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Formation of Silicon Analogues of Thio-isocyanic Acid, HNSiS, and Its Isomers by Neutral−Neutral Reactions of the Fragments: A Computational Study†

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Here, we report the detailed potential energy surface (PES) of the singlet and the triplet [H,N,Si,S] generated using the DFT-based G3B3 methodology and ab initio-based CCSD/6-311G(d,p)//MP2/6-311+G(d,p) methods. The PES reveals a lot of stationary states, thus indicating the possible existence of stable species. While the most stable molecules of the carbon analogues, isocyanic acid, HNCO, and thio-isocyanic acid, HNCS, have been detected in interstellar space, these silicon species have not yet been reported. Considering the potential importance of silicon in interstellar space, this is of interest. The barriers for isomerization and dissociations for these have been calculated, and they ascertain the stability. Thus, the most stable isomer on this surface, HNSiS ($^1A'$) requires about 50 kcal/mol for the lowest isomerization, and the lowest dissociation is 71 kcal/mol. On this surface, some intersystem crossings between the singlets and the triplets occur, and the geometries at these crossing points have also been determined. It is suggested that these silicon analogues of the important thio-fulminic acid and thio-isocyanic acid are stable species, which may be experimentally generated at the laboratory level. The neutral−neutral reactions of the fragments leading to the stable isomers have also been mapped to suggest their possible formation in the interstellar space.

Introduction

While isocyanic acid (HNCO) and its sulfur analogues thio-isocyanic acid (HNCS) have been identified in the interstellar space, the corresponding silicon analogues, (HNSiO) and (HNSiS), have not yet been detected.[1] This is despite the fact that the fragments of these isomers such as SiO, SiN, OH, NH, NO, SiS, and HNO are present in the interstellar space.[1] Given the low temperature and low pressure conditions existing there, it would be of interest to understand the possible formation, stability, and fragmentation of these silicon analogues of the isocyanic acid such as HNSiO and analogues of thio-isocyanic acid HNSiS and their isomers. On the other hand, the laboratory conditions required for isolating these isomers have to be understood, and to date only some calculations on the relative stability of the chainlike isomers of the oxygen analogue, that is, HNSiO, have been reported.[2] This then calls for a detailed study of this species, and, ideally, the potential energy surfaces (PES) by computational methods would give an in-depth picture of these isomers. Recently, the detailed studies of the PES of the isomers of [H,N,C,O] and recently [H,N,C,S] and [H,N,Si,O] have been reported.[3−9] Another analogue of this 16-valence-electron system, but with nitrogen replaced by phosphorus, [H,P,C,O], has also been reported.[10] Although silicon-containing molecules are important both from the reactions in the interstellar space and the semiconductor materials viewpoint, we have not come across any detailed study of the PES or reactions leading to the isomers of [H,N,Si,S].[11] Thus, in this work, we study the stability of these isomers by first generating the singlet and triplet potential energy surfaces, and then we look for the stationary points. With the help of the transition states, we understand the barrier toward isomerization and in some cases also dissociation. The stability of these isomers with respect to its fragments is calculated. We find that on this surface there are some spin-forbidden fragmentations for which we calculate the crossing points. We then finally look into the neutral−neutral reactions of these fragments for generation of the isomers.

Computational Methods

Recent work on silicon species has shown that the widely used B3LYP method with split valence (+polarization/diffuse + polarization) basis sets is quite suitable for geometry and property predictions.[12,13] An accurate estimation of the energies involving a series of single-point calculations on the DFT geometry, such as the compound G3B3 method, is carried out to see its effect on the relative stabilities and isomerization energies.[14] The G3B3 methodology uses the B3LYP/6-31G(d) minimized geometries as the starting point for the higher-level single point corrections and also the ZPVE corrections based at the same level which differ from the more common G3 method in which the MP2-based geometries and HF-based ZPVE are used. The total energies obtained at 0 K by G3B3 methodology are used to calculate the heat of formation (ΔH_f).[15] The triplet isomers are obtained using the unrestricted open-shell methods, and the spin contamination is found to be small, with the maximum $\langle S^2 \rangle$ value of 2.08 obtained only in one or two cases. The heat of formation is estimated using the atomization methods reported in the literature.[15]

All of the DFT calculations are carried out using the Gaussian 98 software package.[16,17] The optimizations are carried out on all of the possible isomers of [H,N,Si,S] and their fragments by the G3B3 method. All geometries are analyzed by harmonic

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TABLE 1: Total Energies (au), Heats of Formation (kcal/mol), and Dipole Moments (D) of the Various Singlet Isomers of [H,N,Si,S] Calculated in This Work[a]

isomers	G3B3(0 K)	ΔH_f (0 K) based on G3B3 methods	dipole moment (D) (G3B3)	CCSD/6-311G(d,p) //MP2/6-311+G(d,p)
HNSiS ^{1}**1**	−742.725288 (0.0)	40.7	1.8	−741.884738 (0.0)
HNSSi ^{1}**2**	−742.624635 (63.2)	103.9	3.6	−741.769467 (72.3)
HSiNS ^{1}**3**	−742.655527 (43.8)	84.5	0.5	−741.822477 (39.1)
HSiSN ^{1}**4**	−742.596590 (80.8)	121.5	3.3	
HSSiN ^{1}**5**	−742.646321 (49.6)	90.3	6.5	−741.807121 (48.7)
HSNSi ^{1}**6**	−742.695559 (18.7)	59.4	2.0	−741.868917 (9.9)
NSi(H)S ^{1}**7**	−742.627242 (61.5)	102.2	5.3	−741.780559 (65.4)
SiN(H)S ^{1}**8**	−742.699134 (16.4)	57.2	2.2	−741.861705 (14.5)
NS(H)Si ^{1}**9**	−742.672180 (33.3)	74.1	2.6	−741.833660 (32.1)

[a] The relative energies are calculated with respect to ^{1}**1** and are shown in parentheses.

vibrational frequencies obtained at the B3LYP/6-31G(d) level and characterized as minima (no imaginary frequency), or as a transition state (one imaginary frequency). The transition state geometries are then used as input for IRC calculations to verify the connectivity of the reactants and products.[18]

For comparison, the PES is also generated using the ab initio CCSD/6-311G(d,p)//MP2/6-311+G(d,p)+ZPVE method. We find that there is a good agreement between the two methods for both geometries and relative energies. The values generated by this method are shown in the tables and figures, and only in the rare case where there is a difference between the two are they discussed in the text along with the reason for the anomaly.

Results and Discussion

Singlet Surface. *Isomers.* Both chainlike isomers and the branched/cyclic isomers stationary on the singlet surface of [H,N,Si,S] (there are nine isomers) are reported for the most stable species along with details such as total energies in Table 1 and geometries in Figure 1. Comparing the structures of the other 16 valence electron systems such as [H,N,C,S], [H,P,C,O], [H,N,Si,O], or [H,N,C,O] to the structures of these isomers, we found that they are almost similar with the chainlike analogues of isocyanic acid with NH (or PH) connectivity being the most stable isomer, that is, HNSiO, HNSiS, HNCO, HNCS, or HPCO.[2−9] The angles in the most stable isomers are almost equal except in the phosphorus analogue where a bond angle of less than 90° was obtained for the angle HPC.[10] Here, this bond angle is around 140°. In three isomers, **3**, **5**, and **6**, the heavy atoms (SiNS) almost lie in a straight line with the angle between them varying from 169.0° to 176°. Isomers **8** and **9** are cyclic isomers which are also the only nonplanar molecules on this surface, while isomer **7** can be at best classified as a branched molecule because the distance between N and S is around 2.184 Å.

The relative energies are calculated with respect to the most stable isomer. The lowest (global minimum) predicted is isomer ^{1}**1**. This is expected as the hydrogen atom in unsaturated structures containing silicon usually goes to the most electronegative element (nitrogen), and this has the lowest energy. Here, the N−Si bond length is 1.563 Å. The next low-lying singlet isomer is **8**, which can be described as the cyclized isomer of **1** and lies about 16.4 kcal/mol above the lowest isomer and is nonplanar. The next low-lying isomer is **6**, which is a linear chain having a SNSi connectivity, while the SSiN connectivity isomer **5** is less stable as the atoms here do not have their valence satisfied unlike in **6**. Isomer **9**, the cyclic nonplanar molecule, lies about 33.3 kcal/mol above the lowest isomer. Isomer **7**, the branched isomer, lies about 61.5 kcal/mol above **1**. The calculated heats of formation are also shown in Table 1. The isomer with the lowest heat of formation is the analogue of isocyanic acid, HNSiS, having a heat of formation of 40.7 kcal/mol. The ab-initio-based MP2 calculations show that the trend is not too different and the relative energies/geometries are almost same. Isomer **4** in this method always optimized to the higher lying excited state and hence is not reported.

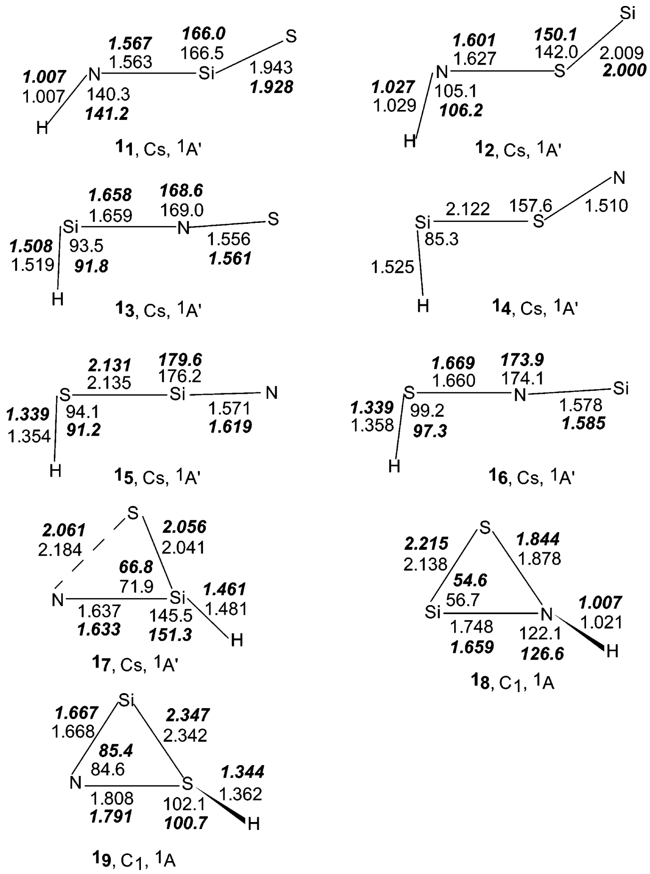


Figure 1. Equilibrium geometries in the singlet state of the [H,N,Si,S] system, optimized at the G3B3 level and MP2 methods (bold italics). Bond lengths are in angstroms, and angles are in degrees.

PES. Interconversions between the isomers can be broadly divided into three types, cyclization (or ring opening), 1,2-H migration, 1,3-H migration, and sometimes combinations between these. The potential energy surfaces generated are shown in Figure 2. The relative energies are indicated in the figures with respect to the most stable isomer. The transition state energies are tabulated in Table 2. The transition state geometries obtained are shown in Figure 3.

Singlet isomer **1** can isomerize to **8** by cyclization. The transition state of the isomerization between ^{1}**1** and ^{1}**8** is

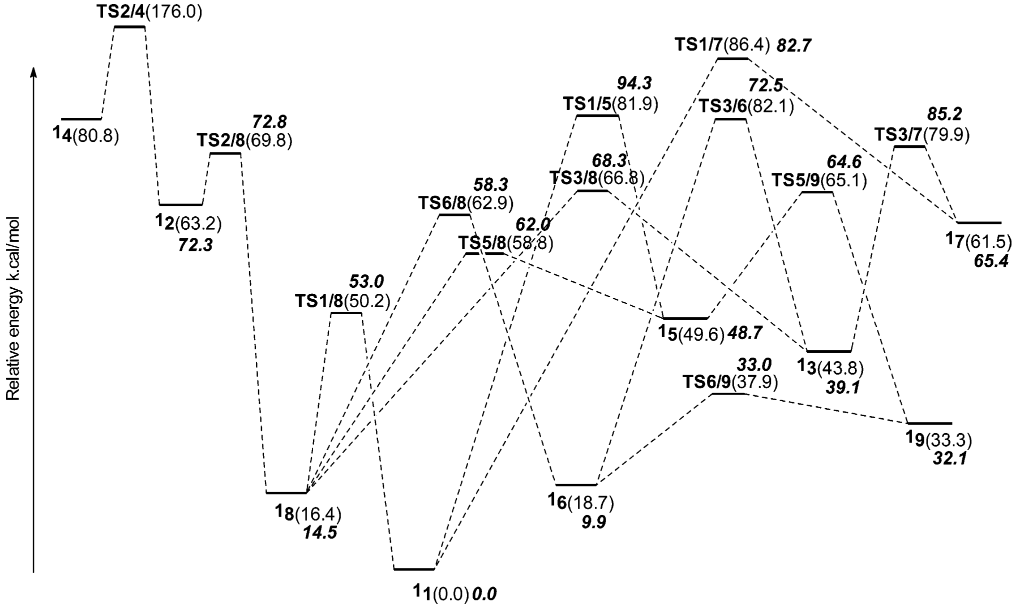


Figure 2. Singlet potential energy surface of the [H,N,Si,S] system. The relative energies (kcal/mol) calculated using G3B3 methods are given in the parentheses, while MP2-based relative energies are given in bold italics.

TABLE 2: Total Energy (au) of the Singlet Transition States for the Isomerizations and Spin-Allowed Dissociations in [H,N,Si,S][a]

transition states singlet	G3B3	CCSD/6-311G(d,p) //MP2/6-311+G(d,p)
TS ^{1}**1**/^{1}**5**	−742.594701 (81.9)	−741.734541 (94.3)
TS ^{1}**1**/^{1}**7**	−742.587584 (86.4)	−741.752992 (82.7)
TS ^{1}**1**/^{1}**8**	−742.645341 (50.2)	−741.800269 (53.0)
TS ^{1}**2**/^{1}**4**	−742.444644 (176.0)	
TS ^{1}**2**/^{1}**8**	−742.614134 (69.8)	−741.768784 (72.8)
TS ^{1}**3**/^{1}**6**	−742.594409 (82.1)	−741.769204 (72.5)
TS ^{1}**3**/^{1}**7**	−742.597914 (79.9)	−741.748982 (85.2)
TS ^{1}**3**/^{1}**8**	−742.618862 (66.8)	−741.775849 (68.3)
TS ^{1}**5**/^{1}**8**	−742.631546 (58.8)	−741.786001 (62.0)
TS ^{1}**5**/^{1}**9**	−742.621582 (65.1)	−741.781812 (64.6)
TS ^{1}**6**/^{1}**8**	−742.625025 (62.9)	−741.791805 (58.3)
TS ^{1}**6**/^{1}**9**	−742.664815 (37.9)	−741.832227 (33.0)
^{2}H + ^{2}NSiS	−742.543309 (114.2)	−741.710164 (109.5)
^{2}SH + ^{2}SiN	−742.556911 (105.7)	−741.742694 (89.1)
^{3}Si + ^{3}HSN	−742.480742 (153.5)	−741.681643 (127.4)
^{2}H + ^{2}SiNS	−742.579204 (91.7)	−741.757371 (79.9)
C−^{2}NSiS + ^{2}H	−742.575934 (93.7)	−741.741812 (90.0)
^{2}SiH + ^{2}NS	−742.545218 (113.0)	−741.727922 (98.4)
^{2}H + ^{2}NSSi	−742.487841 (149.0)	−741.640153 (153.5)

[a] The relative energies are calculated with respect to ^{1}**1** and are shown in parentheses.

nonplanar, and the cyclization takes place with the formation of the N−S bond with a bond length of 2.794 Å and requires 50.2 kcal/mol. The bond length of N−Si elongates from 1.563 Å in **1** to 1.748 Å in **8**. Comparison with the oxygen analogue, that is, HNSiO, reveals that the cyclization there requires much higher energy, around 69 kcal/mol.[9] ^{1}**1** can also isomerize to ^{1}**5** and ^{1}**7** through hydrogen migration. The transition state ^{1}**1**/^{1}**7** is planar, which is a 1,2-H migration with a barrier of 86.4 kcal/mol. The 1,3-H migration to form ^{1}**5** requires a lower activation energy of about 81.9 kcal/mol. The next lowest energy isomer ^{1}**8** can undergo two types of ring-opening reactions. The ring opening with breaking of the N−S bond leads to ^{1}**1**, with a barrier of 33.8 kcal/mol. The nonplanar transition state which is similar to the reactant is probably the reason for the reduced isomerization energy. The ring opening by breaking of the N−Si bond leads to ^{1}**2**, and this has a barrier of 53.4 kcal/mol. The transition state is nonplanar, and the formation of the N−Si bond here requires larger energy than the formation of the N−S bond, which occurs in the isomerization of ^{1}**8**/^{1}**1**. ^{1}**8** can also undergo a combination of isomerization involving H-migration and ring opening. H-Migration from N to S, followed by ring opening, leads to ^{1}**5** and requires an energy of around 42.4 kcal/mol. H-Migration from N to Si followed by ring opening leads to isomer ^{1}**3** with a barrier of around 50.4 kcal/mol. ^{1}**8** can also simultaneously undergo the combination of ring opening with breaking of the S−Si bond and H-migration to S, which lead to ^{1}**6** with a lower barrier of 46.5 kcal/mol.

Isomer ^{1}**6** can cyclize to ^{1}**9**, which requires only 19.2 kcal/mol of energy. Here, an S−Si bond has to be formed, and the transition state is nonplanar with an elongated N−S bond which was 1.660 Å in the chain isomer and optimizes to 1.808 Å in isomer **9**. The H-migration to N in ^{1}**6**, isomerizing to cyclic ^{1}**8**, requires an activation energy of 44.2 kcal/mol. A four-membered ring transition state and activation energy of 63.4 kcal/mol are required for the isomerization of ^{1}**6** to ^{1}**3**, which is a 1,3-H migration. Isomer ^{1}**3** can undergo isomerization to a branched ^{1}**7**, which requires only around 36.1 kcal/mol of energy. The isomerization of ^{1}**5** to ^{1}**9** requires around 15.5 kcal/mol of energy and has a low barrier. Isomer ^{1}**2** can convert to ^{1}**4** by 1,3-H migration, and accordingly the transition state is a four-membered ring and requires a high activation energy of 112.8 kcal/mol. Ring opening of ^{1}**9** to ^{1}**6** requires a low activation energy of only 4.6 kcal/mol. On this surface, we were unable to locate the transition states for isomerization of ^{1}**2** to ^{1}**9**, and ^{1}**5** to ^{1}**7**. Two other transition states that involve isomer ^{1}**4**, which are of high energy, have not been located. The transition states thus show that these isomers are quite stable to isomerization. The predicted (scaled) IR frequencies for the isomers are shown in Table A in the Supporting Information.

Dissociations. The dissociation of the singlet isomers and the recombinations of such fragments can connect to other isomers. Here, we discuss only the important spin-allowed dissociations, and these are shown in Table 2, while the fragment energies are shown in Table C of the Supporting Information. The lowest spin-allowed dissociation for ^{1}**1** is ^{2}NSSi and H, which requires

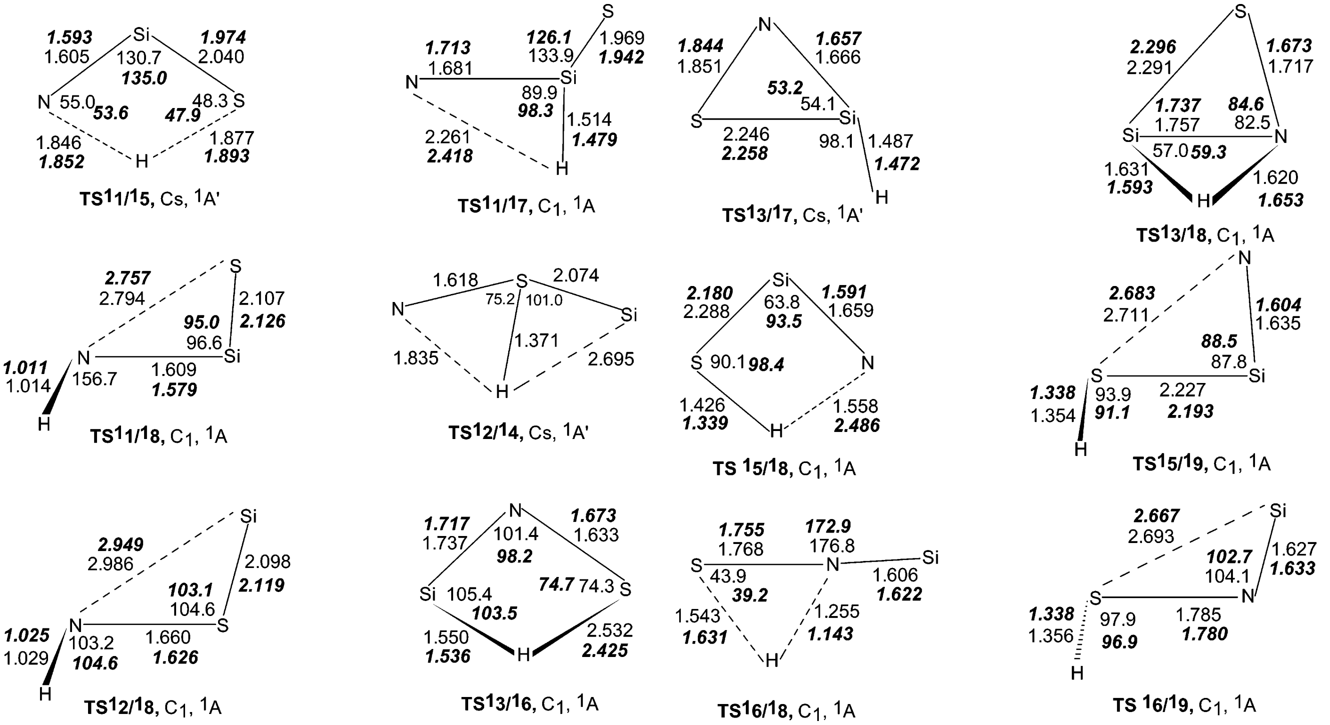


Figure 3. Isomerization transition state geometries in the singlet state of the [H,N,Si,S] system, optimized at the G3B3 level and MP2 methods (bold italics). Bond lengths are in angstroms, and angles are in degrees.

114.2 kcal/mol of energy. We have found no transition states for any of the singlet dissociations despite our best efforts, and hence we feel that all of these spin-allowed dissociations proceed without a barrier. The other dissociations for **1** are of higher energy. For isomer **6** to dissociate to ^{2}SH and ^{2}SiN where an N−S bond has to be broken requires about 87.0 kcal/mol, whereas for isomer **5** where an S−Si bond has to be broken the energy required is 56.1 kcal/mol. The lowest dissociation of isomer **2** to its fragments requires 85.8 kcal/mol, which is an H abstraction. H-Abstraction in isomer **3** requires about 47.9 kcal/mol of energy. Isomer **4** can also undergo dissociation to ^{2}SiH and ^{2}NS, which requires around 32.2 kcal/mol of energy.

Triplet Surface. *Isomers.* The stationary states on this surface are shown in Figure 4, and the energies are given in Table 3. Here again, the global minimum is HNSiS as on the singlet surface, but the difference is that unlike the singlet isomer it is nonplanar with a hydrogen atom out of the plane. The adiabatic energy difference for the singlet and triplet isomer is around 43 kcal/mol, with the triplet having a higher energy. The N−Si bond is slightly longer than that in the singlet isomer, and the NSiS bond angle is smaller. The connectivity HSiNS (isomer ^{3}**3**) is the next most stable isomer lying around 10.1 kcal/mol above ^{3}**1** (Figure 5). Lying close to this isomer just about 3.6 kcal/mol above it is the isomer **8**, which is a branched isomer on this surface. Again, it is quite different in geometry from its singlet counterpart with the SiNS angle becoming much larger and the whole molecule lying in the plane. A general notable feature is that the angles in the cyclic isomers of the singlet states become larger with the change of electronic configuration in the triplet state and thus no cyclic triplet isomer is a minimum on this surface (Figure 6), while in the case of chain isomers the angle between the three heavy atoms decreases in the triplet state when compared to the singlet states. Except for isomer **1**, all other isomers on this surface are planar.

PES. The lowest isomerization on this surface for the most stable isomer **1** is the H-migration from N to the S atom to yield isomer **5**. This requires around 44.1 kcal/mol and involves a planar transition state as shown in Table 4. The next lowest isomerization on this surface for **1** is the 1,2-H migration from N to Si yielding **7**. This requires around 46.5 kcal/mol of energy,

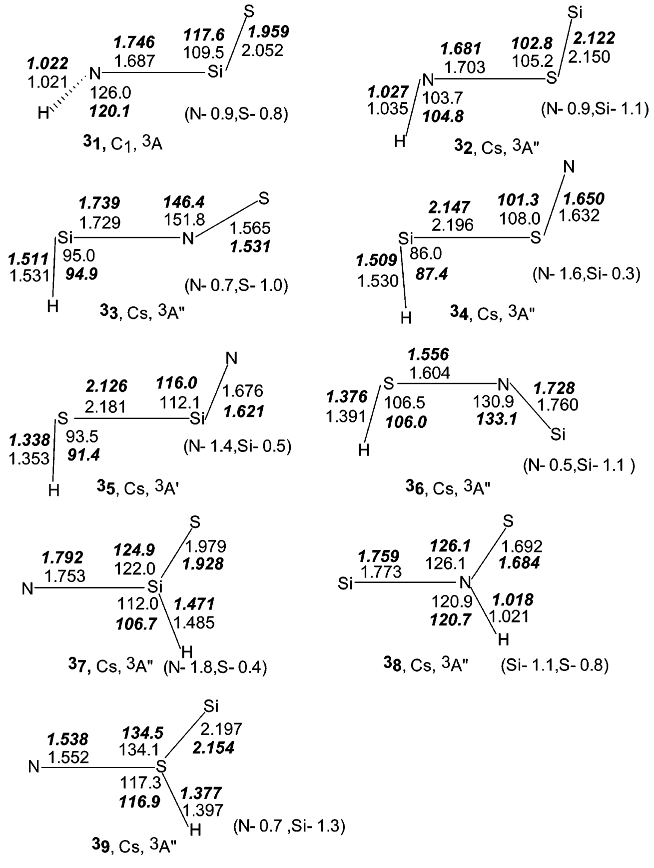


Figure 4. Equilibrium geometries in the triplet state of the [H,N,Si,S] system, optimized at the G3B3 level and MP2 methods (bold italics). Bond lengths are in angstroms, and angles are in degrees. Spin density values are given in parentheses.

TABLE 3: Total Energies (au), Heats of Formation (kcal/mol), and Dipole Moments (D) of the Various Triplet Isomers of [H,N,Si,S] Calculated in This Work[a]

isomers	G3B3(0 K)	ΔH_f (0 K) based on G3B3 energies	dipole moment (D) (G3B3)	CCSD/6-311G(d,p) //MP2/6-311+G(d,p)
HNSiS ^{3}**1**	−742.656644 (0.0)	83.8	1.8	−741.825502 (0.0)
HNSSi ^{3}**2**	−742.612923 (27.4)	111.2	0.6	−741.786214 (24.7)
HSiNS ^{3}**3**	−742.640602 (10.1)	93.9	0.3	−741.815104 (6.5)
HSiSN ^{3}**4**	−742.598562 (36.4)	120.2	2.2	−741.764929 (38.0)
HSSiN ^{3}**5**	−742.608327 (30.3)	114.1	2.9	−741.777788 (29.9)
HSNSi ^{3}**6**	−742.610284 (29.1)	112.9	1.6	−741.781583 (27.6)
NSi(H)S ^{3}**7**	−742.627094 (18.5)	102.3	2.6	−741.805540 (12.5)
SiN(H)S ^{3}**8**	−742.634811 (13.7)	97.5	1.3	−741.819383 (3.8)
NS(H)Si ^{3}**9**	−742.535984 (75.7)	159.5	4.5	−741.694759 (82.0)

[a] The relative energies are calculated with respect to ^{3}**1** and are shown in parentheses.

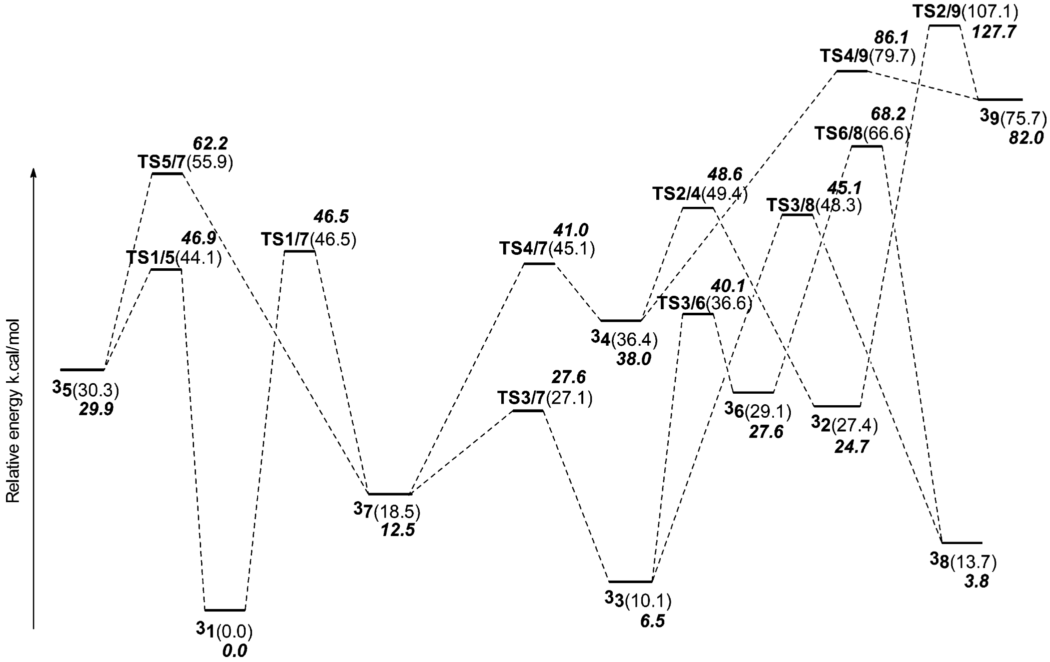


Figure 5. Triplet potential energy surface of the [H,N,Si,S] system. Relative energies (kcal/mol) calculated using G3B3 methods are given in parentheses, while MP2-based relative energies are given in bold italics.

and the transition state is nonplanar with H out of the plane. The N−Si bond length elongates from 1.687 to 1.734 Å in the transition state. Here, the cyclization which is possible on the singlet surface, that is, isomerization of **1** to **8**, is absent. The next lowest isomer **3**, which has the HSiNS connectivity, has a low isomerization energy of 17.0 kcal/mol to isomer **7**. Although both the initial and the final geometries are planar, this has a nonplanar transition state. 1,3-H migration from Si to S in **3** to give **6** requires 26.5 kcal/mol of energy, and the transition state is planar with the SNSi bond angle reducing to 104.7° to accommodate the transfer. 1,2-H migration in this isomer yielding **8** requires a much higher energy of 38.2 kcal/mol, and the transition state shows a lengthened Si−N bond of 1.760 Å. ^{3}**7** isomerization to ^{3}**4** requires around 26.6 kcal/mol, and the transition state is nonplanar. Here, it is required to break the Si−N bond and form the S−N bond. The branched isomer **8** isomerizes to the chainlike isomer **6** through a planar transition state and requires around 52.9 kcal/mol of energy.

Dissociations. The dissociations possible here are shown in Table 4, and, unlike in the case of the singlet, some of them proceed with a barrier and those transition states are shown in Figure 7. In the case of ^{3}**1** dissociation to ^{3}HN and ^{1}SiS, there is no barrier predicted by the G3B3 method, and the energy required to bring about this dissociation is 28.1 kcal/mol. Isomer **2** can dissociate to HNS +^{3}Si endothermically with an energy of 52.9 kcal/mol. The dissociation to ^{3}NH and SSi proceeds through a barrier of 11.3 kcal/mol, and the products lie only ~1 kcal/mol above the reactants. Isomer **3** has its lowest energy dissociation to H + ^{2}SiNS without a barrier and requires 38.5 kcal/mol of energy. In the case of **4**, the lowest dissociation is ^{2}SiH and ^{2}NS and requires 33.5 kcal/mol of energy. The isomer **8** dissociates with a barrier of 15.5 kcal/mol, and the products, which are HNSi and ^{3}S, lie about 9 kcal/mol above the reactants. Finally, in the case of molecule **1**, HNSiS, the DFT method does not predict any barrier for the ^{3}NH + SiS dissociation, while the MP2 method indicates that this molecule requires ~31 kcal/mol as the activation energy for the dissociation. As compared to the oxygen analogue, it is seen that the DFT method did not indicate any barrier unlike in the MP2 case.[9] Recent study of the carbon analogue HNCS using the DFT methodology also seems to indicate barrierless dissociations.[8] This could be an artifact of the DFT calculations where a transition state with a spin density of triplet on the sulfur atom is not be obtained.

MECP. When a singlet state lower in energy than the triplet state dissociates to the lower energy spin-forbidden triplet fragments, then a crossing occurs. This crossing of the triplet and the singlet surfaces that is bound at some lowest point is called the minimum energy crossing point (MECP) and is

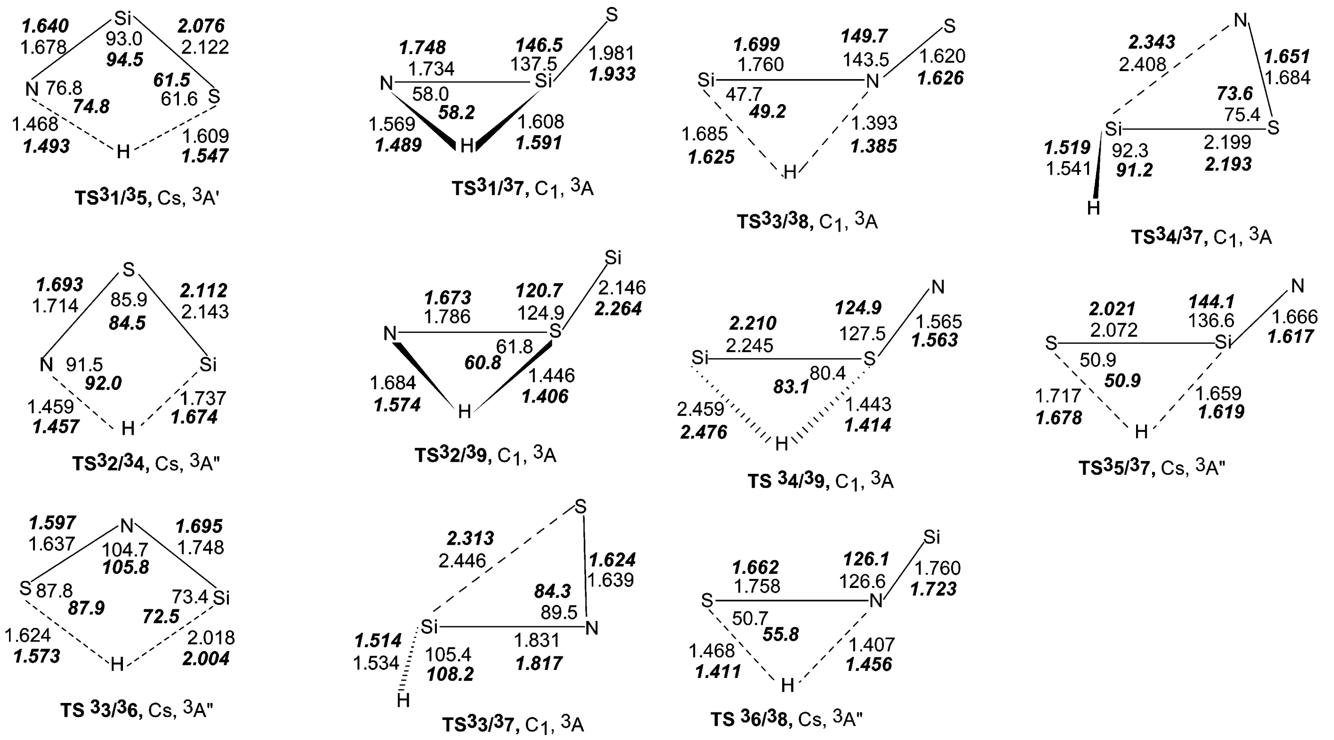


Figure 6. Isomerization transition state geometries in the triplet state of the [H,N,Si,S] system, optimized at the G3B3 level and MP2 methods (bold italics). Bond lengths are in angstroms, and angles are in degrees.

TABLE 4: Total Energy (au) of the Triplet Transition States for the Isomerizations and Spin-Allowed Dissociations in [H,N,Si,S][a]

transition states triplet	G3B3	CCSD/6-311G(d,p) //MP2/6-311+G(d,p)
TS ^{3}**1**/^{3}**5**	−742.586397 (44.1)	−741.750802 (46.9)
TS ^{3}**1**/^{3}**7**	−742.582579 (46.5)	−741.751392 (46.5)
TS ^{3}**2**/^{3}**4**	−742.577936 (49.4)	−741.748095 (48.6)
TS ^{3}**2**/^{3}**9**	−742.486022 (107.1)	−741.622003 (127.7)
TS ^{3}**3**/^{3}**6**	−742.598395 (36.6)	−741.761653 (40.1)
TS ^{3}**3**/^{3}**7**	−742.613505 (27.1)	−741.781440 (27.6)
TS ^{3}**3**/^{3}**8**	−742.579651 (48.3)	−741.753676 (45.1)
TS ^{3}**4**/^{3}**7**	−742.584851 (45.1)	−741.760134 (41.0)
TS ^{3}**4**/^{3}**9**	−742.529697 (79.7)	−741.688319 (86.1)
TS ^{3}**5**/^{3}**7**	−742.567532 (55.9)	−741.726312 (62.2)
TS ^{3}**6**/^{3}**8**	−742.550585 (66.6)	−741.716756 (68.2)
TS/dis (^{3}**1**)		−741.787589 (23.8)
TS/dis (^{3}**2**)	−742.594993 (38.7)	−741.771778 (33.7)
TS/dis (^{3}**8**)	−742.610054 (29.2)	−741.792802 (20.5)
^{1}HNSi + ^{3}S	−742.620459 (22.7)	−741.814976 (6.6)
^{3}HN + ^{1}SiS	−742.611798 (28.1)	−741.799828 (16.1)
^{1}HNS + ^{3}Si	−742.528683 (80.3)	−741.718438 (67.2)
^{2}SiH + ^{2}NS	−742.545218 (70.0)	−741.727922 (61.2)
^{2}SH + ^{2}SiN	−742.556911 (62.6)	−741.742694 (52.0)
^{2}H + ^{2}SiNS	−742.579204 (48.6)	−741.757371 (42.8)
^{2}H + ^{2}NSiS	−742.543309 (71.1)	−741.710164 (72.4)
^{2}H + ^{2}NSSi	−742.487841 (105.9)	−741.640153 (116.3)
^{4}N + ^{2}HSiS	−742.528075 (80.7)	−741.731873 (58.8)

[a] The relative energies are calculated with respect to isomer ^{3}**1** and are shown in parentheses.

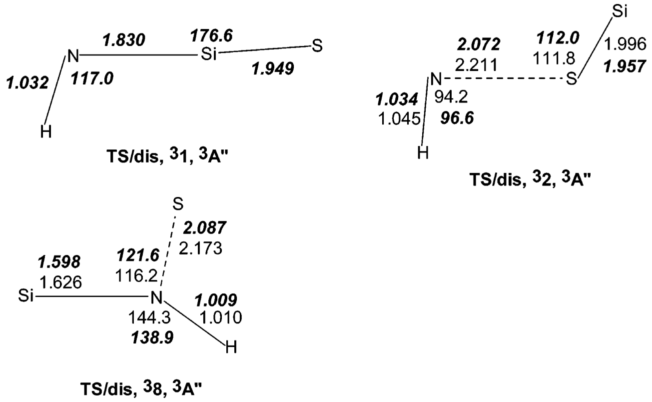


Figure 7. Dissociation transition state geometries in the triplet state of the [H,N,Si,S] system, optimized at the G3B3 level and MP2 methods (bold italics). Bond lengths are in angstroms, and angles are in degrees.

sometimes considered as the transition point for the intersystem crossing.[19] The MECP has been determined by using an external shell and FORTRAN program developed by Harvey et al.[20] In this method, the MECP geometry is generated using the gradients and electronic energies obtained from Gaussian 98 for the two surfaces, under the constraint that the difference in the energies and gradients of the two states is minimum. The MECP geometries have been determined for the important low-lying isomers at the B3LYP/6-31G(d) (G3B3 geometries) level, and these are shown in Figure 8 along with the MP2-generated MECP. The MECPs calculated have been associated with the following reactions, giving rise to singlet/triplet isomers.

$$\mathrm{SiS} + {}^{3}\mathrm{NH} \rightarrow \mathrm{HNSiS}\ (\mathbf{1a})$$

$$\mathrm{HNSi} + {}^{3}\mathrm{S} \rightarrow \mathrm{HNSiS}\ (\mathbf{1b})$$

$$\mathrm{HSN} + {}^{3}\mathrm{Si} \rightarrow \mathrm{HSNSi}\ (\mathbf{6})$$

$$\mathrm{HNS} + {}^{3}\mathrm{Si} \rightarrow \mathrm{HNSSi}\ (\mathbf{8})$$

The idea of finding out the geometry of MECP is to understand the most feasible pathway the reaction would take when the two fragments of different spins interact. The fragments can undergo side-on addition (to form a chainlike isomer) or an insertion type (to form a branched/ring isomer) reaction on collisions to form either the singlet or the triplet isomer. The relative energies discussed below are without the inclusion of the higher order corrections. The location and the assignment

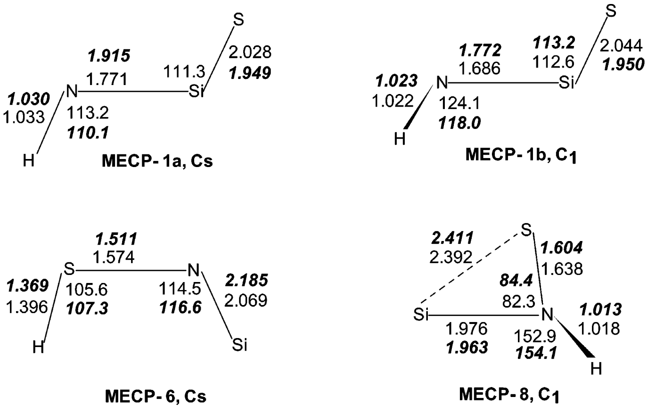


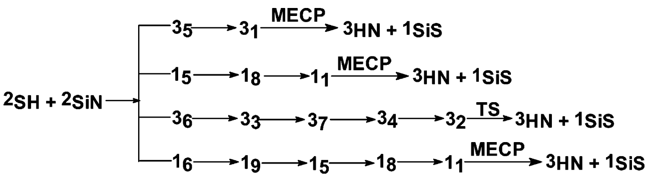
Figure 8. Geometries at the MECP for various isomers in the [H,N,Si,S] system optimized at the B3LYP/6-31G(d) (G3B3 geometries) level and MP2 methods (bold italics). Bond lengths are in angstroms, and angles are in degrees.

of the reaction coordinate of the MECP on the surface are based on the changes in bond length.[3]

Two low-lying reaction coordinates, ^{3}NH + SiS and HNSi + ^{3}S, could contain the MECP for the formation of isomers **1**. MECP **1a** lies around 35.1 kcal/mol above the singlet on the Si−S reaction coordinate. The bond length of Si−S in the singlet is 1.943 Å, which elongates to 2.028 Å in the MECP. This is shorter than the triplet Si−S bond length of 2.052 Å. The MECP lies about 3 kcal/mol above the triplet isomer. This indicates that the singlet has to convert to the triplet isomer with an endothermic energy of 35.1 kcal/mol before it can dissociate to the fragments HNSi and ^{3}S. Another MECP **1b** is lying around 32.2 kcal/mol above the singlet and lies only 0.1 kcal/mol above the triplet isomer on the N−Si reaction coordinate. The N−Si bond changes from 1.563 Å in the singlet and 1.687 Å in the triplet to 1.668 Å in the MECP. Here, the B3LYP method predicts that the singlet has to convert to a triplet before dissociations, while the elongated bond in MP2 suggests proximity to the dissociation. MECP **6** is clearly close to the dissociation to ^{3}Si and HSN. This crossing point lies about 15 kcal/mol above the triplet and 66.1 kcal/mol above the singlet and is about 59.1 kcal/mol below the dissociation channel. The next isomer is the ring **8**, where the MECP **8** is close to the triplet lying only 4.7 kcal/mol above it, while the singlet is about 33.4 kcal/mol lower. The geometry suggests that it is closer to the dissociation to ^{3}Si and HNS.

Reactions

^{2}SH + ^{2}SiN. The side-on addition reaction of ^{2}SH with ^{2}SiN can give rise to isomer **5** either in the singlet or in the triplet form if the reaction proceeds with the bond formation of Si−S, or to singlet or triplet **6** with the bond formation between N and S. The possible pathways are as follows:



The one that forms ^{1}**5** is the most exothermic, releasing 56.1 kcal/mol of energy. The lowest dissociation of ^{1}**5** to ^{2}H and ^{2}NSiS requires an energy of 64.6 kcal/mol, while its isomerization to ^{1}**8** requires a much lower energy of 9.2 kcal/mol as the activation. If ^{1}**5** isomerizes to ^{1}**1**, then the barrier is 32.3 kcal/mol, but the isomerization itself is a exothermic process with a release of 49.6 kcal/mol. The isomerization from ^{1}**8** to ^{1}**1** has an activation barrier of 33.8 kcal/mol. The dissociation of ^{1}**8** requires high energy. ^{1}**1** can finally dissociate to ^{3}NH and SiS by passing through MECP **1b**. Overall, the route is exothermic with the final products lying below the reactants, and all of the transition states are also below the reactants. The second route with the formation of ^{1}**6** is exothermic by 87 kcal/mol. Its isomerization to **9** requires only 19.2 kcal/mol of energy to cross the barrier. All of the dissociations on this reaction pathway require high energy, while the isomerizations require much less.

The side-on addition can also yield the triplet isomers **5** or **6**. Here, the formation of **5** and **6** releases nearly the same exothermic energy. The isomerization from ^{3}**5** to ^{3}**1** requires an activation energy of 14.0 kcal/mol, while the dissociation to H and NSiS requires a high energy of 40.8 kcal/mol. Next, the isomerization from ^{3}**1** to ^{3}**7** is highly endothermic, while the dissociation of ^{3}**1** is lower. The reaction proceeding through the other triplet, that is, **6**, requires 19.5 kcal/mol of energy for dissociation to ^{2}H and ^{2}SiNS, while the isomerization to ^{3}**3** requires only 7.5 kcal/mol of energy. ^{3}**3** can isomerize to ^{3}**7** and requires only 17.0 kcal/mol of energy. The isomerization to ^{3}**4** requires 26.6 kcal/mol of energy, and ^{3}**4** dissociation to ^{2}SiH and ^{2}NS requires 33.5 kcal/mol of energy. The isomerization of ^{3}**4** to ^{3}**2** requires 13.0 kcal/mol of energy, and again the lowest channel for this dissociation has a barrier of 11.3 kcal/mol.

The other possible reaction is the insertion, and it can take the following pathway:

$${}^2\mathrm{SH} + {}^2\mathrm{SiN} \rightarrow {}^1\mathbf{9} \rightarrow {}^1\mathbf{6} \rightarrow {}^1\mathbf{8} \rightarrow {}^1\mathbf{1} \xrightarrow{\text{MECP}} {}^3\mathrm{HN} + {}^1\mathrm{SiS}$$

The possible formation of the singlet isomer of ^{1}**9** is highly exothermic and has a value of 72.3 kcal/mol. The main notable feature of this pathway (singlet) is the high dissociation energies and comparatively lower isomerization energies, and the lowest energy pathway through the singlet yields the ^{1}**1** isomer. The isomerization of ^{1}**9** to ^{1}**6** is predicted to be endothermic by 4.6 and 2.3 kcal/mol for ^{1}**6** to ^{1}**8**.

^{3}NH + ^{1}SiS. The other possible diatomic fragments that can react are those involving ^{3}NH and SiS via the following pathway:

$${}^3\mathrm{NH} + {}^1\mathrm{SiS} \xrightarrow[\text{addition}]{\text{TS}} {}^3\mathbf{2} \rightarrow {}^3\mathbf{4} \rightarrow {}^3\mathbf{7} \rightarrow {}^3\mathbf{3} \rightarrow {}^3\mathbf{6} \rightarrow {}^2\mathrm{H} + {}^2\mathrm{HiNS}$$

Here, the addition reaction yields four pathways. The formation of ^{1}**1** and ^{3}**1** passes through a transition state as predicted by MP2 and is highly endothermic. The ^{1}**2** also turns out be higher in energy than the reactants, and we were unable to locate any transition state. The ^{3}**2** higher in energy than the reactants requires an activation energy of 11.3 kcal/mol to be formed from the reactants, the reaction is endothermic, and the pathway leads to the final products H and ^{2}SiNS.

Conclusions

Silicon analogues of thio-isocyanic acid and its isomers have been investigated by computational methods. G3B3 at the DFT level and MP2 at the ab initio level indicate that there are as many as nine stationary states on the singlet surface and an equal number on the triplet surface which have been characterized as minima. The dissociations and the isomerizations require high energies, indicating that these isomers are quite stable and in some conditions should be able to be generated in the laboratory. The neutral−neutral reactions on this surface mapped using the fragments reveal that, although many of them are barrierless, they are exothermic enough to dissociate to other lower channels. These indicate that in the interstellar space the possibility of detecting HNSiS or the isomers formed from the neutral−neutral reactions is not high but the possibility of the formation of the stable isomers from neutral−ion reactions is not ruled out. More studies in this direction such as mapping the ion−neutral reactions are required.

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Supporting Information Available: Tables and figure of experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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