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Estimating the stability and reactivity of acyclic and cyclic mono-heteroatom substituted germylenes: A density functional theory investigation

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ABSTRACT

DFT computations coupled with appropriate isodesmic reactions are employed to investigate the effects of mono-heteroatom substitution, cyclization and unsaturation on the stability, multiplicity and reactivity of amino-, oxy-, silyl-, phosphino-, and thioalkylgermylenes. The results are based on the references to the parent symmetrical acyclic, saturated/unsaturated cyclic dialkylgermylenes. The calculated singlet–triplet energy gaps (ΔE_{S-T}) demonstrate the following trend: (amino ≈ oxy) > thio > alkyl > phosphino > silyl. Cyclization increases the ΔE_{S-T} of the all germylenes, but unsaturation considerably decreases it. Isodesmic reactions show that π-donor/σ-acceptor amino, oxy and thio stabilize both singlet and triplet germylenes but with a more considerable effect on the former while phosphino acts reversely. The reactivity of the species is discussed in terms of nucleophilicity, electrophilicity and proton affinity issues showing silyl and phosphinoalkylgermylenes more nucleophilic and more basic than amino and oxyalkylgermylenes.

1. Introduction

The chemistry of germylenes (R_2Ge), one of the heavier analogues of carbenes (R_2C), could be very interesting due to their many differences and similarities to carbenes. In contrast to carbon, germanium has low ability to form hybrid orbitals and a typical germanium prefers $(4s)^2(4p)^2$ valence electronic configuration. Hence, in a divalent germylene, two electrons occupy 4s orbital leading to a singlet ground state [1]. The resulted vacant *p*-orbital is subjected to nucleophilic attack of other molecules. Hence, in order to make a germylene stable enough for isolation, the thermodynamic and/or kinetic stabilization of the reactive vacant *p*-orbital is necessary (the lone pair is inert due to its high s-character) [2–6]. The synthesis of a four-membered cyclic germylene **I** (Fig. 1) in 1987 by Veith was indebted to both the electron donating from the adjacent nitrogens (thermodynamic stabilization) and the steric hindrance provided by *t*-Bu groups (kinetic stabilization) [7]. Similarly, after the synthesis of stable imidazol-2-ylidene **II** by Arduengo et al. [8], its germylene analogues were synthesized by Herrmann et al. in 1992 (**III**, Fig. 1) [9]. If the steric hindrance is insufficient the germylene will undergo self-oligomerization, leading to the corresponding polymer, oligomer, or dimer [2]. Therefore, the carbon-substituted germylenes have been also receiving great interest since adjacent carbons are capable of providing substitution sites for bulky groups. The first isolable monomeric acyclic dialkylgermylene **IV** was synthesized by Jutzi et al. [10]. Subsequently, applying 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl ligand, Kira et al. synthesized the stable cyclic dialkylgermylene **V** in 1998 [11]. In this manner, one may find it interesting to combine the stabilizing mesomeric effects of adjacent heteroatom with the steric protection of bulky substituted adjacent carbon atom in one structure. The present study is intending to shed some light on the stabilities and reactivities of mono-heteroatom substituted (Si, N, P, O, and S) germylenes with acyclic, cyclic, and unsaturated cyclic structures (Fig. 2).

2. Materials and methods

Full geometry optimizations are accomplished using hybrid functional B3LYP [12–14] and the 6-31+G* basis set, employing the Gaussian 03 code [15]. The applied basis set comprises Pople's well-known 6-31G* basis set [16,17] and an extra plus due to the importance of diffuse functions [18,19]. To obtain more accurate energetic data, single point calculations are performed at the B3LYP/6-311++G** level. Vibrational frequencies are calculated at the same level of optimization to establish the nature of stationary points as true minima [20]. The NBO [21] population analysis on optimized structures is accomplished at B3LYP/6-311++G** level.

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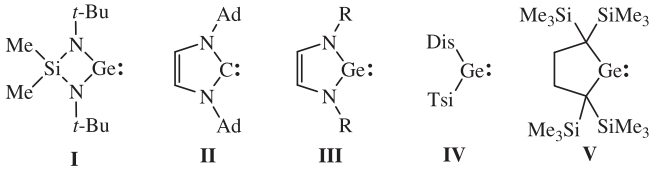


Fig. 1. Stable synthesized divalent species considered in this study.

$\mathbf{1_C}$: X = $C(CH_3)_3$ $\mathbf{2_C}$: Y = $C(CH_3)_2$ $\mathbf{3_C}$: Y = $C(CH_3)_2$
$\mathbf{1_{Si}}$: X = $Si(CH_3)_3$ $\mathbf{2_{Si}}$: Y = $Si(CH_3)_2$ $\mathbf{3_{Si}}$: Y = $Si(CH_3)_2$
$\mathbf{1_N}$: X = $N(CH_3)_2$ $\mathbf{2_N}$: Y = NCH_3 $\mathbf{3_N}$: Y = NCH_3
$\mathbf{1_P}$: X = $P(CH_3)_2$ $\mathbf{2_P}$: Y = PCH_3 $\mathbf{3_P}$: Y = PCH_3
$\mathbf{1_O}$: X = OCH_3 $\mathbf{2_O}$: Y = O $\mathbf{3_O}$: Y = O
$\mathbf{1_S}$: X = SCH_3 $\mathbf{2_S}$: Y = S $\mathbf{3_S}$: Y = S

Fig. 2. The three series of acyclic ($\mathbf{1_X}$), cyclic ($\mathbf{2_Y}$) and cyclic unsaturated ($\mathbf{3_Y}$) germylenes studied in this work.

3. Results and discussion

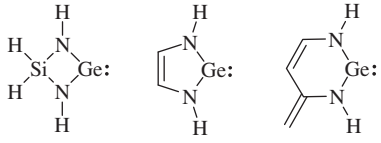
DFT calculations and isodesmic reactions are employed to form a systematic investigation on the effects of mono-heteroatom (Si, N, O, P and S) substitutions on the stability and multiplicity of three series of acyclic ($\mathbf{1_X}$), cyclic saturated ($\mathbf{2_Y}$), and cyclic unsaturated ($\mathbf{3_Y}$) germylenes (Fig. 2). In each series the results are made through comparison to the parent symmetrical dialkylgermylene. To verify the validity of widely accepted B3LYP method for the optimizations and energy calculations, all the acyclic molecules are reoptimized with more accurate but time consuming MP2 method [22,23] (the results are summarized in the Supporting information, Fig. S1). The differences between the results obtained from the two methods are not considerable. Hence, the remaining computations are concentrated on B3LYP.

3.1. Substituent effects on singlet–triplet energy separations (ΔE_{S-T})

Based on the performed calculations on symmetrical di-*t*-butylgermylene $\mathbf{1_C}$, singlet state is 22.7 kcal/mol more stable than its corresponding triplet state (Table S1). The wide C—Ge—C bond angle of this ground state (108.47°) is the result of the steric repulsion between the bulky *t*-butyl groups. This steric repulsion also causes the C—Ge bonds to be longer than a typical H_3C—GeH_3 bond, i.e. 2.028 vs 1.936 Å, optimized at the same level (Table S1). From a structural viewpoint $(t\text{-Bu})_3$-Si substitution instead of $(t\text{-Bu})_3C$ slightly relieves the steric repulsion due to the longer Si—$C_{t\text{-Bu}}$ bonds compared to C—$C_{t\text{-Bu}}$. Hence, the Si—Ge—C bond angle of $\mathbf{1_{Si}}$ is 105.85° and its C—Ge bond is 2.007 Å (Table S1). From an electronic viewpoint, α-silyl substitution decreases the ΔE_{S-T} to 13.3 kcal/mol, the least gap among the studied mono-heteroatom substituted germylenes (Table 1). On the basis of Pauling electronegativities (EN: Si = 1.9), electropositive Si is a σ-donor substituent which is anticipated to cause a small s–*p* gap in favor of the triplet state. Although it decreases the ΔE_{S-T} but is not able to alter the ground state multiplicity due to the low electronegativity difference between Si and Ge. This is in contrast to the silylalkylcarbenes where the presence of silyl substituent alters the ground state from singlet to triplet [24].

The stabilization of germylenes using group 15 (N or P) and 16 (O or S) elements is highly effective due to their π-donating character which stabilizes the reactive vacant *p*-orbital (n → *p* interaction). In the case of nitrogen and oxygen, their strong σ-accepting character also intensifies the singlet state stabilization (Pauling electronegativities, EN: Ge = 2.0, N = 3.0, and O = 3.5). Evidently, the σ-acceptor substituents are anticipated to have a more considerable stabilizing effect on the occupied 4s orbital than the vacant 4p orbital of germylenes and induce a large gap between s- and *p*-orbitals in favor of the singlet state. Therefore, the presence of one amino substituent increases the ΔE_{S-T} from 22.7 kcal/mol of $\mathbf{1_C}$ to 36.4 kcal/mol of $\mathbf{1_N}$ (Table 1). From geometric viewpoint

Table 1
Singlet–triplet energy gap (ΔE_{S-T}, kcal/mol), electron affinity[a] (EA, eV), ionization energy (IE, eV) and proton affinity[b] (PA, kcal/mol) for ground states of the studied germylenes compared to the model compounds of the synthesized NHGe (**VI–VIII**)



Species	ΔE_{S-T}	EA	IE	PA	Species	ΔE_{S-T}	EA	IE	PA
$\mathbf{1_C}$	22.7	−0.948	7.002	231.86	$\mathbf{3_C}$	30.8	−0.932	7.085	217.87
$\mathbf{1_N}$	36.4	−0.225	7.137	227.72	$\mathbf{3_N}$	35.0	−0.418	7.111	211.59
$\mathbf{1_O}$	41.0	−0.609	7.435	210.90	$\mathbf{3_O}$	36.0	−0.866	7.730	195.28
$\mathbf{1_{Si}}$	13.3	−1.322	6.729	238.26	$\mathbf{3_{Si}}$	19.9	−1.331	6.724	227.34
$\mathbf{1_P}$	20.5	−1.080	7.032	231.23	$\mathbf{3_P}$	25.9	−1.163	7.013	218.37
$\mathbf{1_S}$	35.1	−0.820	7.539	215.42	$\mathbf{3_S}$	38.0	−0.904	7.807	203.62
$\mathbf{2_C}$	29.1	−0.871	7.307	220.57	**VI**		−0.063	8.927	344.54
$\mathbf{2_N}$	52.3	−0.197	7.341	216.61	**VII**		0.497	7.136	349.27
$\mathbf{2_O}$	47.8	−0.579	7.686	201.93	**VIII**		−0.277	6.740	344.54
$\mathbf{2_{Si}}$	18.8	−1.265	6.986	229.60					
$\mathbf{2_P}$	27.2	−1.097	7.238	220.75					
$\mathbf{2_S}$	46.4	−0.726	7.818	208.46					

[a] Based on the reaction $(R_1R_2C: + e \rightarrow [R_1R_2CH]^-$.
[b] Based on the reaction $(R_1R_2C: + H^+ \rightarrow [R_1R_2CH]^+$.