Pyridine derived N-heterocyclic germylenes: A density functional perspective

M.Z. Kassaee *, M.R. Momeni, F.A. Shakib, M. Ghambarian

Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

ABSTRACT

Three novel germanimines, 2-, 3-, and 4-germapyridines (**1**, **2**, and **3**, respectively) along with their isomeric germylenes, are compared and contrasted at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G* level of theory. From a thermodynamic viewpoint, two germylenes out of a total of eight singlet minima, 1H-2-germapyridine-2-ylidene (**1a**) and 1H-4-germapyridine-4-ylidene (**3a**), are found 29.2 and 15.4 kcal/mol more stable than their corresponding aromatic germapyridine isomers, respectively. Indeed, **1a** is the global minimum on the potential energy surface of cyclic C_4NGeH_5 with a singlet–triplet energy gap larger than that of Herrmann's germylene, i.e. 57.4 vs. 49.7 kcal/mol. From a kinetic viewpoint, the calculated energy barrier for 1,2-H shift of **1a** to **1** is 70.8 kcal/mol compared to more prohibitive 92.5 kcal/mol for 1,4-H shift of **3a** to **3**. No Ge=Ge doubly bonded minimum structure is found as dimer for **1a**. The doubly bonded dimer of **3a** is 11.2 kcal/mol less stable than its two separate monomers. This study signifies the thermodynamic and kinetic stabilities of divalent **1a** and **3a** hoping to prompt the experimental attentions toward them.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In 1960s, organometallic chemistry encountered the start point of a series of revolutionary studies when the old idea of the unstable double bonds between heavier main group elements was broken down [1–4]. In this way, the valuable studies directed by Satgé introduced first transient intermediates having germanium doubly bonded to nitrogen (germanimines) in 1978 [5,6]. On the other hand, following the pioneering work of Märkl in 1980s [7] and the theoretical calculations of Kiprof and Brown [8], Tokitoh et al. reported the synthesis of the first stable germabenzene in 2002 [9]. Combining these two apparently different subjects, germanimine and germabenzene, one may reaches at germapyridines whose identification opens the gates toward the heavier congeners of our interested pyridine-derived N-heterocyclic carbenes [10] and silylenes [11]. Here, we have considered three *ortho*, *meta*, and *para* germapyridines none of which has been previously under experimental or theoretical investigations. Following the previous reports of our laboratory, now, we are looking for a new generation of N-heterocyclic germylenes. The study of N-heterocyclic germylenes backs to 1987 when Veith succeeded to synthesize a series of metallylenes, including germylene (**I**), with a four-membered structure stabilized by two adjacent nitrogens (Scheme 1) [12]. Some years later and following the synthesis of the first stable carbene by Arduengo in 1991 [13] Hermann's group reported the synthesis of the five-membered N-heterocyclic germylene congener (**II**) in 1992 [14]. After four and five-membered N-heterocyclic germylenes it was time for the synthesis of six-membered ones which was accomplished in 1998 in a push-pull structure (**III**) [15] and in 2006 in a dicoordinated one (**IV**) [16] and will possibly go on with germapyridine-derived ones in future.

Now, we are pleased to report the first theoretical study on the cyclic germapyridines with an especial focus on the corresponding germylenes and show how these novel N-heterocyclic germylenes seem thermodynamically and kinetically more stable than the previously synthesized ones.

2. Computational details

Full geometry optimizations were accomplished without any symmetry constraints by means of hybrid functional B3LYP [17–19] and the 6-31+G* basis set, employing the GAUSSIAN 98 code [20]. The applied basis set was comprised of Pople's well known 6-31G* basis set [21,22] and an extra plus due to the importance of diffuse functions [23,24]. The reliability of the optimized structures was confirmed through altering of the basis set (B3LYP/LANL2DZ) and method (MP2/6-31+G* [25]). To obtain more accurate energetic data, single point calculations were performed at B3LYP/AUG-cc-pVTZ [26] based on the B3LYP/6-31+G* geometries. The transition states (TSs) linking the initial and final structures, were found using the reactants-products quasi-synchronous transit (QST2) algorithm [20]. The frequency calculations were applied to characterize the structures as minimum or TS [27]. Nucleus independent chemical shift (NICS) calculations [28] were

* Corresponding author. Tel.: +98 21 82883441; mobile: +98 912 1000392; fax: +98 21 88006544.
E-mail address: Kassaeem@Modares.ac.ir (M.Z. Kassaee).
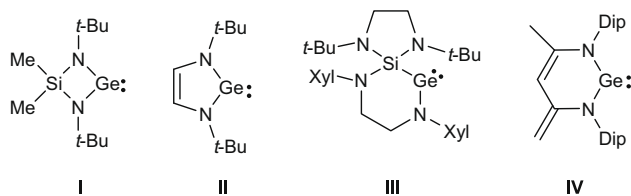
Scheme 1.

performed using the gauge independent atomic orbital (GIAO) method at B3LYP/6-311++G**//B3LYP/6-31+G* level.

The nucleophilicity index, N, which is recently introduced by Domingo et al. [29], is calculated as $N = E_{HOMO(Nu)} - E_{HOMO(TCE)}$, where tetracyanoethylene (TCE) is chosen as the reference. The global electrophilicity, ω [30], is also calculated following the expression, $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu \approx (E_{HOMO} + E_{LUMO})/2$) and η is the chemical hardness ($\eta = E_{LUMO} - E_{HOMO}$) [31].

3. Results and discussion

The B3LYP/6-31+G* is applied to fully optimize 2-, 3-, and 4-germapyridines (**1**, **2**, and **3**) along with their corresponding germylene isomers (Figs. 1 and 2).

3.1. Germapyridines

The optimized geometrical data for germapyridines are validated by the basis set alteration (B3LYP/LANL2DZ, in parenthesis), and the alternate method implication (MP2/6-31+G*, in brackets). The consistency between the geometrical parameters obtained from the three levels of theory convinced us to confine our remaining calculations to B3LYP/6-31+G*, for the sake of time saving. However, both singlet and triplet states of a selected germylene are optimized at the three levels for more confidence which are available at the Supporting information.

Conforming to the aromatic pyridine, our germapyridines are expected to benefit the stabilization of the cyclic electron delocalizations. Hence, the NICS index is calculated as an indicator for this delocalization, using aromatic benzene as the reference (NICS(1) = −10.20 ppm). The resulted NICS(1) values for **1**, **2**, and **3** not only emphasize their aromatic characters (−7.76, −8.70, and −8.68 ppm, respectively) but also appear close to each other. Furthermore, comparison between these values with those of pyridine and germabenzene (−10.10 and −8.92 ppm, respectively) shows that the aromatic characters of these molecules are more

similar to the latter (see the table of NICS data in the Supporting information).

Based on the concept of ISE (isomerization stabilization energy) for evaluation of the aromatic stabilization energy of pyridine and benzene used by Schleyer and Pühlhofer [32], the stabilization energy of our aromatic compounds can also be estimated by the energy of the isodesmic reactions 1–5 (Scheme 2). Compared to the isodesmic reactions used by Schleyer and Pühlhofer, our reactions are modified through introducing a second ring which negates the contamination of the exocyclic double bond. In order to cancel out the anti-syn mismatches [32], the energy of the reactions 1–4 are corrected with that of reaction 5.

Confirming the resulted NICS values, the similarity between aromatic stabilizations of germapyridines **1–3** and the synthesized germabenzene (all about −26.0 kcal/mol) may suggest the accessibility of the formers.

3.2. Germylenes from a thermodynamic viewpoint

Three germylene isomers are considered for each of **1** and/or **2**, while only two are derived from **3** (Fig. 2). Interestingly, two N-heterocyclic germylenes are found more stable than their corresponding germapyridine isomers. Indeed, the singlet germylene **1a** emerges as the global minimum on the potential energy surface of cyclic C$_4$GeNH$_5$ exhibiting 29.2 kcal/mol more stability than its full-valence isomer **1**. A comparable result was also observed for its silylene analogue, 1H-2-silapyridine-2-ylidene, which was 9.80 kcal/mol more stable than its full-valence isomer [11,33]. These are in complete contrast to the carbene congener that was 43.4 kcal/mol less stable than pyridine [10].

The other exciting singlet germylene is **3a** which lies 19.0 kcal/mol higher than singlet **1a** and is 15.4 kcal/mol more stable than its corresponding full-valence isomer **3**. Although most of the remaining germylenes show relative energies resembling those of the corresponding full-valence isomers, our discussion is constrained to **1a** and **3a** (find the discussion of the tabulated data of the other isomers in the Supporting information). The higher relative stability of **1a** is due to the anticipated electron donating characteristic of the adjacent nitrogen in **1a** which induces a moderate aromaticity in the ring (NICS(1) = −6.38 ppm). Our calculations indicate that nitrogen atom stabilizes the singlet state of **1a** to the extent that its ΔE_{s-t} is found as large as 57.4 kcal/mol (Table 1). To reach at a practical comparison, the same calculations are carried out for the parent forms of four- to six-membered N-heterocyclic germylenes (**V**, **VI**, and **VII**) synthesized by Veith, Herrmann, and Driess, respectively. The resulted ΔE_{s-t}s show that Veith structure induces more stability to the singlet germylenic center, compared
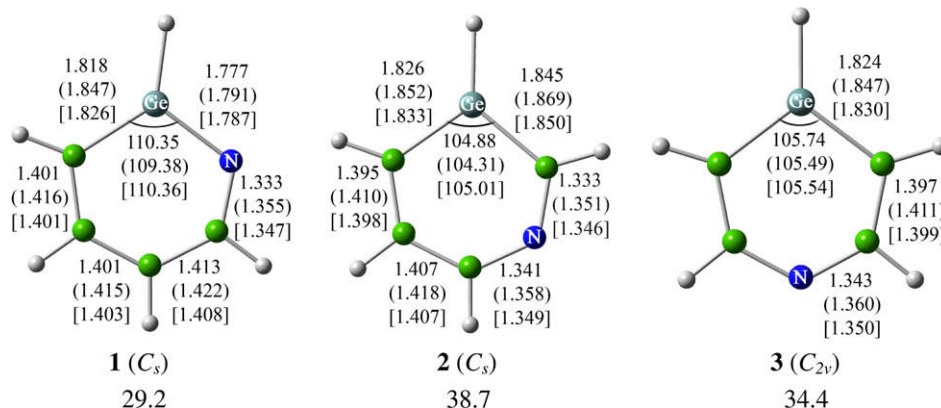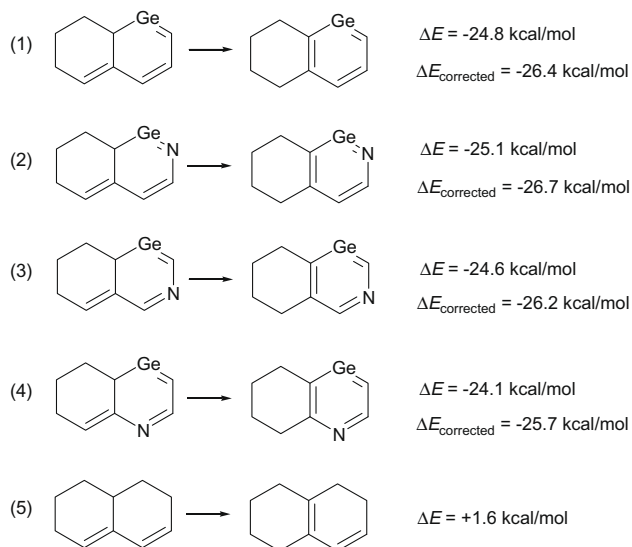

Fig. 1. Principal geometrical parameters (bond length/Å and angle/°) for germapyridines at B3LYP/6-31+G*, B3LYP/LanL2DZ (in parenthesis) and MP2/6-31+G* [in brackets] as well as relative energies (in kcal/mol) at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*.

(1) ΔE = -24.8 kcal/mol

$\Delta E_{\text{corrected}}$ = -26.4 kcal/mol

(2) ΔE = -25.1 kcal/mol

$\Delta E_{\text{corrected}}$ = -26.7 kcal/mol

(3) ΔE = -24.6 kcal/mol

$\Delta E_{\text{corrected}}$ = -26.2 kcal/mol

(4) ΔE = -24.1 kcal/mol

$\Delta E_{\text{corrected}}$ = -25.7 kcal/mol

(5) ΔE = +1.6 kcal/mol

Scheme 2.

Table 1
Singlet–triplet (ΔE_{s-t}), HOMO–LUMO ($\Delta E_{\text{HOMO–LUMO}}$) energy separations (in kcal/mol), minimum vibrational frequencies ($v_{\min}$ in cm^{-1}), and dipole moments (D in Debye) for the scrutinized structures.

Structure	ΔE_{s-t}[a]	$\Delta E_{\text{HOMO–LUMO}}$[b]	$\gamma_{\min}$[c]	D[c]
1	–	106.7	270.31	2.25
1a	57.4	102.5	254.28	2.24
1b	38.0	82.1	137.52	3.15
1c	42.2	77.7	87.08	3.67
2	–	107.1	254.24	2.52
2a	23.3	72.6	161.31	1.75
2b	23.4	71.7	163.11	2.15
2c	27.9	66.9	92.55	2.20
3	–	115.4	270.55	3.04
3a	52.9	94.9	219.08	4.87
3b	29.7	81.8	190.69	1.04
V	73.7	120.4	245.75	0.16
VI	49.7	98.7	405.02	1.32
VII	42.8	78.0	140.43	1.86

[a] At the B3LYP/AUG-cc-pVTZ level.
[b] At the B3LYP/6-311++G** level.
[c] For singlet species at the B3LYP/6-31+G* level.

to Herrmann's and Driess's (Table 1). Interestingly, the calculated ΔE_{s-t} of **1a** is larger than the ΔE_{s-t} of **VI** and **VII** that are 49.7 and 42.8 kcal/mol, respectively (Scheme 3).

The germylene **3a** demonstrates a ΔE_{s-t} as large as 52.9 kcal/mol, very close to that of **1a** which benefits from adjacent nitrogen (Table 2). This calculated ΔE_{s-t} is again more than that of parent germylenes **VI** and **VII**. The possible conjugation of nitrogen lone pair with the empty germylenic *p* orbital in **3a** through intermediacy of a double bond can be considered as the main reason for its

Table 2
Stabilizing energy compared to the parent germylene (ΔE), heat of hydrogenation (ΔE_H), energy barrier ($\Delta E^{\ddagger}$) for isomerizations of the studied germylenes, and dimerization energy (ΔE_{dimer}) (in kcal/mol), at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G* level of theory.

Structure	ΔE[a]	ΔE_H[b]	$\Delta E^{\ddagger}$	ΔE_{dimer}
1a	36.2	−4.8	70.8	–
1b	13.2	−27.8	33.9	−22.3
1c	14.4	−26.6	57.5	−19.8
2a	12.8	−28.1	25.3	−19.1
2b	9.6	−31.3	23.5	−26.9
2c	11.7	−29.2	51.4	−23.5
3a	26.0	−14.9	92.5	11.2
3b	15.9	−25.0	37.7	−8.5
V	38.9	−2.1	–	–
VI	55.1	14.2	–	–
VII	41.2	0.21	–	–

[a] Based on the isodesmic reaction: $R_1R_2Ge: + GeH_4 \rightarrow R_1R_2GeH_2 + H_2Ge$.
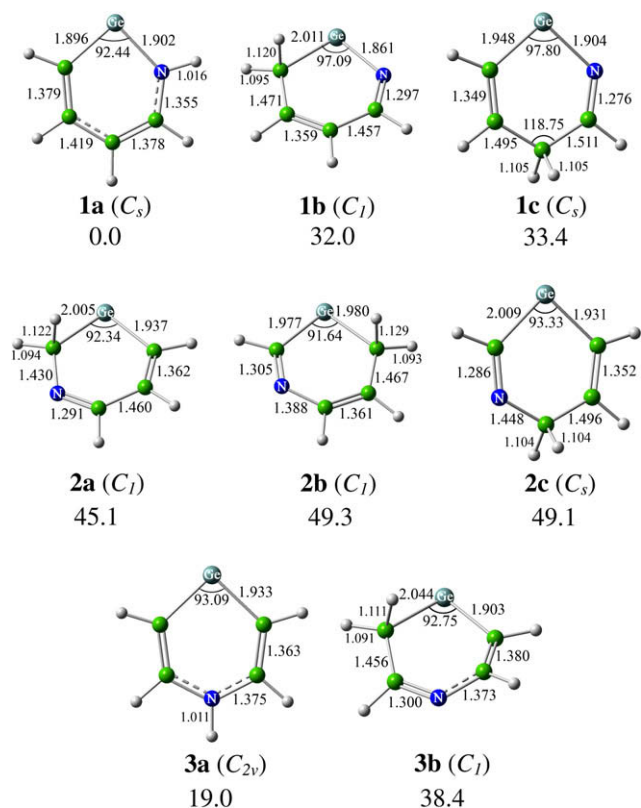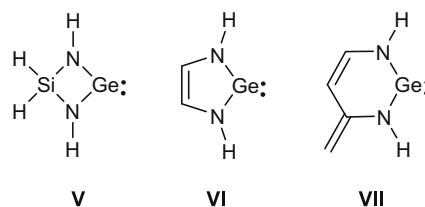[b] Based on the isodesmic reaction: $R_1R_2Ge: + H_2 \rightarrow R_1R_2GeH_2$.

stability. The NICS calculations on this planar molecule (with C_{2v} symmetry) show a moderate aromaticity with the NICS(1) value of −6.58 ppm which reveals the stabilizing effects of the nitrogen atom.

As stated by Hoffmann, Schleyer and Schaefer, a molecule could be called stable if it is computed smallest vibrational frequency is at least 100 cm^{-1} and displays a large HOMO–LUMO energy separation ($\Delta E_{\text{HOMO–LUMO}}$) [34]. Fortunately, besides aromatic germapyridines, **1a** and **3a** fulfill these conditions indicating the smallest vibrational frequencies above 200 cm^{-1} and $\Delta E_{\text{HOMO–LUMO}}$'s about 100 kcal/mol (Table 1). These practical facts open the way for investigations on the stability of these germylenes.

Fig. 2. Principal geometrical parameters (bond length/Å and angle/°) for eight scrutinized N-heterocyclic germylenes at B3LYP/6-31+G* as well as their relative energies (in kcal/mol) at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*.

Scheme 3.

The stabilizing energies of our scrutinized structures on the parent germylene H_2Ge: are measured at B3LYP/AUG-cc-pVTZ (Table 2). The positive ΔE values obtained for all our germylenes indicate their stabilization energy compared to H_2Ge: with the highest one demonstrated by **1a** followed by **3a** ($\Delta E = 36.2$ and 26.0 kcal/mol, respectively). Interestingly, the stabilizing energy of one adjacent nitrogen in the six-membered **1a** is comparable to two nitrogens in the four-membered **V** ($\Delta E = 36.2$ vs. 38.9 kcal/mol) and is close to that of two adjacent nitrogen in the six-membered **VII** ($\Delta E = 36.2$ vs. 41.2 kcal/mol). However, two adjacent nitrogen atoms in the five-membered **VI** have a relatively much greater stabilizing energy on H_2Ge: ($\Delta E = 55.1$ kcal/mol) (Table 2).

The hypothetical hydrogenation of our germylenes may offer a practical criterion for probing their stabilities. Interestingly, the energy difference between the reactive species **1a** and its hydrogenated form is only 4.8 kcal/mol which gives hope for the isolation of the former. Similarly, **V** is only 2.1 kcal/mol higher in energy than its hydrogenated form. This difference for **3a** is 14.9 kcal/mol, while those for all the other studied germylenes exceed 25.0 kcal/mol.

3.3. Germylenes from a kinetic viewpoint

In their valuable study, Hoffmann, Schleyer and Schaefer stated that a stable species should be resistant to fragmentation, isomerization and dimerization [34]. On this basis, identifying the possible reactions threatening our germylenes' stabilities, isomerization to germapyridine and dimerization seem to be worthy of investigation.

3.3.1. Isomerization to germapyridine

Due to structural differences, the germylenes **1a**, **1b**, **2a**, **2b**, and **3b** rearrange to the corresponding germapyridines through 1,2-*H* shift while the others, **1c**, **2c**, and **3a**, go through 1,4-*H* shift (find the transition states for all the germylenes in Supporting information) (Figs. 3 and 4). The thermodynamically stable **1a** shows a prohibitive high energy barrier for 1,2-*H* shift via a planar transition state in a value of 70.8 kcal/mol (Table 2).

However, the interesting result is the barrier found for the isomerization of **3a** to **3** via 1,4-*H* shift. Due to the planar structure
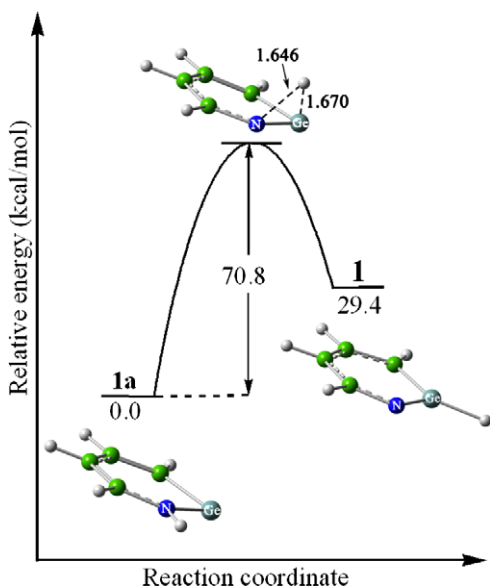

Fig. 3. The transition state obtained for the rearrangement of **1a** to **1** through 1,2-*H* shift at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*.
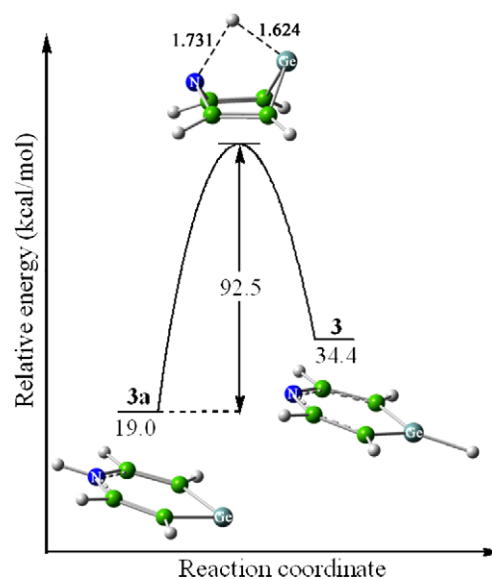

Fig. 4. The transition state obtained for the rearrangement of **3a** to **3** through 1,4-*H* shift at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G*.

of **3a**, the energy required to reach at a boat transition state is 92.5 kcal/mol. This value is significantly higher than that of **1a** which turns the concept of more kinetic stability toward **3a** while the thermodynamic one is toward **1a**. These findings are in accord with those of carbene and silylene analogues in our previous reports [10,11].

3.3.2. Dimerization

Dimerization of heavier group 14 carbene analogues leads to either doubly bonded or, if possible, cyclic bridged dimers (Scheme 4) [35]. In order to reach at a doubly bonded dimer of **1a** two monomers are placed in a same plane and their distance is decreased. This results in no minimum structure but a first-order saddle point. Therefore, one of the monomers is tilted out of the plane and decreasing of the distance leads to a minimum structure with no bond between the two germylenic centers (Fig. 5). Not only the distance between the two divalent germylenes is longer than a single Ge–Ge bond (2.780 vs. 2.440 Å), but also there is no considerable energy difference between the resulted structure and two separate monomers. The same result is obtained for the parent forms of Herrmann's and Veith's molecules.

In contrast, a minimum structure is found as the cyclic bridged dimer of **1a** with two by two equal Ge–N bonds with the lengths of 2.027 and 2.161 Å. Since both these bonds are longer than a typical
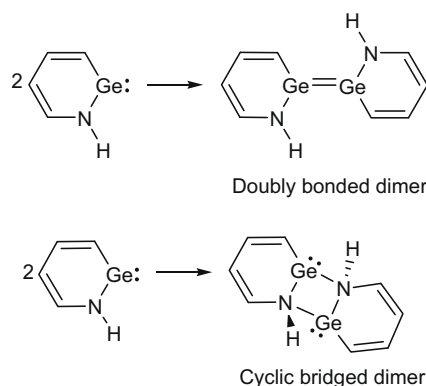
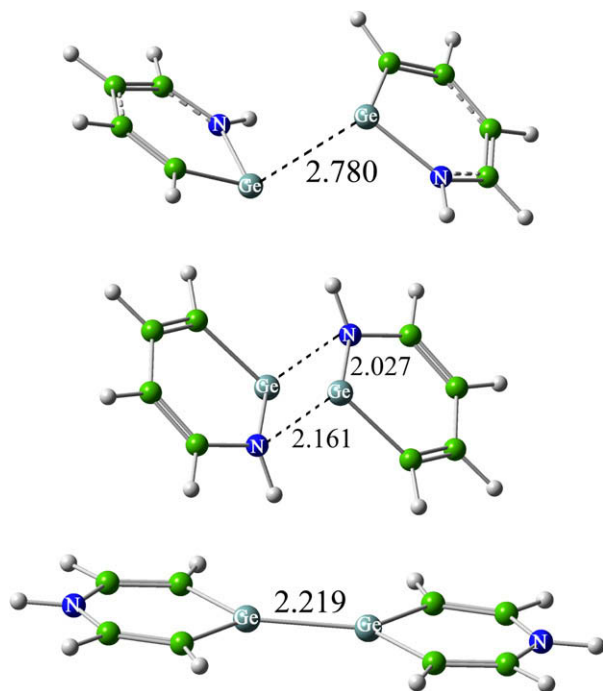**Scheme 4.** Two possible modes of dimerization for **1a**.

Fig. 5. Top: no doubly bonded dimer is found for **1a** (the efforts lead to a minimum structure but with the Ge–Ge bond longer than a single bond); Center: the cyclic bridged dimer of **1a**; Bottom: the doubly bonded dimer of **3a**.

Ge–N bond (1.920 Å), it is not surprising if the energy of this dimer lies 19.4 kcal/mol higher than the total energies of the two separate monomers. Interestingly, its silylene analogue experiences the same situation since no doubly bonded minimum structure is found for the two monomers in a same plane. Tilting one of the monomers leads to a minimum but the distance between the two silylenic centers is longer than a typical single Si–Si bond (2.557 vs. 2.340 Å). Moreover, cyclic bridged dimer is calculated 23.6 kcal/mol less stable than the two separate monomers. Carbene analogue of **1a** shows a completely different behavior where it readily dimerizes to a doubly bonded structure ($\Delta E = -62.0$ kcal/mol) but avoids dimerizing to a cyclic bridged one ($\Delta E = +61.3$ kcal/mol).

Dimerization of **3a**, that is the most thermodynamically stable isomer after **1a**, leads to a doubly bonded minimum structure which is 11.2 kcal/mol higher in energy than the two separate monomers (Fig. 5). The length of Ge=Ge bond (2.219 Å) is indicative of a complete double bond. Endothermicity of this reaction indicates that dimerization is unfavorable for **3a**, just as **1a**. In contrast, dimerization of silylene analogues of **3a** is exothermic with the value of -17.0 kcal/mol leading to a tilted structure with a single Si–Si bond (2.334 Å). The carbene analogue readily dimerizes ($\Delta E = -98.0$ kcal/mol) and forms a nearly double bonded planar structure (with the C=C bond length of 1.385 Å).

3.4. Nucleophilicity and electrophilicity

Metallylenes, including germylenes, are expected to have an inert lone pair due to their high *s*-character while they are highly reactive toward the nucleophilic attack to their empty *p* orbitals [35]. Hence, to classify the reactivity of our germylenes, their nucleophilicity and electrophilicity is evaluated using appropriate indices (Table 3).

While the nucleophilicities of our germylenes stretch in a close range from 3.32 to 3.70 eV, their electrophilicities shows considerable differences. Where the ω values of 1.73 and 1.66 eV for **1a** and

Table 3
The nucleophilicity (N) and the global electrophilicity indices (ω), obtained from the energies of the frontier molecular orbitals, HOMO and LUMO, calculated at B3LYP/6-311++G**.

Structure	HOMO (au)	LUMO (au)	N (eV)	ω (eV)
1	−0.23233	−0.0623	3.14	1.74
1a	−0.22581	−0.0624	3.32	1.73
1b	−0.22517	−0.0943	3.33	2.65
1c	−0.22505	−0.1012	3.34	2.92
2	−0.23109	−0.0604	3.17	1.69
2a	−0.22222	−0.1065	3.41	3.17
2b	−0.22089	−0.1067	3.45	3.19
2c	−0.2175	−0.1108	3.54	3.44
3	−0.24844	−0.0645	2.70	1.81
3a	−0.21159	−0.0603	3.70	1.66
3b	−0.23029	−0.0999	3.19	2.84
V	−0.24977	−0.058	2.66	1.68
VI	−0.19416	−0.037	4.18	1.15
VII	−0.18798	−0.064	4.34	1.73
TCE	−0.34764	−0.1951	0.00	6.57

3a indicate their resistance vs. nucleophilic attack, the high values of 3.17–3.44 eV of **2a–2c** emphasize their high reactivity. Electrophilic behavior of **1a** and **3a** resembles those of **V** and **VI** with ω values of 1.68 and 1.73 eV while **VII** is more resistant to the nucleophilic attack (ω = 1.15 eV).

3.5. Alkylation

We wonder the effect of alkylation on the relative stabilities of the most stable germylenes and their corresponding full-valence isomers. Among *t*-Bu substituted germapyridines (**1$_{t\text{-Bu}}$** and **3$_{t\text{-Bu}}$**) and germylenes (**1a$_{t\text{-Bu}}$** and **3a$_{t\text{-Bu}}$**) we found **1a$_{t\text{-Bu}}$** as the global minimum which is 16.1 kcal/mol more stable than **1$_{t\text{-Bu}}$**. Although this difference in relative energies of **1a$_{t\text{-Bu}}$** and **1$_{t\text{-Bu}}$** is 13.1 kcal/mol less than that between **1a** and **1**, but in contrast to silylene analogue, alkyl substitution can not reverse the relative stabilities [33]. The other stable germylene, **3a$_{t\text{-Bu}}$**, lies 18.3 kcal/mol above the global minimum **1a$_{t\text{-Bu}}$** similar to the relationship of **3a** and **1**. Germapyridine **3$_{t\text{-Bu}}$** is 21.6 kcal/mol higher than the global minimum (**1a$_{t\text{-Bu}}$**) while **3** is 34.4 kcal/mol higher than **1**. Interestingly, substitution causes a moderate decrease in ΔE_{s-t} of **1a** (from 57.4 to 52.8 kcal/mol) and a slight increase for **3a** (from 52.8 to 54.0 kcal/mol).

4. Conclusion

Three germanimines including 2-, 3-, and 4-germapyridines (**1**, **2**, and **3**, respectively) are compared and contrasted at DFT level. NICS criterion indicates aromatic character of the germapyridines closer to the synthesized germabenzene than pyridine. Eight germylene isomers are derived from the germapyridines: Three germylenes for **1**, three for **2**, and only two for **3**. From a thermodynamic point of view, divalent 1*H*-2-germapyridine-2-ylidene (**1a**) and 1*H*-4-germapyridine-4-ylidene (**3a**) are found more stable than their corresponding aromatic germapyridine isomers. These two show singlet–triplet energy gaps of 57.4 and 52.9 kcal/mol, respectively, which are higher than that calculated for the parent form of Herrmann's synthesized germylene, 49.7 kcal/mol. Evidently, **1a** which benefits from a HOMO–LUMO energy separation of 102.5 kcal/mol, is the global minimum on the potential energy surface of cyclic C$_4$NGeH$_5$, 29.2 kcal/mol more stable than its full-valence isomer. The germylene **3a** which is 15.4 kcal/mol more stable than the corresponding full-valence isomer enjoys a HOMO–LUMO energy separation of 94.9 kcal/mol. The germylenes derived from **2** are the least stable ones with the lowest singlet–triplet and HOMO–LUMO energy separations. No Ge=Ge doubly bonded minimum dimer is

found for **1a** and that of **3a** is 11.2 kcal/mol less stable than the two separate monomers. From a kinetic point of view, isomerization of the germylenes to the corresponding aromatic germapyridines is investigated. The calculated energy barrier for the 1,2-*H* shift of **1a** to **1** is 70.8 kcal/mol compared to the more prohibited 92.5 kcal/mol for the 1,4-*H* shift of **3a** to **3**. Thermodynamic confirms kinetic investigations both emphasize the stabilities of germylenes **1a** and **3a** inviting experimental attention toward them. Classifying the nucleophilicity and electrophilicity of our germylenes, we find the least electrophilicity indices for **1a** and **3a** (1.73 and 1.66 eV, respectively), close to that of Veith's synthesized germylene (1.68 eV), demonstrating their resistance against nucleophilic attack.

Appendix A. Supplementary material

Full reference for GUASSIAN 98, the results and discussion of all the studied germylenes, the geometrical parameters of the singlet and triplet states of **1a** at the three levels, transition states obtained for the rearrangement of the scrutinized germylenes to the corresponding germapyridines, the optimized dimers and shapes of frontier molecular orbitals of all the germylenes, NICS calculations for the planar species, and cartesian coordinates for all the calculated structures. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.12.013.

References

[1] J. Satgé, Adv. Organomet. Chem. 21 (1982) 241.
[2] J. Barrau, J. Escudié, J. Satgé, Chem. Rev. 90 (1990) 283.
[3] K.M. Baines, W.G. Stibbs, Adv. Organomet. Chem. 39 (1996) 275.
[4] J. Escudié, H. Ranaivonjatovo, Adv. Organomet. Chem. 44 (1999) 113.
[5] M. Rivière-Baudet, P. Rivière, J. Satgé, J. Organomet. Chem. 154 (1978) C23.
[6] P. Rivière, A. Cazes, A. Castel, M. Rivière-Baudet, J. Satgé, J. Organomet. Chem. 155 (1978) C58.
[7] G. Märkl, D. Rudnik, Tetrahedron Lett. 21 (1980) 1405.
[8] P. Kiprof, A.B. Brown, Internet J. Chem. 2 (1999) 1.
[9] N. Nakata, N. Takeda, N. Tokitoh, J. Am. Chem. Soc. 124 (2002) 6914.
[10] M.Z. Kassaee, F.A. Shakib, M.R. Momeni, M. Ghambarian, S.M. Musavi, Tetrahedron 65 (2009) 10093.
[11] M.Z. Kassaee, H. Zandi, F.A. Shakib, M.R. Momeni, M. Ghambarian, J. Mol. Struct. (Theochem) 913 (2009) 16.
[12] M. Veith, Angew. Chem., Int. Ed. Engl. 26 (1987) 1.
[13] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
[14] W.A. Herrmann, M. Denk, J. Behm, W. Scherer, F.R. Klingan, H. Bock, B. Solouki, M. Wagner, Angew. Chem., Int. Ed. Engl. 31 (1992) 1485.
[15] A. Schäfer, W. Saak, M. Weidenbruch, Z. Anorg. Allg. Chem. 624 (1998) 1405.
[16] M. Driess, S.L. Yao, M. Brym, C. van Wullen, Angew. Chem., Int. Ed. 45 (2006) 4349.
[17] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[18] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[19] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[20] M.J. Frisch et al., GAUSSIAN 98; Gaussian Inc., Pittsburgh, PA, 1998 (see the supporting information for the full reference).
[21] P.C. Hariharan, J.A. Pople, Mol. Phys. 27 (1974) 209.
[22] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654.
[23] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.v.R. Schleyer, J. Comput. Chem. 4 (1983) 294.
[24] M.J. Frisch, J.A. Pople, J.S. Binkley, J. Chem. Phys. 80 (1984) 3265.
[25] (a) C. Moller, M.S. Plesset, Phys. Rev. 46 (1934) 618;
(b) R. Krishan, M.J. Frisch, J.A. Pople, J. Chem. Phys. 72 (1980) 4244.
[26] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
[27] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, John Wiley and Sons, New York, 1986.
[28] (a) P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R.v.E. Hommes, J. Am. Chem. Soc. 118 (1996) 6317;
(b) P.v.R. Schleyer, M. Manoharan, Z. Wang, B. Kiran, H. Jiao, R. Puchta, N.J.R.v.E. Hommes, Org. Lett. 3 (2001) 16.
[29] L.R. Domingo, E. Chamorro, P. Pérez, J. Org. Chem. 73 (2008) 4615.
[30] R.G. Parr, L. Szentpaly, S. Liu, J. Am. Chem. Soc. 121 (1999) 1922.
[31] (a) R.G. Parr, R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 7512;
(b) R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.
[32] P.v.R. Schleyer, F. Pühlhofer, Org. Lett. 4 (2002) 2873.
[33] T. Veszprémi, L. Nyulászi, T. Kárpáti, J. Phys. Chem. A 100 (1996) 6262.
[34] R. Hoffmann, P.v.R. Schleyer, H.F. Schaefer, Angew. Chem., Int. Ed. 47 (2008) 7164.
[35] Y. Mizuhata, T. Sasamori, N. Tokitoh, Chem. Rev. 109 (2009) 3479. and references therein.