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STRUCTURE, STABILITY, DISSOCIATION AND THERMOCHEMISTRY OF SILANITRILES AND SILAISONITRILES: RSiN/ RNSi (R=HBe, HO, HS)

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Abstract

Structure, stability, and dissociation of HBeSiN, HOSiN, HSSiN, and their isomers HBeNSi, HONSi, and HSNSi have been studied in detail using density functional ωB97X-D, M062X, and ab initio MP2, CCSD and CCSD(T) methods. After dissociation of HBeNSi, HONSi, HSNSi, and their isomers, the fragmented atoms have been considered to be either in their ground state or in their valence excited state in various dissociation channels. Only allowed dissociations of these molecules are considered. Various dissociation channels of HBeNSi, HONSi, HSNSi and their isomers have been explored, and an interesting trend has been observed for the dissociation of stable isomers HBeNSi, HOSiN and HSNSi and less stable isomers HBeSiN, HONSi and HSSiN. The effects of substituents on their structural properties, PES for isomerization of RSiN↔RNSi along with their heat of formation, have been calculated using the G3 and G3B3LYP methods. The calculated results agree very well with the available theoretical values.

Keywords: Structure; Stability; Isomerization; Dissociation; Density Functional and ab initio methods; RSiN; RNSi

I. Introduction

Like carbon, silicon-containing molecules have also drawn immense interest in various fields of research such as astrophysics, astrochemistry, atmospheric science, and technology. The detection of CN and subsequent detection of CH_3CN, CH_2CHCN, CH_3CH_2CN, and HC_4CN [I] in the interstellar medium initiated the search for such molecules containing SiN, which was detected in the outer circumstellar envelope IRC +10216 [II]. Herbst et al [III] investigated an extended dense cloud model and reported a set of SiN-containing molecules predicted to be rich in the interstellar region. Apart from their astrophysical implications, SiN-based molecules are potential candidates to show thermal and elastic properties; therefore, they are widely used to prepare insulating layers in electronic fabrication and also as silicon nitride cantilevers [IV]. The reduced molecules from silicon-containing compounds also play an important role in these fields. Simple diatomic hydride BeH is assumed to be crucial in the description of the spherical collapse of the primordial gas clouds [V, VI]. The transient molecules such as SiHO attracted much attention in structural chemistry, reaction dynamics, and interstellar chemistry [VII]. Moreover, the SiHO molecule is thought to be an intermediate in the oxidation process of SiH_4 and plays a major role in the chemical vapor deposition process using the SiH_4 discharge plasma. The radical HSSi has an interest in the fields related to organo-silicon compounds and also in the chemical vapor deposition processes for amorphous silicon films [VIII]. Sulfur hydride SH, which is released in the environment through biogenic and non-biogenic sources, plays a crucial role in the atmospheric sulfur cycle. It is known that the most important reactions of SH in the troposphere are with ozone, molecular oxygen, and nitrogen dioxide [IX]. The species HNO and HSN have special interest both from experimental and theoretical points of view [X-XV]. Apeloig and Albrecht [XVI] studied the relative stabilities and energy barriers separating silanitriles (RSiN) and silaisonitriles (RNSi) using HF, MP2, MP4, and CASSCF methods. Mondal et al**.** [XVII] used the MP2/cc-pVTZ level of theory to investigate the structure and dissociation of MgSiN, MgNSi, and their hydrogenated and protonated forms, and the G3/G3MP2 level to calculate their reaction enthalpies. In 2011, Lauvergnat et al [IV] studied electronic structure calculations and spectral analysis using the RCCSD(T)/aug-cc-pVTZ method on H_2NSi molecules and their three isomers. Very recently, Ghosh et al. [XVIII] used both ab initio and DFT methods to calculate the stability of F-Si-Y (Y=N &P) and F-Ng-SiY (Ng=Kr, Xe, Rn) and their isomer.

In this article, we have modeled the structure and dissociation processes and thermochemistry of RNSi and RSiN (R=HBe, HO, HS) molecules from which atomic and reduced molecular systems are formed. These reduced molecular systems take part in various physical and chemical processes occurred in many areas of physics, chemistry, and technology. For various dissociation processes of these molecules, both ground and valence excited states of the fragmented atoms are considered. The existence of fragmented atoms in their ground and valence excited states was justified experimentally by Eberhardt et al [XIX].

II. Computational details

The structural properties and dissociation pathways of HBeSiN, HOSiN, HSSiN and their isomers HBeNSi, HONSi and HSNSi have been studied in detail

using density functional ωB97X-D, M062X [XX, XXI] ab initio MP2, CCSD and CCSD(T) [XXII-XXVII] methods. In the dissociation processes, the fragmented atoms have been considered to be either in their ground state or in their valence excited states. The dissociation energies are calculated using the energies of the separated fragments. The zero-point energy (ZPE) of molecules is taken into account to calculate the dissociation energies. Isomerization energy at the ab initio level and the Mulliken charges at the MP2/cc-pVTZ level have been investigated. The transition states connecting the RNSi and RSiN isomers are located at the MP2/cc-pVTZ level using the synchronous transit-guided quasi-Newton (STQN) method using the QST2 option. The intrinsic reaction coordinate (IRC) calculations are carried out with both the transition states to verify whether the TSs are connected to the desired minima or not. The electron correlation effects have been taken into account via Moller-Plesset perturbation (MP) theory and coupled cluster techniques. The ab initio methods applied to this work are second-order Moller-Plesset perturbation (MP2) theory and the coupled cluster CCSD and CCSD(T) methods. The CCSD(T) method includes single and double excitations and an estimate of triple excitations by a perturbation treatment, whereas the CCSD method incorporates only single and double excitations. The Gaussian 09 suite of quantum chemistry programs [XXVIII, XXIX] has been used to perform MP2, CCSD, and CCSD(T) calculations. The correlated consistent cc-pVTZ basis set for H, Be, Si, O, S, and N [XXX, XXXI] has been used to calculate the single-point energy of the molecules and fragments employing their geometry optimized by the ab initio methods with 6-311G** basis set for these atoms [XXXII, XXXIII]. Optimized geometries, vibrational frequencies, zero-point energy, and dipole moment of the molecules are calculated by density functional and ab initio methods using the 6-311G** basis set.

The heat of formation (HOF) at 0K and at finite temp (298.15K) is calculated using quantum chemical parameters from G3 and G3//B3LYP [XXXIV, XXXV] calculated in Gaussian 09. The atomization approach of Nicolaides [XXXVI] was used to calculate the heat of formation using the following steps.

$$\Delta H_f^0 = E_M - \sum E_{elements} + \sum \Delta H_{elements}^{Expt}$$

Where ΔH_f^0 → Heat of formation of the molecule at 0K

E_M → Energy of the molecule.

$\sum E_{elements}$ → Sum of energy of constituting atoms.

$\sum \Delta H_{elements}^{expt}$ → Experimental value of heat of vaporization of constituting atoms [XXXVII].

$$\Delta H_f^T = \Delta H_f^0 + \Delta H_M^T - \sum \Delta H_{elements}^T$$

ΔH_f^T → Heat of formation of the molecule at finite (298.15 K) temperature.

ΔH_M^T → Difference between enthalpy at 0K and T K $(H_M^T - H_M^0)$ of the molecule.

$\sum \Delta H_{elements}^T$ → Enthalpy difference (ΔH_T) of atoms at 298 K $(H_{298} - H_0)$.

The change in enthalpy at 298.15K (ΔH 298.15K) for the most favorable dissociation channel is computed using the equation:

$$\Delta H^{298.15K} = \Delta E^{298.15K} + \Delta(PV)$$

Where $\Delta E^{298.15K}$ *and* $\Delta(PV)$ are obtained from the electronic energy at 0 K, and the thermal correlation to enthalpy is obtained from frequency calculation [XXIX].

III. Results and discussion

The ground state energy and zero-point vibrational energy (in parentheses) of HBeNSi, HONSi, HSNSi and their isomers are calculated and summarized in Table I. Both HBeNSi and HSNSi are more stable than their isomers HBeSiN and HSSiN, respectively, but HONSi is less stable than HOSiN. At the CCSD(T)/cc-pVTZ level, the difference in ground-state energy between HBeNSi and HBeSiN is about 82 kcal/mol, and that between HSNSi and HSSiN is about 29 kcal/mol. This difference reduces to about 8 kcal/mol for the HOSiN-HONSi system. It may be noted that the difference in ground-state energies increases by about 5-7 kcal/mol from the MP2 to CCSD(T) method for HBeSiN-HBeNSi and HSSiN-HSNSi systems, but it decreases by about 8 kcal/mol for the HONSi-HOSiN system. The order-stability of the RSiN-RNSi system reverses in the presence of comparatively more electronegative substituent R=OH, which makes the ground-state energies close. For the HBeSiN and HSSiN systems, the relative energy at the CCSD(T)/cc-pVTZ level is 8-13 kcal/mol higher than the MP4/6-311+G** values of Apeloig and Albrecht [XVI]. For the HOSiN system, the CCSD(T) relative energy is very close to their QCISD(T)/6-311G(2df,p) value [XVI].

Table I: Relative energy (kcal/mol) of R-SiN (R=HBe, HO, HS) and their principal isomers at 0 K.

Method	ΔE ($E_{M2} - E_{M1}$)	ΔE ($E_{M4} - E_{M3}$)	ΔE ($E_{M6} - E_{M5}$)
MP2	75.42	16.49	22.23
CCSD	88.38	5.16	35.08
CCSD(T)	81.86	8.15	29.34
Ref[a]. [Theory]	68.9	13.2, 1.8, 3.3, 11.4, 6.5	21.8

The molecules HBeNSi, HBeSiN, HOSiN, HONSi, HSNSi, HSSiN are denoted as M_1, M_2, M_3, M_4, M_5, M_6, and the total energies (a.u.) are denoted as E_{M1}, E_{M2}, E_{M3}, E_{M4}, E_{M5}, E_{M6}, respectively. [a]Apeloig and Albrecht [XVI].

The optimized geometrical parameters and dipole moment of HBeSiN, HOSiN, HSSiN and their silaisonitrile form are calculated consistently in different density functional and ab initio methods and listed respectively in Table II and Table III. In HBeSiN, the Si-N bond length is around 0.05Å lower than that reported by Apeloig and Albrecht, but the Be-Si bond length and ∠BeSiN agree well with their values. According to the calculation of Apeloig and Albrecht, both HOSiN and HSSiN are linear, but our CCSD(T) calculation shows that the molecule is tilted about 7° (∠RSiN

~173°), which is also supported by the CCSD result. This non-linearity/linearity can be explained by the Mulliken charges on individual atoms shown in Table XII. For both HOSiN and HSSiN systems, the charge on the H atom is positive and that on the N atom is negative. So the highly electronegative N atom attracts the electropositive H atom, making these molecules non-linear. In contrast, the charge on the two ends, H and N atoms, of HBeSiN is negative, which prevents the molecule from becoming non-linear. So HBeSiN is found to be linear. For all these three molecules (RNSi, R=HBe, HO and HS), our calculated bond lengths and bond angles (∠Be/O/S-N-Si) agree very well with the results of Apeloig and Albrecht [XVI]. The dipole moment of HBeSiN, HOSiN and HSSiN calculated by the CCSD(T) method is ~3.8 D higher than that of their corresponding isomer. The high dipole moment is due to the position of electropositive and electronegative atoms in the molecule.

Table II: Optimized geometries and dipole moment for RSiN (R=HBe, HO, HS) molecules.

Molecule	R	Method	N–Si (Å)	R–Si (Å)	∠RSiN (deg.)	Dipole Moment (D)
HBeSiN	HBe	ωB97XD	1.561	2.174	179.7	5.31
HBeSiN	HBe	M06-2X	1.559	2.154	180.0	5.39
HBeSiN	HBe	MP2	1.642	2.152	180.0	6.13
HBeSiN	HBe	CCSD	1.581	2.156	180.0	4.77
HBeSiN	HBe	CCSD(T)	1.599	2.150	180.0	6.13
HBeSiN	HBe	Ref [XVI]	1.651	2.147	180.0	
HOSiN	HO	ωB97XD	1.554	1.617	177.4	5.26
HOSiN	HO	M06-2X	1.553	1.614	175.8	5.32
HOSiN	HO	MP2	1.600	1.640	179.5	5.76
HOSiN	HO	CCSD	1.575	1.624	165.7	4.39
HOSiN	HO	CCSD(T)	1.584	1.634	172.6	5.65
HOSiN	HO	Ref [XVI]	1.606	1.656	179.5	
HSSiN	HS	ωB97XD	1.555	2.107	177.5	4.88
HSSiN	HS	M06-2X	1.555	2.104	174.3	4.99
HSSiN	HS	MP2	1.619	2.129	179.5	5.66
HSSiN	HS	CCSD	1.577	2.115	161.4	4.38
HSSiN	HS	CCSD(T)	1.588	2.127	173.9	5.70
HSSiN	HS	Ref [XVI]	1.625	2.133	180.0	

Table III: Optimized geometries and dipole moment for RNSi (R=HBe, HO, HS) molecules

Molecule	R	Method	N–Si (Å)	R–N (Å)	∠RNSi (deg.)	Dipole Moment (D)
HBeNSi	HBe	ωB97XD	1.567	1.503	180.0	1.84
HBeNSi	HBe	M06-2X	1.569	1.500	180.0	2.01
HBeNSi	HBe	MP2	1.589	1.516	180.0	2.29
HBeNSi	HBe	CCSD	1.575	1.507	180.0	1.89
HBeNSi	HBe	CCSD(T)	1.585	1.511	180.0	2.36
HBeNSi	HBe	Ref [XVI]	1.592	1.515	180.0	
HONSi	HO	ωB97XD	1.554	1.338	173.7	1.50
HONSi	HO	M06-2X	1.555	1.341	174.2	1.55

HONSi	HO	MP2	1.582	1.345	174.8	1.84
HONSi	HO	CCSD	1.562	1.351	174.0	1.42
HONSi	HO	CCSD(T)	1.575	1.356	173.8	1.82
HONSi	HO	Ref [XVI]	1.586	1.355	175.9	
HSNSi	HS	ωB97XD	1.561	1.656	174.8	1.05
HSNSi	HS	M06-2X	1.563	1.656	174.8	1.14
HSNSi	HS	MP2	1.583	1.668	174.6	1.59
HSNSi	HS	CCSD	1.567	1.667	174.4	0.92
HSNSi	HS	CCSD(T)	1.577	1.670	174.2	1.58
HSNSi	HS	Ref [XVI]	1.587	1.669	175.2	

The calculated dissociation energies of HBeNSi and HBeSiN through various dissociation channels are presented in Table IV and Table V. Four dissociation channels have been considered on the basis of availability of fragment radicals and atoms in the interstellar region, and the fragmented atoms and molecules are considered in their ground state (in Table IV) and in valence excited state (in Table V). The dissociation energy for HBeSiN is found to be less than that of its isomer for both in the ground state and in the valence excited state. The higher dissociation energy is obtained for the first dissociation channel where HBeNSi/HBeSiN dissociated to two fragmented atoms. The lowest dissociation energy is estimated for the last channel where the molecule dissociated to two diatomic molecules. In the last dissociation channel, the BeH molecule, which is assumed to play an important role in different processes occurred in cosmology, and the SiN molecule, which was detected in the outer circumstellar envelope, are released from the molecule. The dissociation energy for the second channel is close to that for the third one. These two dissociation energies are separated by 0.65 eV. The dissociation energy depends on the nature of the fragmented atoms and molecules. As HBeNSi is more stable than HBeSiN, the dissociation energy of the former for all four dissociation channels is higher than that of the corresponding channel of the latter. The probability of formation of SiN and HBe from a less stable molecule is more than that from the more stable one. Only three dissociation channels are allowed by the selection rule. The dissociation energy depends on the nature of the valence excited state of the fragmented atoms. In the first dissociation channel, the two fragmented atoms Si and N are in their valence excited states, and hence the dissociation energy for this channel is highest among all the three channels. The dissociation energy decreases with a reduced number of fragmented atoms in the dissociation channel. The last channel is the most energetically favorable one where N is produced in its valence excited state.

Table IV: Dissociation energies (eV) of HBeNSi and HBeSiN molecules at various dissociation channels when atoms are in the ground state.

Dissociation Scheme	MP2 HBeNSi	MP2 HBeSiN	CCSD(T) HBeNSi	CCSD(T) HBeSiN
HBe($X\ ^2\Sigma^+$) + Si(^3P) + N(^4S)	10.86	7.59	10.42	6.87
HBeSi($X\ ^2A''$) + N(^4S)	8.54	5.27	7.93	4.38
HBeN($X\ ^3\Sigma^-$) + Si(^3P)	7.78	4.51	7.28	3.73
SiN($X\ ^2\Sigma^+$) + HBe($X\ ^2\Sigma^+$)	7.13	3.86	6.34	2.79

Table V: Dissociation energies (eV) of HBeNSi and HBeSiN molecules at various dissociation channels when fragmented atoms are in a valence excited states.

Dissociation Scheme	MP2 HBeNSi	MP2 HBeSiN	CCSD(T) HBeNSi	CCSD(T) HBeSiN
HBe(X $^2\Sigma^+$) + Si(^{1}D) + N(^{2}D)	15.47	12.20	14.07	10.52
HBe(X $^2\Sigma^+$) + Si(^{3}P) + N(^{2}D)	14.17	10.90	13.16	9.61
HBeSi(X ^{2}A") + N(^{2}D)	11.85	8.58	10.68	7.13

The dissociation energies of HONSi and HOSiN in various dissociation channels are calculated in Table VI. In these dissociation channels, the fragmented atoms are in their ground states. Comparing Tables IV and VI, it is observed that the lowest dissociation energy of HOSiN is obtained for the channel where HOSiN dissociated to a triatomic and an atom, whereas for HBeSiN the lowest dissociation energy is calculated for the channel where HBeSiN dissociated to two diatomics. For a particular channel, the dissociation energy of HOSiN is lower than that of HBeNSi for the corresponding channel. The dissociation energy of HBeSiN for the channel where two diatomics are produced is about 1 eV lower than that of HOSiN for the corresponding channel. In the last channel, HOSi is released from the molecule.

Table-VI: Dissociation energies (eV) of HONSi and HOSiN molecules at various dissociation channels when atoms are in the ground state

Dissociation Scheme	MP2 HONSi	MP2 HOSiN	CCSD(T) HONSi	CCSD(T) HOSiN
HO(X $^2\Pi$) + Si(^{3}P) + N(^{4}S)	8.03	8.75	7.42	7.77
HON(X ^{3}A") + Si(^{3}P)	5.12	5.83	4.64	4.99
SiN(X $^2\Sigma^+$) + HO(X $^2\Pi$)	4.30	5.02	3.34	3.69
HOSi(X ^{2}A′) + N(^{4}S)	2.67	3.38	2.34	2.69

In Table VII, after dissociation of HONSi and HOSiN, the fragmented atoms in three allowed dissociation channels are in valence excited states. It is important to note that for all three dissociation channels shown in Table V, the dissociation energy of HBeNSi is about 3.5 eV greater than that of HBeSiN, whereas the dissociation energy of HONSi is very close to that of HOSiN. The difference between the two dissociation energies is 0.35 eV, which is one-tenth of that for HBeSiN and HBeNSi. Unlike HBeSiN, HOSiN is more stable than its isomer HONSi. So, for all three channels, the dissociation energy of HOSiN is greater than that of HONSi.

Table-VII: Dissociation energies (eV) of HONSi and HOSiN molecules at various dissociation channels when fragmented atoms are in a valence excited state.

Dissociation Scheme	MP2 HONSi	MP2 HOSiN	CCSD(T) HONSi	CCSD(T) HOSiN
HO($X\ ^2\Pi$) + Si(^1D) + N(^2D)	12.64	13.36	11.07	11.42
HO($X\ ^2\Pi$) + Si(^3P) + N(^2D)	11.34	12.06	10.17	10.52
HOSi($X\ ^2A'$) + N(^2D)	5.98	6.70	5.09	5.44

The dissociation energies of HSNSi and HSSiN in various dissociation channels are calculated in Table VIII. In these dissociation channels, the fragmented atoms are in their ground states. The dissociation pattern of HSSiN/HSNSi is similar to that of HBeSiN/HBeNSi shown in Table IV. Like HBeNSi, HSNSi is more stable than its isomer. It is important to note that for all dissociation channels, the dissociation energy of HBeNSi is much greater than that of HSNSi. In HBeNSi, Be is much less electronegative than N, whereas in HSNSi, the electronegativity of S is comparable to that of N. So the bond between the atoms Be and N is much stronger than that between S and N. Therefore, the energy required to break the Be-N bond would be greater than that required to break the S-N bond. This is reflected in the bond dissociation energies of HBeNSi and HSNSi systems. It is interesting to note that the dissociation energy of HSNSi for the second channel is about 1 eV greater than that for the third channel. In the second dissociation channel, where the SHN molecule is released, the N-Si bond breaks, keeping the S-N bond intact. But in the third channel, the S-N bond breaks and N is produced in its ground ^4S state along with the HSSi molecule. The electronegativity of Si (1.9) is much less than that of N (3.0) and S (2.58), and hence the strength of the NSi bond is greater than that of the S-N bond. Therefore, the higher dissociation energy for the second dissociation channel is due to the N-Si bond, which is stronger than the SN bond. For HBeNSi, the Si-producing channel is energetically lower than the N-producing channel, which is opposite to that observed for HSNSi. These two channels of HBeNSi are separated by 0.65 eV of energy. The lower dissociation energy for the Si-producing third channel is due to the strength of the NSi bond, which is slightly weaker than that of the Be-N bond. In HSNSi, the N-Si bond is stronger than the S-N bond, which makes the Si-producing channel energetically higher. If the second and third channels are considered as formation reactions of HSSiN and HSNSi, then these reactions must be insertion reactions of Si and N atoms into S-N and Si-S bonds, respectively. The last dissociation channel, where HS is released from the molecule, is the energetically most favorable one. Indeed, the electronegativity of Be (1.57), Si (1.9), S (2.58), and N (3.0) is responsible for the interesting pattern of the dissociation energies.

Table VIII: Dissociation energies (eV) of HSNSi and HSSiN molecules at various dissociation channels when atoms are in the ground state

Dissociation Scheme	MP2 HSNSi	MP2 HSSiN	CCSD(T) HSNSi	CCSD(T) HSSiN
HS($X\ ^2\Pi$) + Si(^{3}P) + N(^{4}S)	8.30	7.34	7.74	6.47
HSN($X\ ^1A'$) + Si(^{3}P)	5.74	4.78	5.24	3.97
HSSi($X\ ^2A'$) + N(^{4}S)	4.71	3.74	4.26	2.99
SiN($X\ ^2\Sigma^+$) + HS($X\ ^2\Pi$)	4.57	3.61	3.66	2.39

The dissociation energies of the HSNSi-HSSiN system at various dissociation channels are summarized in Table IX. In these channels, fragmented atoms are in the valence excited states. It can be noted that four dissociation channels are allowed by the selection rule, whereas for the HBeNSi-HBeSiN and HONSi-HOSiN systems only three dissociation channels, as shown in Tables V and VII, respectively, are permitted. The dissociation energy for all the channels of HSNSi is lower than that of HBeNSi/HBeSiN. This reduction of dissociation energy is mainly due to the strength of the S-N bond, which is weaker than that of the Be-N bond. In the third channel, although the Si-N bond breaks in both cases, the dissociation energy of HSNSi is about 3.7 eV lower than that of HBeNSi. This is due to the ground-state energy of the parent and fragmented triatomic which is different in the two cases.

Table-IX: Dissociation energies (eV) of HSNSi and HSSiN molecules at various dissociation channels when fragmented atoms are in a valence excited state.

Dissociation Scheme	MP2 HSNSi	MP2 HSSiN	CCSD(T) HSNSi	CCSD(T) HSSiN
HS($X\ ^2\Pi$) + Si(^{1}D) + N(^{2}D)	12.91	11.95	11.39	10.12
HS($X\ ^2\Pi$) + Si(^{3}P) + N(^{2}D)	11.61	10.65	10.49	9.22
HSSi($X\ ^2A'$) + N(^{2}D)	8.02	7.05	7.01	5.74
HSN($X\ ^1A'$) + Si(^{1}D)	7.04	6.08	6.15	4.87

As seen from Tables II and III, the dipole moment of HBeSiN is about three times greater than that of HBeNSi. The increase in the dipole moment of HBeSiN is due to the presence of both electropositive atoms adjacent to each other and on one side of the highly electronegative nitrogen atom. The dipole moment of HSSiN is slightly lower than that of HBeSiN. This slight reduction of the dipole moment of HSSiN is due to the more electronegative S atom in the place of Be. This relatively large dipole moment of HBeSiN, HOSiN, and HSSiN will make the isomers observable via MW spectroscopy. The dipole moment would be further reduced slightly if the S atom is replaced by more electronegative O, which we observed in HOSiN. As the two electropositive atoms, Be and Si reside at the two ends of HBeNSi, the dipole moment

of the molecule would be small. The dipole moment would be decreased further if a less electropositive atom appears in the place of Be.

The barriers for the RSiN↔RNSi isomerization reactions are summarized in Table X, and the structures of transition states are depicted in Fig I. The isomerization reactions are studied at the MP2/cc-pVTZ level. The RSiN↔RNSi (R=HBe, HO, HS) isomerization proceeds through a reactant-like transition state that has a bent structure and is close in energy to the RSiN form for HBe and HS substituents, and for the HO substituent, the energy of the transition state is close to the RNSi form. For HBeSiN, the isomerization barrier is calculated to be 16.46 kcal/mol at the MP2/cc-pVTZ level of theory, whereas for HSSiN the corresponding barrier is 48.86 kcal/mol. Therefore, HBeNSi↔HBeSiN conversion is easier than HSNSi↔HSSiN. In the case of HOSiN, the barrier is 64.11 kcal/mol. The barrier for isomerization is very sensitive to the level of computation. In the calculation of Apeloig and Albrecht [XVI], the isomerization barrier for HOSiN varies from 34.2 to 55.3 kcal/mol, and that depends upon the method and basis set. Moreover, the barrier increases with improvement of both method and basis set. The basis sets used in the calculation of Apeloig and Albrecht are much smaller than those used in our calculation.

Table-X: Calculated Barriers (kcal/mol) for the RSiN↔RNSi Isomerization[a] at MP2/cc-pVTZ level.

R	RSiN → RNSi	Other values[b]	RNSi → RSiN	Other values[b]
HBe	**16.46**	13.2	92.14	82.1
HO	64.11	55.3, 37.5, 34.2, 35.8, 45.3	**47.62**	42.1, 35.7, 31.1, 29.4, 33.8
HS	**48.86**	42.1	71.19	63.9

[a]The lower barrier in each case is given in boldface, [b]Apeloig and Albrecht [XVI].

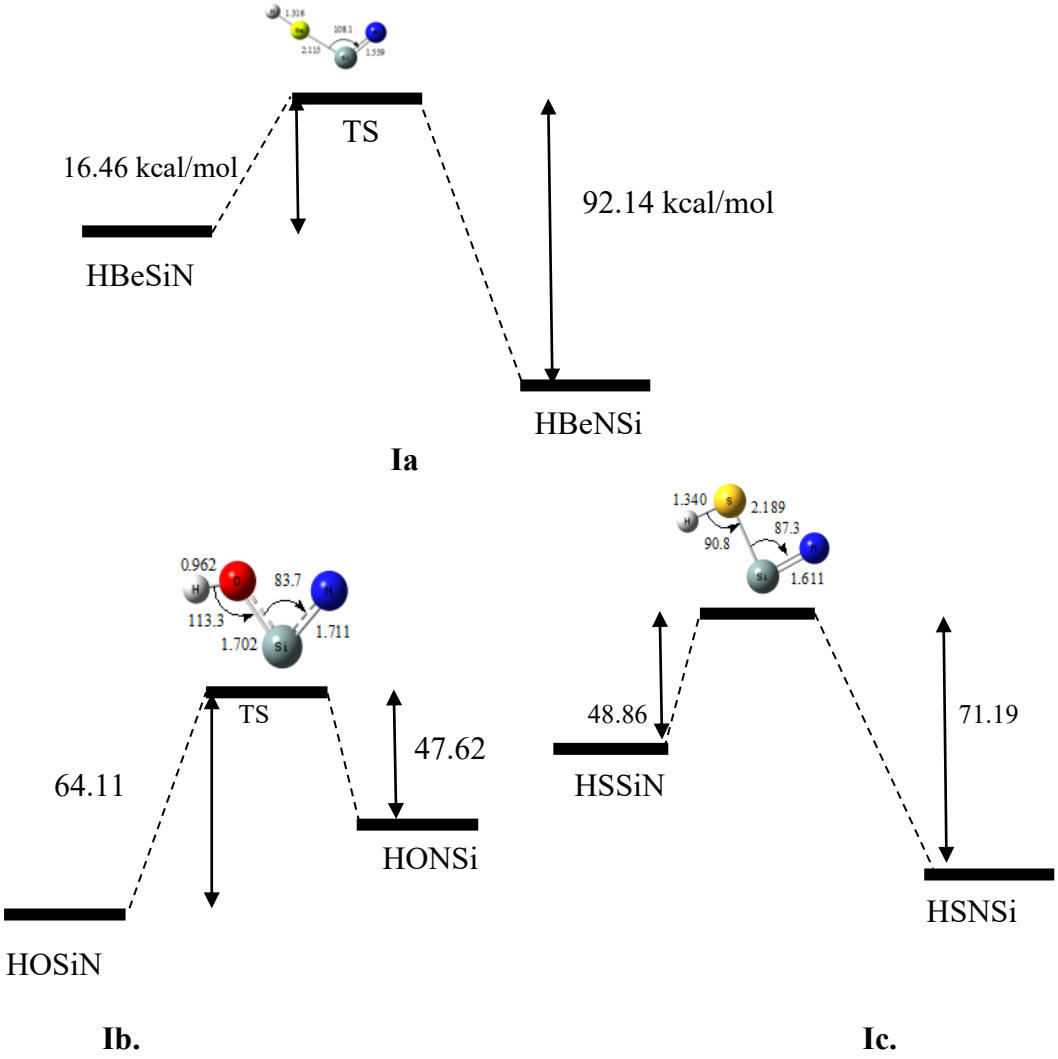

Fig. I Activation energy (kcal/mol) and TSs for RNSi↔RSiN (**Ia**. R=HBe, **Ib**. R=HO & **Ic.** R=HS) isomerization calculated at the MP2/cc-pVTZ level (bond length in Å and angle in deg)**.**

In Table XI, the heat of formation of all these SiN-based molecules is summarized. The HOF is calculated using both the G3 and G3B3LYP methods. Our calculated results for the heat of formation both at 0K and 298 K are very consistent. It is observed that the HOF for HBeSiN/HSSiN is more than that of its NSi isomeric part, which suggests the stability of the NSi isomer is more than that of the respective SiN isomer. Some kinds of stability-order reversal have been observed for the HOSiN molecule. Similar results have been reported in the recent literature [XVIII], where the stability of the F-SiN is found to be more stable than that of the F-NSi isomer, and the insertion of a noble gas (Ng=Kr, Xe, and Rn) increases the stability of F-Ng-NSi more than that of the F-Ng-SiN isomer. The presence of a noble gas atom made the molecule thermodynamically unstable, and they are stable only kinetically. The

calculated HOF for these molecules and the activation energy from their potential energy surface, as indicated in Table X, justify the reason for showing such a stability order upon isomerization. The results from both G3/G3B3LYP calculations, the HOF of HBeSiN and HSSiN, vary from 88 kcal/mol to 127 kcal/mol, which is much higher than that of the HOF of HOSiN (~34 kcal/mol) upon isomerization; the value becomes less for HBeNSi/HSNSi but more for HONSi. The presence of a more electronegative HO^- radical in HOSiN has made it more stable compared to HBeSiN/HSSiN. The Mulliken charge analysis in Table XII shows a qualitative explanation for the arising of such stability on isomerization. In the supplementary copy, the ground state energy and zero-point energy values of the molecules at MP2, CCSD, and CCSD(T) levels have also been enlisted in Table IA.

Table XI: Heat of formation (kcal/mol) at 0K (ΔH_f^0) and 298.15K ($\Delta H_f^{298.15}$) for all the molecules and their isomers at G3 and G3//B3LYP level.

Molecule	Heat of formation at 0K:G3	Heat of formation at 0K:G3//B3LYP	Heat of formation at 298.15 K: G3	Heat of formation at 298.15 K: G3//B3LYP
HBeSiN	129.27	127.97	126.68	125.36
HBeNSi	46.65	46.60	43.86	43.80
HOSiN	34.25	33.43	31.47	30.88
HONSi	43.26	42.46	40.32	39.54
HSSiN	89.94	88.78	87.34	86.42
HSNSi	58.35	57.88	55.59	55.12

Table XII: Mulliken charges of HBeNSi/HBeSiN, HONSi/HOSiN and HSNSi/HSSiN at MP2/cc-pVTZ level.

Molecule	H	Be/O/S	N	Si
HBeNSi	-0.14	0.10	-0.24	0.27
HBeSiN	-0.13	0.29	-0.41	0.25
HONSi	0.25	-0.27	-0.24	0.26
HOSiN	0.26	-0.39	-0.46	0.59
HSNSi	0.09	0.03	-0.44	0.32
HSSiN	0.14	-0.12	-0.44	0.42

IV. Conclusion

Structure, stability, and dissociation of RSiN (R=HBe, HO, HS) molecules and their isomers have been studied in detail using ab initio MP2, CCSD, and CCSD(T) methods. For HBeSiN and HSSiN systems, HBeNSi and HSNSi are more stable than their isomers, HBeSiN and HSSiN, respectively. This trend reverses for the HOSiN-HONSi system, where HOSiN is more stable than its isomer. The electronegativity of the substituent group dictates the stability of the molecules. An interesting trend has been observed for the dissociation energies of these molecules. For HBeNSi and HSNSi systems, the lowest dissociation energy has been obtained for the channel where the molecule dissociates to two diatomics, but for HOSiN systems, the molecule produces a triatomic and nitrogen atom for the lowest dissociation energy. For the dissociation channels where the fragmented atoms and molecules are in the ground state, the dissociation energies of HBeNSi and HSNSi are well separated

from those of their isomers HBeSiN and HSSiN, respectively, but for the HOSiN-HONSi system, the dissociation energies of HOSiN for various dissociation channels are very close to that of HONSi, making it difficult to distinguish. For the HBeNSi system, the Si-producing channel is energetically lower than the N-producing channel, whereas for the HSNSi systems, the N-producing channel is energetically favored.

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Supplementary

Table-IA: Ground state energy E_g (a.u) and zero-point energy ZPE (a.u) of the molecules.

Molecule	MP2 (E_g)	MP2 (ZPE)	CCSD (E_g)	CCSD (ZPE)	CCSD(T) (E_g)	CCSD(T) (ZPE)
HBeNSi	-359.0021697	0.013250*	-359.0154772	0.013150	-359.0348204	0.012993
HBeSiN	-358.8796564	0.010932	-358.8729222	0.011433	-358.9025799	0.011213
HONSi	-419.3324874	0.018104	-419.3379173	0.018465	-419.3669447	0.017581
HOSiN	-419.3572895	0.016624	-419.3438304	0.016148	-419.3782003	0.015844
HSNSi	-741.9781066	0.013969	-741.9986874	0.014076	-742.0268055	0.013797
HSSiN	-741.9411412	0.012423	-741.9409902	0.012277	-741.9781669	0.011913

* Zero Point Energy (using 6-311G** basis set) and Energy (E_g) in cc-pVTZ//6-311G** basis set.

Conflict of Interest:

The authors declare that there was no relevant conflict of interest regarding this paper.

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