Exploring the Nature of Silicon-Noble Gas Bonds in H₃SiNgNSi and HSiNgNSi Compounds (Ng = Xe, Rn)

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Abstract: Ab initio and density functional theory-based computations are performed to investigate the structure and stability of H₃SiNgNSi and HSiNgNSi compounds (Ng = Xe, Rn). They are thermochemically unstable with respect to the dissociation channel producing Ng and H₃SiNSi or HSiNSi. However, they are kinetically stable with respect to this dissociation channel having activation free energy barriers of 19.3 and 23.3 kcal/mol for H₃SiXeNSi and H₃SiRnNSi, respectively, and 9.2 and 12.8 kcal/mol for HSiXeNSi and HSiRnNSi, respectively. The rest of the possible dissociation channels are endergonic in nature at room temperature for Rn analogues. However, one three-body dissociation channel for H₃SiXeNSi and one two-body and one three-body dissociation channels for HSiXeNSi are slightly exergonic in nature at room temperature. They become endergonic at slightly lower temperature. The nature of bonding between Ng and Si/N is analyzed by natural bond order, electron density and energy decomposition analyses. Natural population analysis indicates that they could be best represented as (H₃SiNg)+(NSi)⁻ and (HSiNg)⁺(NSi)⁻. Energy decomposition analysis further reveals that the contribution from the orbital term (ΔEorb) is dominant (ca. 67%–75%) towards the total attraction energy associated with the Si-Ng bond, whereas the electrostatic term (ΔEelstat) contributes the maximum (ca. 66%–68%) for the same in the Ng–N bond, implying the covalent nature of the former bond and the ionic nature of the latter.
Keywords: *ab initio* study; dissociation channels; kinetic stability; natural population analysis; electron density analysis; energy decomposition analysis

1. Introduction

Having a late break-through in 1962 with the discovery of Xe+[PtF₆]⁻, chemistry related to the noble gas (Ng) compounds has been developing very rapidly, especially during the last two decades. This is due to the outcome of the huge efforts made by both experimentalists [1–19] and theoreticians [20–46] towards the syntheses and/or predictions of stable Ng-containing compounds. The first compound having the Xe–C bond was reported as XeCH₃⁺ many years ago in 1961 by Field et al. [47], and the very next year, the same group [48] detected ArCH₃⁺ and KrCH₃⁺ in mass spectrum. A few years later in 1979, Turbini et al. [49] detected Xe(CF₃)₂ by means of mass spectroscopic techniques. Subsequently, detection of a few pentafluorophenylxenon cation [50–52] derivatives was also reported in 1989. Thereafter, plenty of examples with Ng–C bonds, *viz.* HXeCCH [53–55], HKrCCH [55], HXeCC [53,55], HXeCCXeH [53,55], HXeCN [5], HKrCN [5], HNgCCF [56], HCCNgF [56], ClXeCN [57], BrXeCN [57], HXeC₃N [58], HKrC₃N [58], HXeC₄H [11] and HKrC₄H [11], were made available in the literature as experimentally-detected compounds using a low temperature matrix-isolation technique. Moreover, several theoretically-predicted compounds with Ng–C bonds, some unusual highly-coordinated Ng(CCH)₄ and Ng(CCH)₆ clusters (Ng = Kr, Xe) [59] and polymer, H–(Xe–C₂)n–Xe–H (n ≥ 1) [60], were found to be metastable species.

On the other hand, there are only a few examples of the systems having Si-Ng bonds, which were experimentally obtained or theoretically predicted to be viable. The generation of the F₃SiXe⁺ by Grandinetti et al. [61] in an ion-molecule reaction between the protonated SiF₄ and Xe, F₃Si–FH⁺ + Xe → Xe–SiF₃⁺ + HF, provided the first system with the Si–Ng bond. Through so-called direct addition of SiF₃⁺ and Ng, Cunje et al. [62] were successful in producing not only XeSiF₃⁺, but also ArSiF₃⁺ and KrSiF₃⁺ at room temperature and high pressure. Two other isomers of NgSiF₃⁺ with Si–Ng–F and F–Ng–F types of linkages were also proposed [62]. The metastability of the first neutral compound, FArSiF₃, with the Si–Ar chemical bond, was predicted by Cohen et al. [63]. Prompted by this study, Yockel et al. [64] found viable FKrSiF₃ as the first example having the Si–Kr bond in a neutral system. Lundell and coworkers [65] further assessed the stability and bonding of FxeSiF, the first neutral compound with the Si–Xe covalent bond. Roithová et al. [66] showed that SiF₃²⁺ could behave as a superelectrophilic reagent and that NgSiF₃²⁺ (Ng = Ne, Ar) could be formed as a result of the thermal ion-molecule reaction, F₃Si²⁺ + Ng → NgSiF₂⁺ + F. Recently, Savoca et al. [67] detected SiₓXe⁺ via infrared (IR) multiple photon dissociation spectroscopy. More recently, we studied the Ng binding ability of the SiH₃⁺ cluster, as well as the effect of H substitution of SiH₃⁺ by halide groups (−X) on its ability in binding Ng [68].

In this manuscript, we have reported two new viable compounds, H₃SiNgNSi and HSiNgNSi (Ng = Xe, Rn), with Si-Ng covalent bonds. Crabtree and coworkers [69] very recently detected highly stable silicon nitrides, H₃SiNSi and HSiNSi by chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. H₃SiNSi has a C₃ᵥ point group symmetry with a linear Si–N–Si moiety,
whereas HSiNSi possesses a planar geometry (C₅) with a slightly bent Si–N–Si arrangement, and for both of them, the minimum energy structures have a singlet spin state. We have assessed in silico the structure, stability and the nature of bonding in H₃SiNgNSi and HSiNgNSi compounds. They are found to be metastable systems. The nature of bonding therein is analyzed by natural population analysis (NPA), Wiberg bond indices (WBI) calculation [70], electron density analysis [71] and energy decomposition analysis (EDA) [72–75]. It may be noted that except for RnSiX₃⁺ (X = H, F–Br) [68], there is no study with the compound having the Si–Rn bond. In that sense, for the first time, we reported here the neutral Rn-containing compounds, H₃SiRnNSi and HSiRnNSi, with the Si–Rn covalent bond.

2. Results and Discussion

2.1. Structure and Stability

The optimized geometries of H₃SiNSi and HSiNSi compounds and their Ng inserted analogues, H₃SiNgNSi and HSiNgNSi, are provided in Figure 1. Similar to their mother moieties, the minimum energy structure of H₃SiNgNSi corresponds to the C₃ᵥ point group with the 1A₁ electronic state, whereas HSiNgNSi has a planar geometry with the Cₛ point group and 1A' electronic state. On the other hand, the transition states (TSs) corresponding to the dissociations of H₃SiNgNSi and HSiNgNSi into Ng and H₃SiNSi or HSiNSi have Cₛ (TS-1 in Figure 1) and C₁ (TS-2 in Figure 1) symmetry, respectively, in which the NSi fragment remains attached with H₃SiNg or HSiNg fragments in a tilted fashion. The geometrical parameters of H₃SiNgNSi and HSiNgNSi compounds obtained at the ωB97X-D/def2-QZVPPD and CCSD(T)/def2-TZVP levels are provided in Table S1 (Supplementary Information), whereas the same for the minimum energy and TS structures of H₃SiNgNSi and HSiNgNSi obtained at the MP2/def2-QZVPPD level are given in Table 1. The geometrical parameters of H₃SiNSi and HSiNSi are also provided in Table S2 (Supplementary Information). The Si–Ng bond distance in H₃SiNgNSi is somewhat shorter than that in HSiNgNSi. This may be due to the positive charges on the Ng centers in H₃SiNgNSi and HSiNgNSi compounds. The positive charge on the Ng center in H₃SiNgNSi (+0.61 |e| on Xe and +0.68 |e| on Rn) is larger than that in HSiNgNSi (+0.50 |e| on Xe and +0.57 |e| on Rn). The chemical inertness of Ng atoms originates from the filled valence shell. Hence, a more positively-charged Ng center would be more effective in taking part in chemical bond formation. The larger interaction energy between H₃Si and NgNSi than that between HSi and NgNSi corroborates well with the stronger bond formation in the former cases than the latter ones (vide infra).

The N–Si bond gets slightly elongated in the Ng inserted analogues compared to those in H₃SiNSi and HSiNSi. The Si–Ng–N and Ng–N–Si moieties in the H₃SiNgNSi compound are linear. However, the same in the HSiNgNSi compound are slightly bent from the linear arrangement (≤0.5°). Since in TS-1 and TS-2, the NSi fragment is bonded to the Ng center in a tilted fashion, having the mode with imaginary frequency as the bending of Si–Ng–N and Ng–N–Si angles, the <Si–Ng–N and <Ng–N–Si get shortened (96.0°–126.2°) compared to those in the corresponding minimum energy structures (≈180.0°). In the TSs, the Si–Ng bond distance is found to decrease by about 0.1 Å, while the Ng–N bond distance increases by 0.3–0.2 Å compared to those in the corresponding minimum energy structures.
Figure 1. Pictorial depictions of the energy minimum structures and the transition states (TSs) of $\text{H}_3\text{SiNSi}$, $\text{HSNiSi}$, $\text{H}_3\text{SiNgNSi}$ and $\text{HSiNgNSi}$ compounds. Point groups along with their electronic states are given in parentheses. TS-1 and TS-2 are associated with the dissociation of $\text{H}_3\text{SiNgNSi}$ and $\text{HSiNgNSi}$, producing Ng and $\text{H}_3\text{SiNSi}$ or $\text{HSiNSi}$.

Table 1. The geometrical parameters (in Å and degrees) of the optimized geometries of $\text{H}_3\text{SiNgNSi}$ and $\text{HSiNGNSi}$ compounds (both minimum energy structures and transition states) studied at the MP2/def2-QZVPPD level.

| Nature of Stationary Points | Compounds          | $r_{\text{H-Si}}$ | $r_{\text{Si-Ng}}$ | $r_{\text{Np-N}}$ | $<\text{H-Si-Ng}$ | $<\text{Si-Ng-N}$ | $<\text{Ng-N-Si}$ |
|----------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Minimum                    | $\text{H}_3\text{SiXeNSi}$ | 1.471               | 2.588               | 2.338               | 1.600               | 107.0               | 180.0               |
| Energy                     | $\text{H}_3\text{SiRnNSi}$ | 1.472               | 2.688               | 2.382               | 1.598               | 107.8               | 180.0               |
| Structures                 | $\text{HSiXeNSi}$     | 1.508               | 2.653               | 2.375               | 1.603               | 88.7                | 179.5               |
|                           | $\text{HSiRnNSi}$     | 1.510               | 2.747               | 2.420               | 1.601               | 89.0                | 179.7               |
| Transition                 | $\text{H}_3\text{SiXeNSi}$ | 1.462(3)            | 2.486               | 2.683               | 1.616               | 103.9, 99.5         | 110.6               |
|                           | $\text{H}_3\text{SiRnNSi}$ | 1.463(5)            | 2.573               | 2.733               | 1.616               | 104.1, 99.3         | 103.7               |
|                           | $\text{HSiXeNSi}$     | 1.504               | 2.511               | 2.576               | 1.626               | 87.6                | 100.7               |
|                           | $\text{HSiRnNSi}$     | 1.505               | 2.590               | 2.623               | 1.625               | 87.7                | 96.0                |
The stability of these Ng inserted compounds is understood by computing ZPE-corrected dissociation energy (D₀), as well as dissociation enthalpy (ΔH) and free energy change (ΔG) at 298 K for different possible dissociation channels. We have considered the higher spin states of all of the dissociated products. The spin state, which gives the lowest energy, is taken into consideration. We have computed ΔG values for the different possible dissociation channels of H₃SiNgNSi and HSiNgNSi at both the MP2/def2-QZVPPD (see Table S3 in the Supplementary Information) and ωB97X-D/def2-QZVPPD levels (see Table 2), and those for the D₀ and ΔH are given in Tables S4 and S5 (Supplementary Information). We found that the D₀, ΔH and ΔG values obtained at the MP2 level are larger than those obtained at the ωB97X-D level in most cases, particularly in Xe analogues. In some cases, this provides qualitatively wrong results. For example, with respect to most of the dissociation channels, the Xe inserted compounds are less likely to be dissociated than those of the Rn analogues, implying larger stability of the former compounds than the latter ones. However, in general, it is expected that due to larger polarizability, Rn would make a somewhat stronger bond than that of Xe. It was already reported in the literature that the MP2 level of computation can produce inaccurate dissociation energy diagrams for the Ng inserted compounds [76]. Our results corroborate that the stability of Ng inserted compounds should not be analyzed based on MP2 results alone. Therefore, we have given special emphasis to the results obtained at the ωB97X-D level to assess the stability of these studied compounds with respect to the different dissociation channels.

We have considered two-body (2-B) as well as three-body (3-B) dissociation channels comprising both neutral and ionic fragments. For H₃SiNgNSi, except for the 2-B dissociation channel producing H₃SiNSi and Ng, all other dissociation channels are endergonic in nature at room temperature. Though dissociation of H₃SiNgNSi into H₃SiNSi, and Ng is exergonic by −119.3 kcal/mol for Xe and −110.5 kcal/mol for Rn, the dissociation is kinetically protected by 19.3 and 23.3 kcal/mol for Xe and Rn analogues, respectively. For H₃SiXeNSi, except this 2-B dissociation, another 3-B dissociation producing H₃Si, Ng and NSi is slightly exergonic in nature (−0.2 kcal/mol) at room temperature. However, it becomes endergonic (2.6 kcal/mol) at a slightly lower temperature (250 K), as the contribution from the favorable ΔS term becomes smaller at a lower temperature.

In the case of HSiRnNSi, except for the dissociation into HSiNSi and Rn, all other dissociation channels are endergonic in nature. However, for HSiXeNSi, in addition to the dissociation into HSiNSi and Xe, two other 2-B and 3-B dissociations are slightly exergonic in nature at 298 K. In both Xe and Rn analogues, the dissociation producing HSiNSi and Ng is highly exergonic, being −121.1 kcal/mol for Xe and −113.0 kcal/mol for Rn. This dissociation is found to be kinetically protected by the free energy barrier of 9.2 kcal/mol for Xe and 12.8 kcal/mol for Rn analogues. The 2-B dissociation of HSiXeNSi producing HSiXe and NSi and the 3-B dissociation producing HSi, Xe and NSi are exergonic by −3.6 and −5.8 kcal/mol, respectively, at 298 K. We have computed ΔG values at a lower temperature and have found that at 180 K, ΔG values become slightly positive (0.5 and 0.2 kcal/mol for 2-B and 3-B dissociations, respectively), and at 150 K, it becomes 1.6 kcal/mol for the 2-B dissociation and 1.7 kcal/mol for the 3-B dissociation. It may be noted that activation free energy barriers obtained at the MP2 level are quite close to those obtained at the ωB97X-D level (see Table S3).
Table 2. Free energy change ($\Delta G$, kcal/mol) at 298 K for different dissociation channels of H$_3$SiNgNSi and HSiNgNSi compounds at the $\omega$B97X-D/def2-QZVPPD level.

| Processes                      | $\Delta G$ H$_3$SiNgNSi | $\Delta G$ HSiNgNSi | $\Delta G$‡a |
|-------------------------------|--------------------------|---------------------|--------------|
| Xe Rn                         |                          |                     |              |
| H$_3$SiNgNSi $\rightarrow$ H$_3$SiNg$^+$ + NSi$^-$ | 105.3                    | 110.7               |              |
| H$_3$SiNgNSi $\rightarrow$ H$_3$Si$^+$ + Ng + NSi$^-$ | 165.2                    | 166.1               |              |
| H$_3$SiNgNSi $\rightarrow$ H$_3$Si$^+$ + Ng + NSi$^-$ | -119.3                   | -110.5              |              |
| H$_3$SiNgNSi $\rightarrow$ H$_3$Si$^+$ + Ng + NSi$^-$ | 64.4                     | 73.0                |              |
| H$_3$SiNgNSi $\rightarrow$ H$_3$Si$^+$ + Ng + NSi$^-$ | 236.9                    | 239.2               |              |
| H$_3$SiNgNSi $\rightarrow$ HSi$^+$ + HNgH + NSi$^-$ | 149.4                    | 149.8               |              |
| H$_3$SiNgNSi $\rightarrow$ HSi$^+$ + HNgH + NSi$^-$ | 268.1                    | 268.4               |              |
| H$_3$SiNgNSi $\rightarrow$ HSi$^+$ + HNgH + NSi$^-$ | 355.1                    | 355.5               |              |
| H$_3$SiNgNSi $\rightarrow$ HSi$^+$ + HNgH + NSi$^-$ | 19.3                     | 23.3                |              |

$\Delta G$‡a is the activation free energy barrier for the processes, H$_3$SiNgNSi $\rightarrow$ H$_3$SiNSi + Ng and HSiNgNSi $\rightarrow$ HSiNSi + Ng.

Hu and co-workers [77] argued that to have a half-life in the order of $\sim$10$^2$ s at 100, 200 and 300 K, a system of type XNgY must have a minimum energy barrier of 6, 13 and 21 kcal/mol, respectively. Therefore, H$_3$SiNgNSi could be detected at as high as a 250–300 K temperature range, whereas HSiNgNSi could be detected around the 150–200 K temperature range.

2.2. Nature of Bonding

The NPA charge at each atomic center and the WBI values of Si–Ng and Ng–N bonds are tabulated in Table 3. The H and N centers are electronegative in nature, while Si and Ng centers are electropositive in nature. The Si center attached to N (0.77–0.80 $|e|$) carries a slightly more positive charge than that of Si in the –SiH$_3$ fragment (0.51–0.63 $|e|$). On the other hand, N attains a large negative charge of $\sim$1.50 $|e|$ for Xe analogues and $\sim$1.52(4) $|e|$ for Rn analogues. Note that the net charge on the NSi fragment ranges from $\sim$0.71 $|e|$ to $\sim$0.75 $|e|$. Therefore, they could be best represented as (H$_3$SiNg)$^+$,(NSi)$^-$ and (HSiNg)$^+$,(NSi)$^-$ . Obviously, the Ng–N bond would be of the ionic type. The low WBI values ($\sim$0.2) for the Ng–N bonds dictate their ionic nature of interaction. In contrast, the quite high WBI values ($\sim$0.65) for the Si–Ng bonds imply that the bonds are of the covalent type, and almost a single bond is formed therein.
Table 3. Natural population analysis (NPA) charge on each atomic center \((q_k, \text{ au})\) and Wiberg bond indices (WBI) values of Si–Ng and Ng–N bonds computed at the MP2/def2-QZVPPD level.

| Compounds       | H  | Si  | Ng  | N   | Si  | Si–Ng | Ng–N |
|-----------------|----|-----|-----|-----|-----|-------|------|
| \(\text{H}_3\text{SiXeNSi}\) | -0.17 | +0.63 | +0.61 | -1.50 | +0.79 | 0.64  | 0.22 |
| \(\text{H}_3\text{SiRnNSi}\) | -0.17 | +0.56 | +0.68 | -1.52 | +0.80 | 0.65  | 0.22 |
| \(\text{HSiXeNSi}\) | -0.33 | +0.56 | +0.50 | -1.50 | +0.77 | 0.63  | 0.18 |
| \(\text{HSiRnNSi}\) | -0.33 | +0.51 | +0.57 | -1.54 | +0.79 | 0.66  | 0.17 |

Electron density analysis [71] provides additional insight into the nature of bonding. Different topological descriptors of electron density and electron localization function (ELF) computed at the bond critical points (BCPs) of Si–Ng and Ng–N bonds are given in Table 4. The concentration and depletion of electron density at the BCPs are indicated by the negative and positive values of \(\nabla^2 \rho (r_c)\), respectively. In general, the occurrence of electron density concentration and depletion at the BCPs indicates the covalent and noncovalent type of bonding, respectively. However, many failures ([71,78–83] pp. 312–314) of this descriptor in representing a covalent bond, especially for the systems with heavy atoms, are documented in the literature. The local electron energy density \((H(r_c))\), which is the sum of local kinetic energy density \((G(r_c))\) and local potential energy density \((V(r_c))\), is also commonly applied to interpret the nature of a bond.

Table 4. Calculated topological properties (au) at the bond critical points of Ng–Si and Ng–N bonds obtained from the .wfn files generated at the MP2/def2-QZVPPD level.

| Compounds       | \(\rho (r_c)\) | \(\nabla^2 \rho (r_c)\) | \(G(r_c)\) | \(V(r_c)\) | \(H(r_c)\) | ELF  |
|-----------------|----------------|--------------------------|-----------|-----------|-----------|------|
| \(\text{H}_3\text{Si} \rightleftharpoons \text{XeNSi}\) | 0.078           | -0.093                   | 0.016     | -0.055    | -0.039    | 0.868|
| \(\text{H}_3\text{SiXe} \rightleftharpoons \text{NSi}\) | 0.073           | 0.140                    | 0.057     | -0.079    | -0.022    | 0.295|
| \(\text{H}_3\text{Si} \rightleftharpoons \text{RnNSi}\) | 0.075           | -0.061                   | 0.018     | -0.051    | -0.033    | 0.824|
| \(\text{H}_3\text{SiRn} \rightleftharpoons \text{NSi}\) | 0.073           | 0.139                    | 0.058     | -0.081    | -0.023    | 0.284|
| \(\text{HSi} \rightleftharpoons \text{XeNSi}\) | 0.069           | -0.056                   | 0.017     | -0.049    | -0.032    | 0.786|
| \(\text{HSiXe} \rightleftharpoons \text{NSi}\) | 0.068           | 0.137                    | 0.053     | -0.072    | -0.019    | 0.278|
| \(\text{HSi} \rightleftharpoons \text{RnNSi}\) | 0.066           | -0.042                   | 0.017     | -0.045    | -0.028    | 0.769|
| \(\text{HSiRn} \rightleftharpoons \text{NSi}\) | 0.068           | 0.132                    | 0.053     | -0.073    | -0.020    | 0.276|

Even if \(\nabla^2 \rho (r_c) > 0\), but \(H(r_c) < 0\), then also the bond might be considered as a covalent type [84]. In our cases, \(\nabla^2 \rho (r_c)\) is negative in the Si–Ng bonds, implying their covalent nature. However, \(H(r_c)\) is negative in both Si–Ng and Ng–N bonds and slightly more negative in Si–Ng bonds than that in Ng–N bonds. The contour plots of \(\nabla^2 \rho (r)\) are displayed in Figure 2.
Figure 2. Contour plots of the Laplacian of the electron density of H$_3$SiXeNSi and HSiXeNSi clusters at a particular plane computed at the MP2/def2-QZVPPD/WTBS level (WTBS is used for Xe and Rn; The green-colored region shows the area of $\nabla^2 \rho(r) > 0$, whereas the blue-colored region shows the area of $\nabla^2 \rho(r) < 0$).

In between Si and Ng centers, a well-defined region having $\nabla^2 \rho(r) < 0$ is developed, whereas in between Ng and N centers, the valence orbitals only undergo slight deformation in their shapes. Note that though H$(r_e)$ is negative in Ng–N bonds, the charge distribution shows that it would be better to consider them as ionic bonds rather than the covalent ones. To prove this, we have further computed ELF [85] at the BCPs of Si–Ng and Ng–N bonds, and the corresponding color-filled maps of ELF are provided in Figure 3. Generally, a high value of ELF at a certain point is an indicator of the localized electrons therein. It further implies the existence of covalent bonds or lone pairs or core electrons.

A typical covalent bond possesses a large ELF value in between two bonded centers, whereas in the case of an ionic bond, the ELF value at the interstitial positions of the two atoms is very low. In our cases, the ELF values at the BCPs of Si–Ng bonds are quite high (~0.8) being close to the limiting value of 1.0 for a perfect localization case, whereas they are quite small (~0.3) for the Ng–N cases, corroborating well with their ionic nature. The color-filled maps of ELF further dictate the large degree of electron localization in between Si and Ng centers, whereas it is very small in between Ng and N centers (see Figure 3).
Figure 3. Color-filled maps of the electron localization function of H$_3$SiXeNSi and HSiXeNSi clusters at a particular plane computed at the MP2/def2-QZVPPD/WTBS level (WTBS is used for Xe and Rn).

The total interaction energy ($\Delta E_{\text{int}}$) is divided into the Pauli repulsion ($\Delta E_{\text{pauli}}$), electrostatic ($E_{\text{elstat}}$), orbital ($\Delta E_{\text{orb}}$) and dispersion ($\Delta E_{\text{disp}}$) energy terms in EDA to get further insight into the nature of Si–Ng and Ng–N bonds (see Table 5). The NPA charge on each atomic center is used as a guiding tool to impose the charges on the fragments used in our energy partitioning schemes. Since H$_3$SiNgNSi and HSiNgNSi could be best represented as (H$_3$SiNg)$^+$($\text{NSi}$)$^-$ and (HSiNg)$^+$($\text{NSi}$)$^-$, we have used [H$_3$SiNg]$^+$ or [HSiNg]$^+$ and [NSi]$^-$ as two fragments to know the nature of the Ng–N bond. As Tonner and Frenking [86] argued, when two different fragmentation schemes are possible, the most favorable one is given by the smallest size of the $\Delta E_{\text{orb}}$ term. Therefore, we also performed EDA following the radical fragmentation scheme, and indeed, the ionic fragmentation gives a smaller $\Delta E_{\text{orb}}$ value than that of the radical one. On the other hand, since the total charges on the fragments, [H$_3$Si] or [HSi] and [NgNSi], are well below 0.5 |e|, we have partitioned H$_3$SiNgNSi and HSiNgNSi into neutral [H$_3$Si] or [HSi] and [NgNSi] fragments to explore the nature of Si–Ng bond, as the total charges on them are below 0.5 |e|. 
Table 5. Energy decomposition analysis (EDA) results of the H₃SiNgNSi and HSiNgNSi molecules studied at the revPBE-D3/TZ2P//MP2/def2-QZVPPD level. All of the energy terms are in kcal/mol.

| Compounds          | Fragments       | ΔE_{int} | ΔE_{Pauli} | ΔE_{elstat} | ΔE_{orb} | ΔE_{disp} |
|--------------------|-----------------|----------|------------|-------------|----------|-----------|
| H₃SiXeNSi          | [H₃Si] + [XeNSi] | −46.0    | 210.4      | −82.0 (32.0%) | −172.6 (67.3%) | −1.7 (0.7%) |
|                    | [H₃SiXe]⁺ + [NSi]⁻ | −128.1   | 111.6      | −159.4 (66.5%) | −78.6 (32.8%) | −1.7 (0.7%) |
| H₃SiRnNSi          | [H₃Si] + [RnNSi] | −49.9    | 198.8      | −80.0 (32.2%) | −166.9 (67.1%) | −1.8 (0.7%) |
|                    | [H₃SiRn]⁺ + [NSi]⁻ | −132.9   | 113.0      | −166.6 (67.7%) | −77.4 (31.5%) | −1.9 (0.8%) |
| HSiXeNSi           | [HSi] + [XeNSi] | −37.8    | 169.6      | −51.0 (24.6%) | −155.4 (74.9%) | −1.0 (0.5%) |
|                    | [HSiXe]⁺ + [NSi]⁻ | −120.4   | 103.4      | −148.0 (66.2%) | −74.0 (33.1%) | −1.7 (0.8%) |
| HSiRnNSi           | [HSi] + [RnNSi] | −41.0    | 163.9      | −50.9 (24.8%) | −153.0 (74.7%) | −1.1 (0.5%) |
|                    | [HSiRn]⁺ + [NSi]⁻ | −123.7   | 105.3      | −154.4 (67.4%) | −72.7 (31.7%) | −1.9 (0.8%) |

(The percentage values within the parentheses show the contribution towards the total attractive interaction ΔE_{elstat} + ΔE_{orb} + ΔE_{disp}).

In the Ng–N bonds, the contribution from ΔE_{elstat} towards the total attraction is the maximum ranging within 66%–68%. ΔE_{orb} contributes around 31%–33% towards the total attraction in these bonds. In cases of Si–Ng bonds, ΔE_{orb} is the largest contributor towards the total attraction (ca. 67%–75%), implying their covalent nature. In both Ng–N and Si–Ng bonds, ΔE_{disp} is found to be less important, as it contributes the least.

3. Experimental Section

The geometry optimization and the frequency calculation are performed at several levels, viz. ωB97X-D/def2-QZVPPD [87,88], MP2/def2-QZVPPD [89] and CCSD(T)/def2-TZVP [90], to ensure that the results obtained are not an artifact of the calculation at a particular level. For the core electrons of Xe and Rn, a quasi-relativistic pseudopotential is used [91]. At both the ωB97X-D/def2-QZVPPD and MP2/def2-QZVPPD levels, H₃SiNgNSi and HSiNgNSi (Ng = Ar–Rn) are found to be minima on the potential energy surface (PES). However, at the CCSD(T)/def2-TZVP level, the calculations for Ar and Kr inserted analogues do not converge; rather, the compounds dissociate into two fragments during optimization. Hence, we exclude those systems from the discussion. The occurrence of only one imaginary frequency with a mode, which leads to the desired products, implies the transition states (TSs) corresponding to the dissociations of H₃SiNgNSi and HSiNgNSi into Ng and H₃SiNSi or HSiNSi. All of these computations are performed by using the Gaussian 09 program package [92]. The atoms-in-molecules (AIM) analysis [71] is carried out by using Multiwfn software [93] at the MP2/def2-QZVPPD/WTBS level. All of electron WTBS [94,95] basis set is used for Xe and Rn.

The energy decomposition analysis (EDA) [72–75] is performed at the revPBE-D3/TZ2P//MP2/def2-QZVPPD [96–98] level using the ADF (2013.01) program package [99]. Scalar relativistic effects are considered for the heavier atoms using the zeroth-order regular approximation (ZORA) [100–102].

4. Conclusions

H₃SiNgNSi and HSiNgNSi (Ng = Xe, Rn) could be considered as metastable compounds. The 2-B dissociation pathways producing Ng and H₃SiNSi or HSiNSi are found to be highly exergonic in
nature at room temperature. However, they are found to be kinetically stable along the same dissociation channel due to their activation free energy barriers of 19.3 and 23.3 kcal/mol for $\text{H}_3\text{SiXeNSi}$ and $\text{H}_3\text{SiRnNSi}$, respectively, and 9.2 and 12.8 kcal/mol for $\text{HSiXeNSi}$ and $\text{HSiRnNSi}$, respectively. The Rn analogues have thermochemical stability with respect to all other possible dissociation channels. However, for $\text{H}_3\text{SiXeNSi}$, another 3-B dissociation channel producing $\text{H}_3\text{Si}$, Xe and NSi is slightly exergonic in nature at 298 K, but at a slightly low temperature (250 K), it turns out to be endergonic in nature. On the other hand, for $\text{HSiXeNSi}$ one 2-B ($\text{HSiNg}$ and NSi) and 3-B ($\text{HSi}$, Ng and NSi) dissociation paths are slightly exergonic in nature at room temperature. At low temperature (around 150–180 K), they become endergonic. The rest of the dissociation paths are not feasible. According to the argument of Hu et al. [77], $\text{H}_3\text{SiNgNSi}$ could be stable enough to be detected at the 250–300 K temperature range, whereas $\text{HSiNgNSi}$ needs a lower temperature (150–200 K) to be detected. The NPA charge suggests that they could be best represented as ($\text{H}_3\text{SiNg}^+$(NSi)$^-$ and ($\text{HSiNg}^+$(NSi)$^-$). Consequently, the WBI values for the Ng–N bonds are found to be quite low (~0.2), whereas the same for the Ng–Si bonds are quite large (~0.65), signifying the covalent nature of the bond. Large ELF values (~0.8) and negative values of $\nabla^2\rho(r_c)$ at the Si–Ng bond critical points further imply its covalent character. As expected from the ionic nature of Ng–N bonds, the maximum contribution in the total attraction energy comes from the $\Delta E_{\text{elstat}}$ (ca. 66%–68%). On the other hand, $\Delta E_{\text{orb}}$ is the main contributing term (ca. 67%–75%) in the total attraction energy of Si–Ng bonds, showing their covalent nature.

**Supplementary Materials**

Supplementary materials can be found at http://www.mdpi.com/1422-0067/16/03/6402/s1.

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**Author Contributions**

Sudip Pan performed the computations and wrote the manuscript. Ranajit Saha helped in preparing the manuscript. Pratim K. Chattaraj guided throughout the work, analyzed the results and reviewed the manuscript.

**Conflicts of Interest**

The authors declare no conflict of interest.

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