Effects of α-mono heteroatoms (N vs. P), and β-conjugation on cyclic silylenes

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ABSTRACT

Following the quest for stable silylenes, we have found high thermodynamic and kinetic viabilities for a series of novel cyclic alkylaminosilylenes [CAASs: including 1_N–4_N)] over their corresponding cyclic alkylphosphinosilylenes (CAPSs: 1_P–4_P, respectively), at *ab initio* and DFT levels, coupled with appropriate isodesmic reactions. Among silylenes scrutinized, 4_N immerged the most promising for its higher singlet–triplet energy difference ($\Delta E_{S–T}$), wider band gap ($\Delta E_{HOMO–LUMO}$), higher heat of hydrogenation (ΔE_H), significant resistance to dimerization and resistance to rearrangement to its full valence octet isomer, etc. Unsaturation destabilized 2_N, 3_N, and 3_P through cross conjugation.

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1. Introduction

Divalent compounds of group 14 elements are among the most important reactive intermediates [1]. Considerable progress in the chemistry of these compounds was achieved with the synthesis and isolation of a number of stable *N*-heterocyclic carbenes [2–4] and their heavier analogs [5–9]. These discoveries have stimulated further research on the stability and electronic structures of these interesting divalent species [10]. In contrast to carbenes, silylenes generally possess a singlet ground state, due to the large energy gap and spatial differences between their silicon 3*s* and 3*p* orbitals (Fig. 1) [11].

In 1990s it was found that electronegative atoms could donate their lone pair electrons into the empty *p* orbital of the divalent carbon or silicon and stabilize their singlet states [12–16]. The largest effect was achieved with amino substituents [14]. In 1991, Arduengo synthesized the first commercially presentable stable carbene (**I**) which contained two α-nitrogens [2]. It benefited from spatial, electronic, and aromatic factors. Then, Bertrand and coworkers synthesized the first mono substituted *N*-heterocyclic carbene (**II**) which was a superior organocatalyst for being more nucleophilic (Fig. 2) [17]. In 1994, the first stable silylene (**III**) was synthesized by Denk et al. [5]. Consequently, silylenes **VI** and **V** were synthesized (Fig. 2) [18,19].

Following our interest in stable carbenes [20], silylenes [21] and germylenes [22], here we compare the effects of α-N, α-P, and β-conjugation on the stability and reactivity of silylenes with five- and six-membered rings at B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G* and MP2/6-311++G**//MP2/6-31+G* levels, coupled with appropriate isodesmic reactions (Fig. 3).

2. Computational methods

Full geometry optimizations are accomplished without any symmetry constraints by means of hybrid functional B3LYP [23,24], MP2 [25,26], and the 6-31+G* basis set, employing the Gaussian 98 code [27]. The applied basis set is comprised of Pople's well known 6-31G* basis set [28,29] and an extra plus due to the importance of diffuse functions [30,31]. To obtain more accurate energetic data, single point calculations are performed at two levels including B3LYP/AUG-cc-pVTZ//B3LYP/6-31+G* [32] and MP2/6-311++G**//MP2/6-31+G*. The transition states (TSs), linking the initial and final structures, are found using the reactants-products quasi-synchronous transit (QST3) algorithm calculations [33]. The frequency computations are applied to characterize the structures as a minimum or TS, without or with only one imaginary frequency, respectively [34,35]. Because of the size problem, dimerization calculations were performed at B3LYP/6-311+G** and MP2/6-311++G**. The nucleophilicity index, *N*, introduced by Domingo et al. [36] is calculated as $N = E_{HOMO(Nu)} − E_{HOMO(TCNE)}$, where tetracyanoethylene (TCNE) is chosen as the reference. The global electrophilicity, ω 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 ($\eta = E_{LUMO} − E_{HOMO}$) [37].

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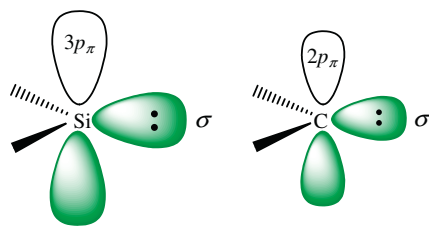*E-mail address:* kassaeem@modares.ac.ir (M.Z. Kassaee).

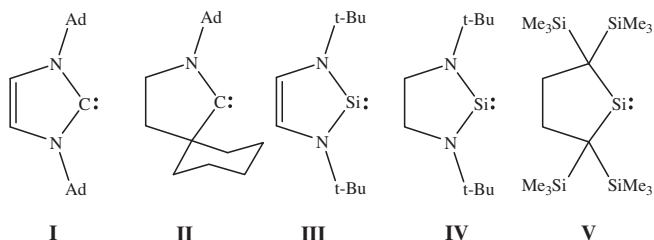**Fig. 1.** Orbitals of singlet silylene and carbene.

Fig. 2. Samples of synthesized stable divalent.

3. Results and discussion

Ab initio and DFT calculations along with appropriate isodesmic reactions are employed to examine the effects of α-mono amino and phosphino groups, as well β-conjugation on the thermodynamic and kinetic stabilities of eight cyclic silylenes (Fig. 3). Major routes that we have adopted include: Multiplicity change (path a), [1,2] H shift rearrangements (path b, and c), heat of hydrogenations (path d, and e), dimerizations (path f, and g), besides nucleophilicity and electrophilicity (path h, and i).

3.1. Singlet–triplet energy separation (ΔE_{S-T}), band gaps ($\Delta E_{HOMO-LUMO}$) (Fig. 4: path a)

According to West and Hill: "The stability of a silylene is related to its singlet–triplet energy gap, ΔE_{S-T} [18]". We calculated ΔE_{S-T} and band gaps ($\Delta E_{HOMO-LUMO}$) for our silylenes at two levels of theory: B3LYP/AUG-cc-pVTZ and MP2/6-311++G** (Table 1).

All of our CAASs and CAPSs appear remarkably stable for showing rather large ΔE_{S-T} and $\Delta E_{HOMO-LUMO}$ values that are comparable to those of stable silylenes III[5] and V [19] (Figs. 2 and 3, Table 1). Every CAAS (1_N, 2_N, 3_N and 4_N) turns out more stable than its corresponding CAPS (1_P, 2_P, 3_P and 4_P, respectively). This is due to higher singlet state stabilization of CAASs through π-donating/σ-accepting interactions of the α-amino group [14]. Among silylenes
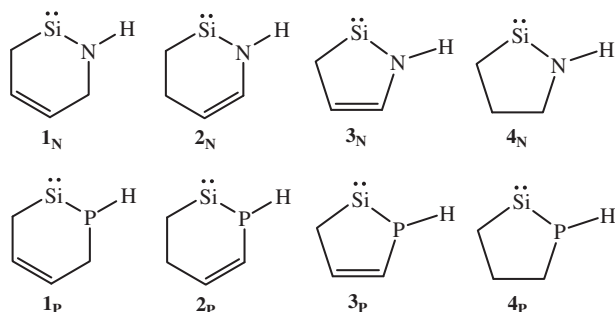

Fig. 3. Cyclic alkylaminosilylenes (CAASs: 1_N–4_N) are compared and contrasted to each other and to their correspounding cyclic alkylphosphinosilylenes (CAPSs: 1_P–4_P).

scrutinized, 4_N, followed by 1_N, immerge as the most promising for their relatively higher ΔE_{S-T} and $\Delta E_{HOMO-LUMO}$.

β-Conjugation lowers the stability of 2_N (ΔE_{S-T} = 41.2 kcal/mol) compared to 1_N (ΔE_{S-T} = 50.1 kcal/mol) because of cross conjugation. The same phenomenon is responsible for lowering of ΔE_{S-T} values of 3_N and 3_P compared to 4_N and 4_P, respectively.

From another prospective, Hoffmann et al. have emphasized that a molecule could be called stable if its computed smallest vibrational frequency is at least 100 cm^{-1} [38]. In that sense, all our scrutinized silylenes could be called "stable" because their smallest vibrational frequencies (υ_{min}) exceed 100 cm^{-1} at B3LYP/6-31+G* level (Fig. 3, Table 1). Also their dipole moments (D) fall within the anticipated range and those reported for the synthesized silylenes III, [5] and V [19] (Fig. 2, Table 1).

3.2. Rearrangements of silylenes to full valence structures through [1, 2] H shifts (Fig. 4: path b, and c)

At the first glance intermolecular rearrangements of our sextet silylenes to their full valence octet isomers seem not only possible but very probable (Fig. 4: path b, and c). However, prohibitively high energy barriers ($\Delta E^{\ddagger b}$ and $\Delta E^{\ddagger c}$) for both types of [1,2] H shift to full valence octet structures at B3LYP/AUG-cc-pVTZ and MP2/6-311++G** levels indicate that such intramolecular rearrangements are not so likely (Table 2). This makes our silylenes appear stable not only thermodynamically, but kinetically. Every CAAS (1_N–4_N) shows a relatively higher barrier of energy for [1,2] H shifts then its corresponding CAPS (1_P–4_P), respectively. Among CAASs, structures 1_N and 4_N rearrange to 1_N (full valence) and 4_N (full valence) respectively through [1,2] H shifts via near planar transition states (Fig. 5). Again, thermodynamically stable 4_N is also kinetically stable due to its high energy barriers for hydrogen shift ($\Delta E^{\ddagger b}$ = 53.7 and $\Delta E^{\ddagger c}$ = 64.0 kcal/mol) (Table 2). Barriers for rearrangements of 1_N are also considerable ($\Delta E^{\ddagger b}$ = 43.6 and $\Delta E^{\ddagger c}$ = 48.1 kcal/mol), although they appear smaller than those of 4_N.

3.3. Evaluation of stability through heat of hydrogenations (Fig. 4: path d, and e)

Heats of hydrogenation (ΔE_H^d) are estimated for all our silylenes at B3LYP/AUG-cc-pVTZ and MP2/6-311++G** levels (Fig. 4: path d; Table 2). The higher is the ΔE_H^d value, the more is the stability of a silylene [38]. Accordingly, the highest stability is demonstrated by 4_N (ΔE_H^d = −31.4 kcal/mol). Interestingly, every CAAS appears more stable than its corresponding CAPS for showing a higher ΔE_H^d. We estimated relative stabilities for our silylenes using the parent silylene: SiH$_2$ as the reference in an isodesmic reaction (Fig. 4: path e; Table 2). The results are similar to those obtained from heats of hydrogenation. The highest stability is shown by 4_N (ΔE_{ism}^e = 27.4 kcal/mol). In addition, CAASs (ΔE_{ism}^e = 21.3 − 27.4 kcal/mol) are more stable than their corresponding CAPSs (ΔE_{ism}^e = 12.4 − 15.1 kcal/mol).

3.4. Dimerization of silylenes through head-to-head and head-to-tail processes (Fig. 4: path f, and g)

While dimerization of a carbene often leads to a much more stable olefin product, dimerization product of a silylene usually is as unstable as its monomer [39,40]. Nevertheless, Trinquier [41–43], Apeloig and Müller [44] have suggested at least two different routes for dimerization of silylenes. The first path is the "classical" route where the filled orbital of one silylene overlaps with the empty *p*-orbital of the other forming a head-to-head disilene (Fig. 4, path f) [39]. In the second path, the lone pair orbital of a substituent on silylene interacts with an empty 3*p*-orbital of the other silylene forming a head-to-tail bridged dimmer (Fig. 4, path g). In this work we probe both types of dimerizations where