not show notable a difference between the normal (1_R) and abnormal (2_R) germanium-germylene bonding mode. Furthermore, stereoelectronic effects of the substituents modify the N(1)-Ge(2')-N(4) bond angles. For example, benzo substituent features the significantly largest N(1)-Ge(2')-N(4) bond angles for abnormal and normal germylenes (81.45 (1) Å vs. 83.90 (2) Å in singlets and 80.48 (1) Å vs. 83.25 (2) Å in triplets). Likewise, fluorine substituent makes the smallest N(1)-Ge(2')-N(4) bond angle in both abnormal and normal germylenes (75.03 (1) Å vs. 80.93 (2) Å in singlets and 73.45 (1) Å vs. 79.94 (2) Å in triplets) (Table 3).

Substituent effects on normal (1_R) and abnormal (2_R) vinylidene germylenes

Worthington and Cramer in 1997 claimed that vinylidene ($\text{H}_2\text{C}=\text{C}$) could have two symmetry-distinct triplet states with similar energy that in one of them, an electron from the $\text{C}=\text{C}$ σ (sp) orbital promotes to the vacant p orbital and in the other one electron from π orbital promote to the p orbital [29, 60]. In 2011, Momeni et al. studied triplet NHC vinylidene silylenes and confirmed their latter choice for the silylidene structures. They indicated that silylidene prefers to form $\pi^1 p^1$ triplet state over $n^1 p^1$, due to the high energy gap between the $3s$ and $3p$ orbitals of Si (Fig. 3) [29]. So, due to the high similarity between silylene and germylene, we guess that vinylidene germylenes behave in the same manner trans to silylene and our results confirm this.

Our NBO analysis shows that the formal charge of Ge(1') in the triplets, because of electron transfer from the π orbital to

Table 1 Calculated second-order perturbation stabilization energies ($E^{(2)}$), for the intermolecular interactions ($LP_{N(4)} \rightarrow \pi^*_{Ge(2')-Ge(1')}$; $P_{Ge(1')} \rightarrow \sigma^*_{N(1)-Ge(2')}$; $P_{Ge(1')} \rightarrow \sigma^*_{N(4)-Ge(2')}$) and occupancy number of $4P_y$ ($Ge(1')$) using NBO analysis at the B3LYP/6-311++G** level of theory for normal 1_R and abnormal 2_R (a) singlet and (b) triplet species

Structures	Donor \rightarrow acceptor	Donor \rightarrow acceptor	Donor \rightarrow acceptor	Occupancy number
(a) Singlet				
$1_{R(s)}$	$LP_{N(4)} \rightarrow \pi^*_{Ge(2')-Ge(1')}$	$P_{Ge(1')} \rightarrow \sigma^*_{N(1)-Ge(2')}$	$P_{Ge(1')} \rightarrow \sigma^*_{N(4)-Ge(2')}$	4Py
$1_{H(s)}$	40.32	4.95	4.95	0.02
$1_{OH(s)}$	1.22	4.55	4.55	0.01
$1_{F(s)}$	7.12	2.33	2.33	0.01
$1_{SH(s)}$	14.10	4.80	4.80	0.01
$1_{OCH3(s)}$	16.76	4.70	4.70	0.16
$1_{CN(s)}$	11.81	4.26	4.26	0.01
$1_{CF3(s)}$	13.60	5.28	5.28	0.53
$1_{Ph(s)}$	0.91	–	–	0.50
$2_{H(s)}$	49.39	1.17	8.32	0.02
$2_{OH(s)}$	6.18	3.43	3.87	0.10
$2_{F(s)}$	16.18	1.46	3.12	0.15
$2_{SH(s)}$	22.22	2.63	3.83	0.01
$2_{OCH3(s)}$	16.80	3.16	3.99	0.40
$2_{CN(s)}$	20.60	2.09	4.27	0.00
$2_{CF3(s)}$	21.32	1.68	5.48	0.02
$2_{Ph(s)}$	2.37	–	9.51	0.22
(b) Triplet				
$1_{R(t)}$	$LP_{N(4)} \rightarrow \pi^*_{Ge(2')-Ge(1')}$	$P_{Ge(1')} \rightarrow \sigma^*_{N(1)-Ge(2')}$	$P_{Ge(1')} \rightarrow \sigma^*_{N(4)-Ge(2')}$	4Py
$1_{H(t)}$	–	1.78	1.78	0.84
$1_{OH(t)}$	–	2.25	2.25	0.45
$1_{F(t)}$	–	2.49	2.49	0.83
$1_{SH(t)}$	–	1.44	1.44	0.86
$1_{OCH3(t)}$	–	1.47	1.47	0.85
$1_{CN(t)}$	–	2.04	2.04	0.83
$1_{CF3(t)}$	–	2.33	2.33	0.60
$1_{Ph(t)}$	–	–	–	0.63
$2_{H(t)}$	1.46	1.12	1.69	0.86
$2_{OH(t)}$	0.54	1.73	1.79	0.85
$2_{F(t)}$	2.35	1.29	2.10	0.83
$2_{SH(t)}$	4.76	–	2.47	0.85
$2_{OCH3(t)}$	0.53	1.80	1.82	0.84
$2_{CN(t)}$	2.23	1.84	1.95	0.83
$2_{CF3(t)}$	1.95	1.84	1.95	0.82
$2_{Ph(t)}$	0.58	–	2.87	0.45

the vacant p orbital, is more than their corresponding singlets (Table 4).

Also, on the basis of the NBO analysis, the triplet state of vinylidene germylenes has a semioccupied $4P_y$ orbital with occupancy number of 0.5–0.8 e, where $4P_y$ occupancy number in singlet is about zero (Table 1).

So, α -germanium substituent due to its electropositive character is a triplet state stabilizer and permits the promotion of an electron from a π orbital to the vacant p orbital (Scheme 2). The molecular electrostatic potential (MEP) and HOMO-LUMO molecular orbitals for singlet and triplet germylenes are shown (Fig. 4).

MEP may be used to predict reactive sites for electrophilic and nucleophilic attack and can be determined experimentally by X-ray diffraction techniques or theoretical calculations. It has its origin in the charge distribution within the molecule. The backbone is formed by the atoms whose nuclei are the centers of positive charge. The electrons with a negative charge are distributed around these nuclei occupying their respective orbitals [63–67].

In the MEP, the color coding from blue to red regions correspond to highly electron deficient to electron-rich regions while green regions suggest almost electrically

Table 2 Thermodynamic parameters for singlet (s) and triplet (t) states of normal and abnormal structures including stability (ΔE_{S-T} /kcal/mol), calculated at two levels of theory, along with B3LYP/6-311++G** which computed the frontier molecular orbital energies (HOMO/kcal/mol andLUMO/kcal/mol), band gap ($\Delta E_{HOMO-LUMO}$ /kcal/mol), nucleophilicity (N /ev), global electrophilicity (ω /ev), and the nucleus-independent chemical shift (NICS) calculated at 1 Å above the ring center

Structures	E_{HOMO}	E_{LUMO}	$\Delta E_{HOMO-LUMO}$	N	ω	NICS(1)	ΔE_{S-T}^a (ΔE_{S-T}^b)
(a) Singlet							
1 _{H(s)}	-113.13	-92.05	21.07	4.56	1.11	-14.82	-
1 _{OH(s)}	-117.90	-96.22	21.68	4.30	11.46	-12.04	-
1 _{F(s)}	-134.42	-110.44	23.97	3.64	13.55	-15.30	-
1 _{SH(s)}	-119.49	-95.74	23.75	4.30	10.57	-12.41	-
1 _{OCH3(s)}	-113.59	-93.15	20.43	4.54	11.33	-12.99	-
1 _{CN(s)}	-144.14	-118.83	25.31	3.21	14.81	-14.33	-
1 _{CF3(s)}	-133.68	-106.95	26.73	3.67	11.74	-15.72	-
1 _{PH(s)}	-116.89	-94.18	22.70	4.40	10.63	-16.19	-
2 _{H(s)}	-103.85	-84.50	19.35	4.96	1.02	-11.31	-
2 _{OH(s)}	-110.20	-90.12	20.08	4.69	10.83	-11.77	-
2 _{F(s)}	-124.38	-102.69	21.68	4.07	12.88	-12.53	-
2 _{SH(s)}	-108.95	-88.28	20.67	4.74	10.20	-11.64	-
2 _{OCH3(s)}	-105.67	-86.14	19.52	4.88	10.20	-12.97	-
2 _{CN(s)}	-131.31	-109.21	22.10	3.77	14.18	-12.94	-
2 _{CF3(s)}	-120.95	-97.62	23.33	4.22	11.09	-13.29	-
2 _{PH(s)}	-105.01	-68.49	36.52	4.91	4.46	-1.87	-
(b) Triplet							
1 _{H(t)}	-123.297	-37.63	85.66	4.12	0.87	-8.04	-14.54 (-11.49)
1 _{OH(t)}	-125.34	-43.62	81.70	4.03	1.89	-8.74	-14.77 (-11.52)
1 _{F(t)}	-137.72	-60.06	77.10	3.52	2.73	-8.85	-13.90 (-11.45)
1 _{SH(t)}	-126.10	-47.15	78.95	4.00	2.06	-7.89	-12.07 (-9.19)
1 _{OCH3(t)}	-123.36	-39.09	84.26	4.12	1.69	-9.10	-15.03 (-11.73)
1 _{CN(t)}	-149.37	-73.49	75.88	2.99	3.54	-7.47	-10.23 (-7.26)
1 _{CF3(t)}	-137.92	-60.98	76.93	3.48	2.78	-7.32	-9.58 (-6.49)
1 _{PH(t)}	-122.58	-44.38	78.20	4.15	1.93	-6.98	-11.91 (-8.50)
2 _{H(t)}	-114.61	-37.03	77.58	4.50	0.81	-3.32	-16.17 (-13.15)
2 _{OH(t)}	-119.97	-40.33	79.64	4.26	1.75	-8.16	-15.85 (-13.44)
2 _{F(t)}	-131.34	-53.56	77.01	3.77	2.38	-8.18	-15.84 (-13.41)
2 _{SH(t)}	-118.54	-48.98	69.56	4.32	2.18	-8.20	-14.89 (-11.91)
2 _{OCH3(t)}	-115.91	-35.99	79.91	4.44	1.56	-8.64	-16.25 (-13.59)
2 _{CN(t)}	-139.78	-85.47	54.31	3.40	5.06	-8.32	-13.35 (-10.26)
2 _{CF3(t)}	-130.21	-63.08	67.12	3.82	3.01	-8.47	-13.02 (-9.52)
2 _{PH(t)}	-112.95	-51.23	61.72	4.57	2.36	-0.53	-13.40 (-11.10)

^aB3LYP/6-311++G**^bM06/6-311++G**

neutral region. MEP (Fig. 4) of title molecule visibly suggests that the major negative potential region lies around oxygen and nitrogen atoms, while germanium (Ge(2')) atoms of tetrazol rings bear maximum burnt of positive potential.

Singlet-triplet energy gap (ΔE_{S-T}) for normal (1_R) and abnormal (2_R) vinylidene germylenes

The singlet-triplet splittings are predicted as the energy differences between the neutral ground state and the lowest triplet

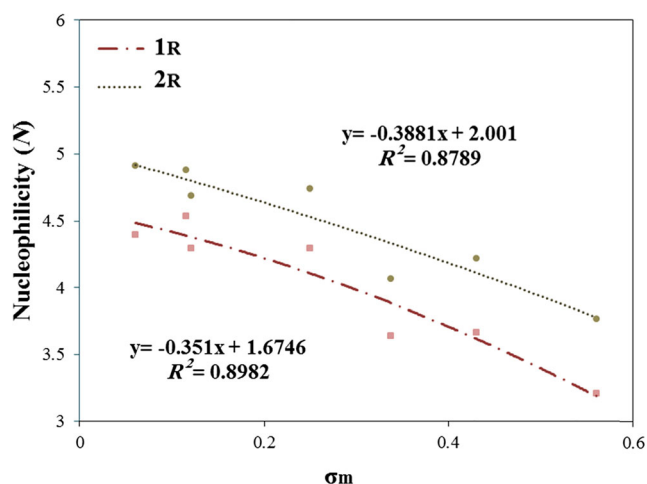


Fig. 1 Correlation between nucleophilicity (N) and Hammett substituent constants (σ_m) for our normal (1_R) vs. abnormal (2_R) tetrazole-5-vinylidene germylenes

state. Stability of every germylene is assumed to depend on its ΔE_{S-T} values which is calculated at B3LYP/6-311++G** and M06/6-311++G** levels of theory (Table 2). In fact, in germylenes, the np valence electrons are spatially separated from ns valence electrons, as a result of Pauli repulsion with the $(n-1)p$ electrons in the inner shells. On the other hand, the electron-electron repulsion between the paired electrons in germylenes is less than their analogues which is due to the larger size of the lone pair orbital that makes the singlet state for these elements to be favored. So germanium prefers to have nonbonding electrons in atomic orbitals with a higher percentage of s character and we can say that the higher s character in the germylenes suggests the stabilization of the singlet state, leading to an increase in singlet-triplet energy gap (ΔE_{S-T}) value as observed [24]. Consequently, the

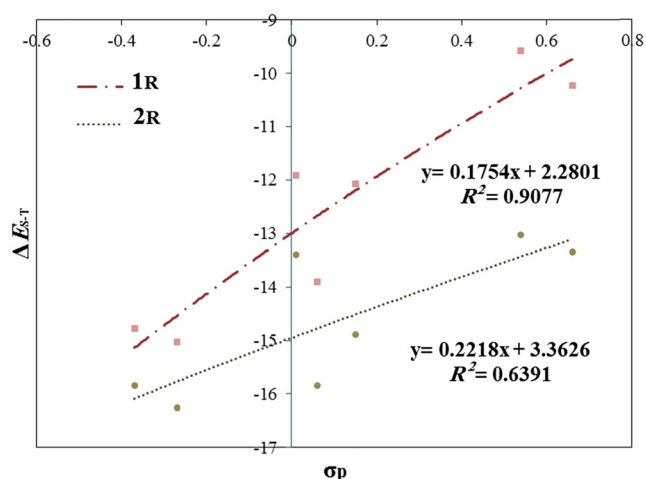


Fig. 2 Correlations between ΔE_{S-T} and Hammett substituent constants (σ_p) for our normal (1_R) vs. abnormal (2_R) tetrazole-5-vinylidene germylenes

probability of triplet stabilization has been investigated through a decrease in ΔE_{S-T} . So, the variation of ΔE_{S-T} can provide useful means in determining the stability of the triplet states compared with the singlets.

Interestingly, a total of sixteen triplet germylenes are encountered as global minimum with rather high stabilities. In accordance with Worthington and Cramer [60] statements and in contrast to Momeni's [29], findings on the stabilization of vinylidene silylenes, our results indicate that in the case of vinylidene germylenes, substituent effect on vinylidene multiplet splitting and the stabilizing $P_{Ge(1')} \rightarrow \sigma^*_{N(4)-Ge(2')}$ interaction is detectable in our triplets (Table 1). So, we confirm that σ -electron-withdrawing interactions bring effects on the germylene ($Ge(1')$) p orbital stabilization, preferentially.

Every triplet abnormal is more stable than its corresponding normal. The ΔE_{S-T} (kcal/mol) for our scrutinized normal vinylidene germylenes immerge consistent with the order of 1_{CF_3} (-9.58) $>$ 1_{CN} (-10.23) $>$ 1_{Ph} (-11.91) $>$ 1_{SH} (-12.07) $>$ 1_F (-13.90) $>$ 1_H (-14.54) $>$ 1_{OH} (-14.77) $>$ 1_{OMe} (-15.03). This order is maintained for abnormal vinylidene germylenes: 2_{CF_3} (-13.02) $>$ 2_{CN} (-13.35) $>$ 2_{Ph} (-13.40) $>$ 2_{SH} (-14.89) $>$ 2_F (-15.84) $>$ 2_{OH} (-15.85) $>$ 2_H (-16.17) $>$ 2_{OMe} (-16.25). Clearly, normal isomers have a rather manifest consistency trends with the abnormal. However, every triplet abnormal isomer shows more stability than its corresponding normal. For instance, stability of triplet 2_{CF_3} ($\Delta E_{S-T} = -13.02$ kcal/mol) is more than that of its corresponding 1_{CF_3} ($\Delta E_{S-T} = -9.58$ kcal/mol). In abnormal isomers, the N(4) nitrogen atom (adjacent to the $Ge(2')$) does not carry any steric effects due to substituent. So, its ability to stabilize with $P_{Ge(1')} \rightarrow \sigma^*_{N(4)-Ge(2')}$ interaction is higher than that in the case of normal isomers with 1,4-substitution pattern. In the confirmation, NBO analyses show that the donation of $P_{Ge(1')} \rightarrow \sigma^*_{N(4)-Ge(2')}$ in the abnormal germylenes is more than that of $P_{Ge(1')} \rightarrow \sigma^*_{N(1)-Ge(2')}$. Another factor that has an effect on triplet abnormal stabilization is the donation of $LP_{N4} \rightarrow \pi^*_{Ge(2')-Ge(1')}$ interaction (Scheme 2), which in the abnormal germylenes is approximately twice of that on the normals (Table 1).

The ΔE_{S-T} also changes as a function of different electronic effects of various types of substituents (1_R and 2_R). In our results, a decrease in ΔE_{S-T} via an increase in the π -electron-donating effect of substituents is detected. Clearly, 1_R and 2_R substituents affect the triplet state through π -donating $LP_{N(1,4)} \rightarrow \pi^*_{Ge(2')-Ge(1')}$ interactions (Table 1, Scheme 3, $a \rightarrow m$ and $a' \rightarrow m'$). Among normal germylenes, 1_{OMe} is the most stable ($\Delta E_{S-T} = -15.03$ kcal/mol) structure, while the least stable structure is 1_{CF_3} with $\Delta E_{S-T} = -9.58$ kcal/mol. Also in abnormal germylenes, the highest ΔE_{S-T} is detectable for 2_{OMe} with $\Delta E_{S-T} = -16.25$ kcal/mol, while the lowest is detectable for 2_{CF_3} with -13.02 kcal/mol (Table 2).

Table 3 Geometrical parameters containing bond angles (deg), bond lengths (Å), and dihedral angle ($\text{Ge}_2\text{-N}_1\text{-N}_2\text{-N}_3$, $\text{Ge}_1\text{-Ge}_2\text{-N}_1\text{-X}$, D) in degrees, at B3LYP/6-311++G** level of theory

	$\text{N}_1\text{-Ge}_2$	$\text{Ge}_2\text{-N}_4$	$\text{N}_1\text{-Ge}_2\text{-N}_4$	$\text{Ge}_2\text{-Ge}_1$	$\text{Ge}_2\text{-N}_1\text{-N}_2\text{-N}_3$	$\text{Ge}_1\text{-Ge}_2\text{-N}_1\text{-X}$	$\text{Ge}_1\text{-Ge}_2\text{-N}_1$	$\text{Ge}_1\text{-Ge}_2\text{-N}_4$
(a) Structures (singlet)								
1 _H	1.85	1.85	80.12	2.41	0.04	0.18	139.94	139.94
1 _{OH}	1.87	1.87	78.00	2.41	10.1	28.53	140.21	140.17
1 _F	1.93	1.93	75.03	2.40	20.57	59.85	135.99	135.99
1 _{SH}	1.87	1.87	80.93	2.40	0.81	3.89	139.41	139.64
1 _{OCH₃}	1.87	1.87	78.10	2.42	1.81	5.16	140.72	141.16
1 _{CN}	1.89	1.89	79.41	2.39	0.01	0.00	140.29	140.29
1 _{CF₃}	1.89	1.89	77.82	2.39	0.02	0.00	141.04	140.17
1 _{Pb}	1.87	1.87	81.45	2.39	1.46	0.38	139.70	138.83
2 _H	1.91	1.91	84.36	2.43	0.00	0.01	133.33	142.29
2 _{OH}	1.91	1.85	82.77	2.42	7.70	21.48	133.90	143.07
2 _F	1.98	1.87	80.93	2.40	13.93	57.31	133.80	139.10
2 _{SH}	1.91	1.85	84.46	2.42	1.83	5.22	131.51	144.01
2 _{OCH₃}	1.91	1.85	82.78	2.42	6.59	13.43	133.58	143.56
2 _{CN}	1.97	1.84	83.28	2.41	0.00	0.01	130.77	145.94
2 _{CF₃}	1.94	1.84	83.02	2.41	0.01	0.04	128.07	148.89
2 _{Pb}	1.92	1.84	83.90	2.41	0.94	175.33	109.02	166.71
(b) Structures (triplet)								
1 _H	1.86	1.86	78.98	2.46	0.00	0.09	140.50	140.50
1 _{OH}	1.88	1.88	76.35	2.46	0.87	6.26	141.81	141.81
1 _F	1.89	1.89	73.45	2.46	0.13	1.19	143.25	143.27
1 _{SH}	1.87	1.87	79.70	2.46	0.90	4.20	140.09	140.20
1 _{OCH₃}	1.88	1.88	76.92	2.46	0.80	4.70	141.33	141.73
1 _{CN}	1.90	1.90	78.16	2.45	0.01	0.02	140.67	141.15
1 _{CF₃}	1.88	1.88	78.78	2.46	0.00	0.02	141.06	141.10
1 _{Pb}	1.87	1.87	80.48	2.45	0.41	2.94	139.71	139.80
2 _H	1.92	1.84	82.98	2.46	0.00	0.00	131.93	145.08
2 _{OH}	1.92	1.86	81.47	2.45	2.01	10.00	135.14	143.29
2 _F	1.95	1.87	79.54	2.45	0.03	0.13	135.58	144.86
2 _{SH}	1.92	1.85	83.05	2.45	0.68	5.65	134.31	142.61
2 _{OCH₃}	1.92	1.85	81.68	2.42	2.00	6.30	134.95	143.34
2 _{CN}	2.00	1.83	81.56	2.44	0.00	0.16	132.08	146.35
2 _{CF₃}	1.97	1.84	81.59	2.45	0.00	0.00	136.08	142.32
2 _{Pb}	1.95	1.82	83.25	2.45	1.12	4.76	134.82	141.90

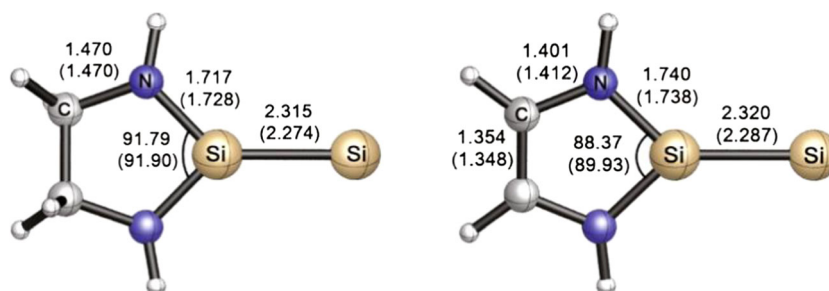
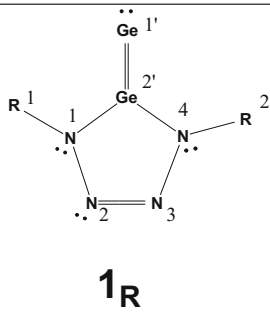
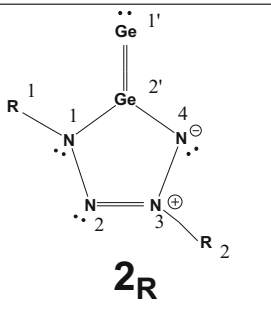
Fig. 3 Scrutinized N-heterocyclic vinylidene silylenes in Momeni et al. studies [22]

Table 4 The NBO analyses including atomic charges for normal (**1**) and abnormal (**2**) vinylidene germylenes, calculated at B3LYP/6-311++G** level of theory



1_R

vs.

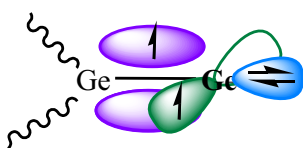


2_R

Singlet species	Atomic Charges						Triplet species	Atomic Charges					
	Ge ₁ '	Ge ₂ '	N ₁	N ₂	N ₃	N ₄		Ge ₁ '	Ge ₂ '	N ₁	N ₂	N ₃	N ₄
1_H	-0.16	1.00	-0.82	-0.01	-0.01	-0.82	1_H	-0.30	1.14	-0.82	-0.02	-0.02	-0.82
1_{OH}	0.11	0.75	-0.31	-0.05	-0.05	-0.31	1_{OH}	0.00	0.82	-0.28	-0.07	-0.07	-0.28
1_{OMe}	0.09	0.76	-0.30	-0.05	-0.05	-0.30	1_{OMe}	-0.01	0.83	-0.27	-0.06	-0.06	-0.27
1_F	0.24	0.65	-0.17	-0.04	-0.04	-0.17	1_F	0.06	0.78	-0.16	-0.05	-0.05	-0.16
1_{SH}	0.13	0.81	-0.79	-0.02	-0.02	-0.79	1_{SH}	0.00	0.93	-0.77	-0.03	-0.03	-0.77
1_{Ph}	-0.01	0.86	-0.57	-0.04	-0.04	-0.57	1_{Ph}	-0.01	0.86	-0.57	-0.04	-0.04	-0.57
1_{CN}	0.28	0.76	-0.65	0.02	0.02	-0.65	1_{CN}	0.15	0.90	-0.66	0.01	0.01	-0.66
1_{CF3}	0.24	0.77	-0.68	0.00	0.00	-0.68	1_{CF3}	0.09	0.91	-0.68	-0.01	-0.01	-0.68
2_H	-0.12	0.98	-0.72	-0.81	-0.06	-0.08	2_H	-0.29	1.10	-0.73	-0.78	-0.03	-0.09
2_{OH}	0.06	0.77	-0.27	-0.08	0.30	-0.72	2_{OH}	-0.04	0.82	-0.25	-0.07	0.29	-0.70
2_{OMe}	0.03	0.77	-0.25	-0.07	0.30	-0.69	2_{OMe}	-0.05	0.82	-0.23	-0.07	0.29	-0.68
2_F	0.16	0.67	-0.13	-0.08	0.38	-0.58	2_F	0.03	0.78	-0.13	-0.06	0.37	-0.59
2_{SH}	0.06	0.80	-0.69	-0.09	-0.06	-0.73	2_{SH}	-0.04	0.86	-0.67	-0.09	-0.07	-0.70
2_{Ph}	0.00	0.82	-0.49	-0.08	0.02	-0.71	2_{Ph}	-0.07	0.84	-0.48	-0.07	0.02	-0.70
2_{CN}	0.20	0.75	-0.56	-0.02	-0.03	-0.64	2_{CN}	0.07	0.84	-0.54	-0.01	-0.04	-0.65
2_{CF3}	0.14	0.77	-0.61	-0.04	-0.03	-0.67	2_{CF3}	0.02	0.85	-0.58	-0.03	-0.04	-0.67

Nucleus-independent chemical shift (NICS) for normal (**1_R**) and abnormal (**2_R**) vinylidene germylenes

The nucleus-independent chemical shift (NICS) is a computational method that evaluates the absolute magnetic shielding at the center of a ring. The NICS values are reported with a reversed sign to make them compatible with the chemical shift conventions of NMR spectroscopy. Positive NICS values indicate antiaromaticity while rather high negative values point out aromaticity [68]. NICSs are calculated at 0.5, 1, 1.5, and

**Scheme 2** The π^1p^1 triplet germanium germylene

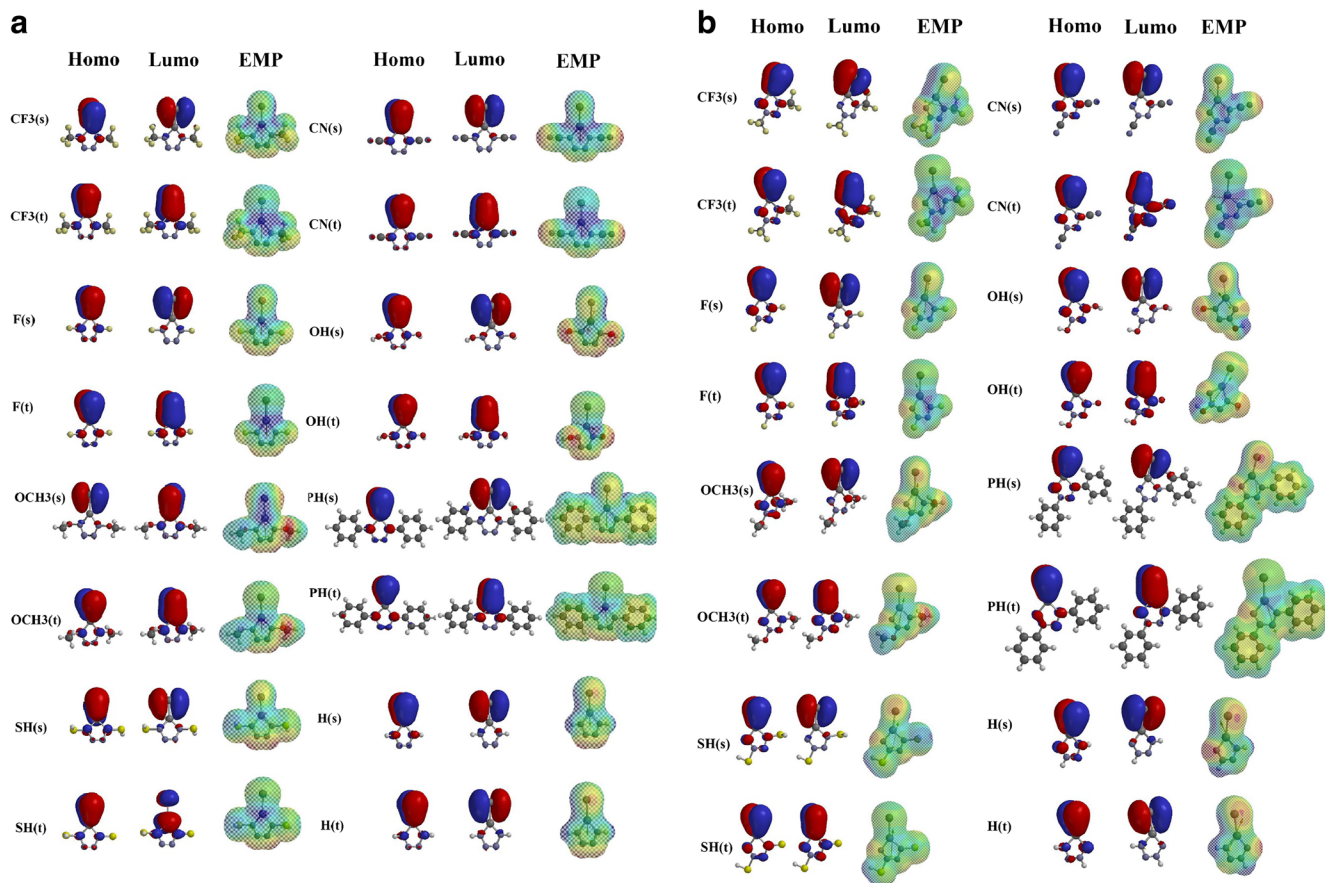
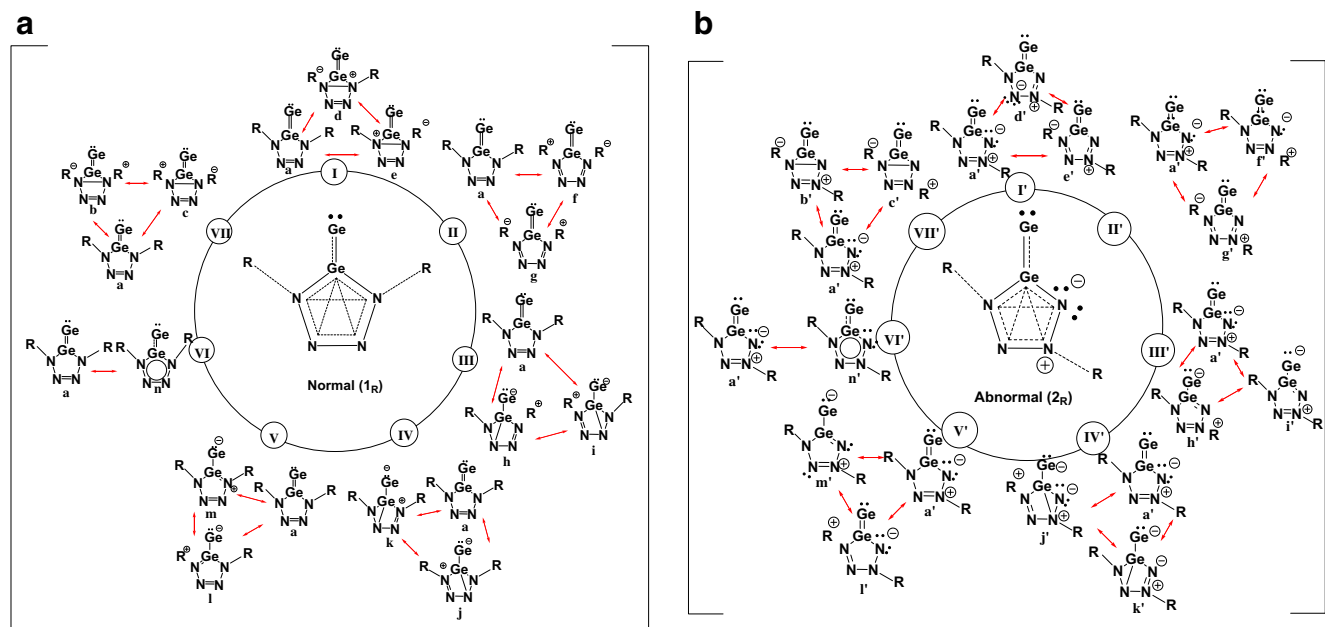


Fig. 4 Shapes of electrostatic potential maps (EMP) and HOMO-LUMO molecular orbitals for singlet and triplet **a** normal 1_R and **b** abnormal 2_R vinylidene gemylenes

2 Å above the ring center for singlet and triplet normal and abnormal vinylidene gemylenes, at B3LYP/6-311++G** level of theory. Our NICS calculations show that every normal 1_R

congress is more aromatic than its corresponding abnormal, 2_R . However, singlet state of 2_{Ph} shows the smallest NICS value (Table 2).



Scheme 3 Electron delocalizations through seven sets of possible canonical forms (I–VII) for our **a** normal 1_R and **b** abnormal 2_R gemylenes

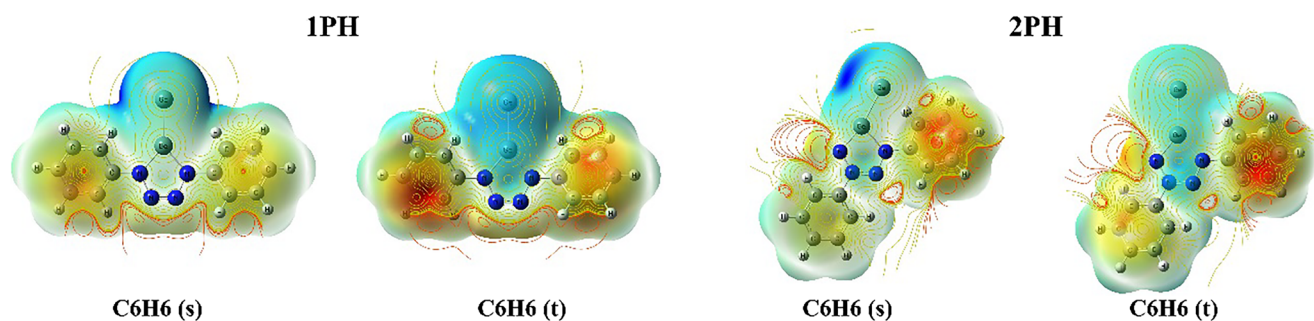


Fig. 5 Shapes of total density EMP and contours for singlet and triplet 1_{Ph} and 2_{Ph}

Negative charge of Ge(1') in singlet state of 2_{Ph} is less than singlet state of 1_{Ph} , which is in contrast to the other structures (Table 4). We found that 2_{Ph} in singlet state has $LP_{Ge(1')} \rightarrow \sigma^*_{C-C}$ (0.75 kcal/mol) and $LP_{Ge(1')} \rightarrow \sigma^*_{C-H}$ (1.91 kcal/mol) electron donation interactions which make Ge(1')–Ge(2') to be more skew than that of triplet and normal isomers (Fig. 5). In this case, the antiaromaticity value decreases and on the other hand, there is no antiaromaticity in singlet state of 2_{Ph} .

The resonance hybrid structures (Scheme 3) for vinylidene germynes coupled with the electrostatic potential maps (Fig. 4) reveal the electronic effects on (a) normal 1_R and (b) abnormal 2_R isomers (Fig. 6).

Conclusions

We have reached at two sets of normal and abnormal exocyclic vinylidene triplet germynes (1_R and 2_R) that appear rather more stable than several other calculated triplet germynes. Investigating the effects of the R groups ($R = H, CF_3, CN, C_6H_6, SH, F, OMe, \text{ and } OH$) leads us to the ΔE_{S-T} values of $-9.58, -10.23, -11.91, -12.07, -13.90, -14.77,$ and -15.03 kcal/mol for normal vinylidene germynes and $-13.02, -13.35, -13.40, -14.89, -15.84, -15.85$ and -16.25 kcal/mol for abnormal isomers, respectively, at the B3LYP/6-311++G** level. Clearly, every triplet abnormal isomer shows more stability than its corresponding normal. Variation of the substitution pattern in normal (1_R) and

abnormal (2_R) isomers effects on σ -donor capacities of the species. It is found that the abnormal isomers with 1,3-substitutions are stronger electron donors than their normal congeners. Also, in our results, a decrease in ΔE_{S-T} via an increase in π -electron-donating effect of substituents is detected. The geometrical parameters (bond lengths, angles) of the reported germynes are performed at B3LYP/6-311++G** level of theory. NICS calculations show that every normal isomer appears more aromatic than its corresponding abnormal, except for singlet state of 2_{Ph} which appears less antiaromatic than the others. All the results indicate the role of aromaticity and delocalization of the π -system as a stabilizing factor. Furthermore, all abnormal 2_R isomers have wider band gaps and more nucleophilicity (N) but less electrophilicity (ω) than their normal 1_R isomers. Our Hammett studies indicate that 1_R is more sensitive to the electronic effects of substituents, R , than 2_R . Electron-donating species increase N in both 1_R and 2_R , while electron-withdrawing groups increase stability.

Consequently, we have found abnormal forms of tetrazol-5-vinylidene germynes with electron-donating substitutions could decrease the ΔE_{S-T} value enough to bring the resulting novel stable triplet germynes which indicate more stability and nucleophilicity (N) than their corresponding normals.

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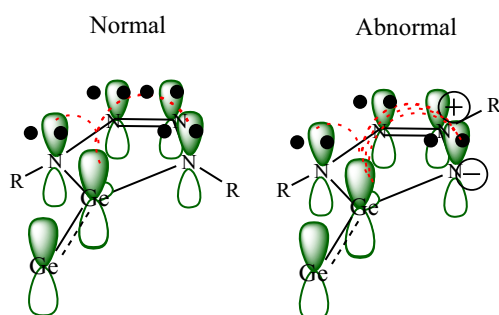


Fig. 6 The π -interaction between germanium and the adjacent nitrogens

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