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A quest for triplet silylenes $XHSi_3$ at ab initio and DFT levels ($X = H$, F, Cl and Br)

M.Z. Kassaee *, S.M. Musavi, M. Ghambarian

Department of Chemistry, Tarbiat Modarres University, P.O. Box 14155-4838, Tehran, Iran

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Abstract

Four ground state triplet silylenes are found among 30 possible silylenic $XHSi_3$ structures ($X = H$, F, Cl and Br), at seven ab initio and DFT levels including: B3LYP/6-311++G**, HF/6-311++G**, MP3/6-311G*, MP2/6-311+G**, MP4(SDTQ)/6-311++G**, QCISD(T)/6-311++G** and CCSD(T)/6-311++G**. The latter six methods indicate that the triplet states of 3-flouro-1,2,3-trisilapropadienylidene, 1-chloro-1,2,3-trisilapropargylene and 3-chloro-1,2,3-trisilapropargylene are energy minima. These triplets appear more stable than their corresponding singlet states which cannot even exist for showing negative force constants. Also, triplet state of 1-flouro-1,2,3-trisilapropargylene is possibly accessible for being an energy minimum, since its corresponding singlet state is not a real isomer. Some discrepancies are observed between energetic and/or structural results of DFT vs. ab initio data.

Keywords: Silylene; H_2Si_3; $FHSi_3$; $ClHSi_3$; $BrHSi_3$; 3-Flouro-1,2,3-trisilapropadienylidene; 1-Chloro-1,2,3-trisilapropargylene; 3-Chloro-1,2,3-trisilapropargylene; 1-Flouro-1,2,3-trisilapropargylene; Ab initio; DFT

1. Introduction

Recently much attention has been directed to the question of singlet/triplet energy gaps, in the heavier carbene analogues consisting of: silylenes [1], germylenes [2], stannylenes and plumbylenes [3]. Quantum chemical calculations on several silylenes and germylenes have shown their ground states to be mostly singlet, in contrast to carbenes, where the triplet is of lower energy [4,5]. Both electronic and steric effects might affect singlet–triplet energy separations (ΔE_{t-s}) [6]. The lowest electronic states of methyl-, silyl-, and lithium-substituted silylenes have been investigated. Methyl group acts like halogens. It increases the singlet–triplet energy splittings of group 14 divalent species. SiH_3 behaves as an electropositive substituent and decreases this energy gap. When it gets to the more electropositive lithium-substituted silylenes, the ground state switches from singlet to the triplet state. The effects of the electropositive substituents on ΔE_{t-s} prevail against those of the electronegative ones [7–9].

To understand the molecules scrutinized in this work, we take up the properties of multiple-bonds. In a multiple-bond, made from the second row elements, the bond length is inversely proportional to the corresponding bond order. Such is not usually the case for the multiple-bonds, made from the third period onward. They often have long bond distances and low π-bond energies, which may be due to the poor overlap of their p-orbitals, that makes their corresponding molecules extremely unstable [10,11]. However, evidence confirming that these compounds exist in cryogenic matrix or gas phase, as short-lived species, has accumulated from studies arising from the latter half of the 1960s to the 1970s. Stable compounds having P=C bonds [12], as well as Si=C [13], Si=Si [14], and P=P [15] have been synthesized and isolated for the first time in 1978 and 1981, respectively. Consequently, attention has expanded to silicon–silicon double bonds and triple bonds containing silicon [16–18], as well as the small silicon-containing rings [19]. More recently, Kira et al. reported

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* Corresponding author. Tel.: +98 912 1000392; fax: +98 21 8006544.
E-mail address: Kassaeem@Modares.ac.ir (M.Z. Kassaee).

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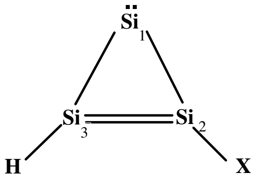
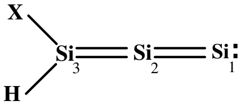
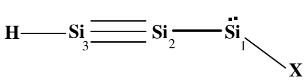


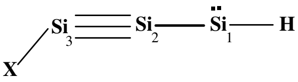
2-X-1,2,3-trisilacyclopropenylidene (singlet $\mathbf{1}_{\mathbf{s\text{-}X}}$; triplet, $\mathbf{1}_{\mathbf{t\text{-}X}}$)



3-X-1,2,3-trisilapropadienylidene (singlet $\mathbf{2}_{\mathbf{s\text{-}X}}$; triplet $\mathbf{2}_{\mathbf{t\text{-}X}}$)



1-X-1,2,3- trisilapropargylene (singlet $\mathbf{3}_{\mathbf{s\text{-}X}}$; triplet $\mathbf{3}_{\mathbf{t\text{-}X}}$)



3-X-1,2,3-trisilapropargylene (singlet $\mathbf{4}_{\mathbf{s\text{-}X}}$; triplet $\mathbf{4}_{\mathbf{t\text{-}X}}$)

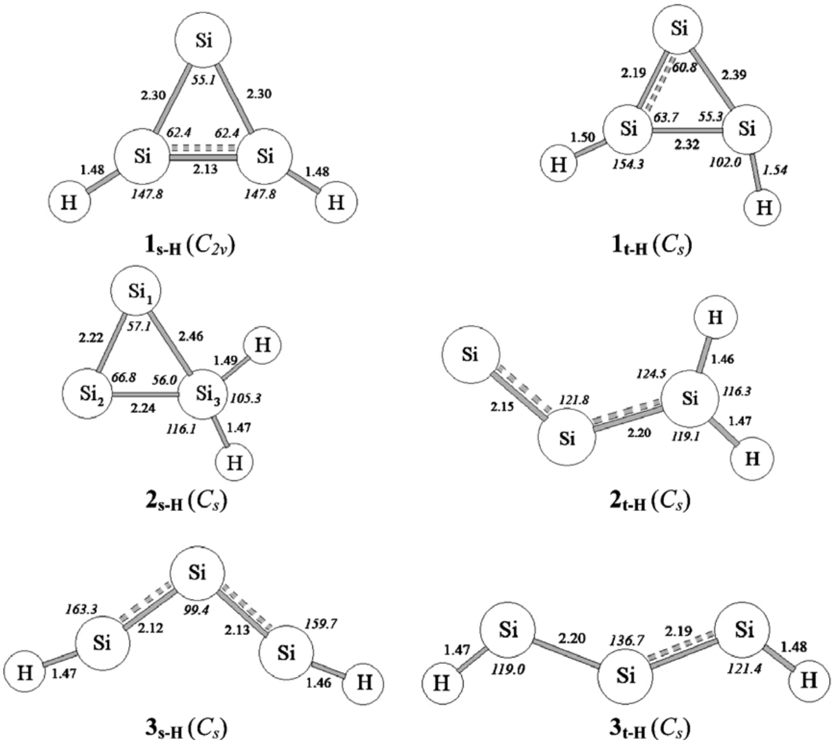
Fig. 1. The four structures considered for singlet (**s**) and/or triplet (**t**) states of silylenic $XHSi_3$ (where X = H, F, Cl and Br).

interesting examples of cyclic disilenes [20], spiropentasiladiene [21], 4-silatriafulvene [22], a silicon-containing fused bicyclic compound with a highly strained bridgehead double bond [23], and a disilane with a long Si–Si bridge [24]. Also, a stable silicon analogue of an allene, with a core of Si=Si=Si unit, with sp-hybridized silicon atoms, was synthesized [25]. Unlike its linear carbon counterpart, trisilaallene is 'bent', but the compound is relatively stable. Finally, the synthesis and characterization of the first disilyne with a Si≡Si triple-bond is reported by Sekiguchi and coworkers [26]. The structure and bonding of Si compounds are inherently complex. The well established bonding rules of carbon chemistry are of little help in deducing the compounds of Si and the other heavier group 14 analogues [27].

Following up on our studies on divalent species of group 14 elements [3,28–34], as well as the specific studies of Maier et al. on the small and matrix isolable silylenes C_2HXSi [35]; a quest is made for triplet silylenes $XHSi_3$ at ab initio and DFT levels (X = H, F, Cl and Br) (see Fig. 1).

2. Computational methods

Full geometrical optimizations are performed on singlet and triplet H_2Si_3 silylenes, as well as their halogen substituted analogues consisting of $FHSi_3$, $ClHSi_3$ and $BrHSi_3$, each with four skeletal arrangements containing: 2-X-1,2,3-trisilacyclopropenylidene (**1**), 3-X-1,2,3-trisilapropadienylidene (**2**), 1-X-1,2,3-trisilapropargylene (**3**), and 3-X-1,2,3-trisilapropargylene (**4**), at the HF, DFT, the second and third-order MØller–Plesset (MP2, MP3) methods, where X = H, F, Cl and Br (Fig. 1). All optimizations are performed with no imposed constraints, making the starting structures free to transform through optimizations. For Hartree–Fock (HF) calculations, the 6-311++G** basis set is employed. Likewise, for DFT calculations the, Becke's hybrid three-parameter functional combined with the Lee–Yang–Parr non-local correlation functional B3LYP [36] with the 6-311++G** basis set is employed. For MP2, 6-311+G** and MP3, the 6-311G* basis sets is used. The MP2/6-311+G** optimized geometries are submitted as input for single-point calculations at the fourth-order MP (MP4), QCISD(T) [37–39] and CCSD(T) levels [40] with the 6-311++G** basis set. Singlet states are



$\mathbf{1}_{\mathbf{s\text{-}H}}$ (C_{2v}) $\mathbf{1}_{\mathbf{t\text{-}H}}$ (C_s)

$\mathbf{2}_{\mathbf{s\text{-}H}}$ (C_s) $\mathbf{2}_{\mathbf{t\text{-}H}}$ (C_s)

$\mathbf{3}_{\mathbf{s\text{-}H}}$ (C_s) $\mathbf{3}_{\mathbf{t\text{-}H}}$ (C_s)

Fig. 2. MP2/6-311+G** optimized geometries and point groups of six silylenic H_2Si_3 structures, with bond lengths given in angstroms (Å) and bond angles in degrees (°).