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Ab Initio Study of the Isomers: HNNSi, HSiNN, and HNSiN

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We report on new structural, energetics, and vibrational frequency data for three isomers on the potential energy surface [H, Si, N, N] calculated at the UHF, MP2, and CCSD(T)/6-311G(2d) levels of theory. Similarly to SiNN, conventional methods fail to predict a thermodynamic stability for the isomer HSiNN. However, at the CCSD(T) level, the species HSiNN was found to lie 13.63 kcal mol^{-1} lower in energy than HNNSi; the isomer HNSiN was located 47.62 kcal mol^{-1} above the global minimum. After including the zero-point energy corrections, the isomer HSiNN becomes almost isoenergetic with its dissociation products HSi and N_2; its detection might be likely only at low temperatures.

Understanding the chemistry of silicon in interstellar space has been a challenge to scientists[1—3] and, in this respect, the recent detection of SiN[4] in outer space has brought a new impetus into this research area and also a renewed interest in the gas phase chemistry of silicon-nitrogen species. In this context, the interplay of laboratory spectroscopic investigations with ab initio theoretical studies has been of special relevance to the identification of new molecules in interstellar space.

In the case of the basic unit SiN, experimental knowledge accumulated to date has been reported by Ito et al.,[5] Elhanine et al.,[6] and Naulin et al.;[7] theoretically, the studies of Bruna et al.,[8] Cai et al.,[9] and Borin[10] contain the most detailed descriptions of this system. The simplest triatomics, HSiN and HNSi, resulting from the incorporation of a hydrogen atom into the basic unit, SiN, have been extensively studied, both experimentally and theoretically, over a long period of time.[11—22] The addition of another hydrogen to the triatomic species gives rise to a more complex [H, H, Si, N] potential energy surface (PES) which, together with its ionized counterpart [H, H, Si, N]$^+$, have also been the subject of various theoretical and experimental investigations.[23—29]

Of relevance to the gas phase chemistry of silicon-nitrogen species are also the isomers of the triatomics, Si_2N[30] and SiN_2,[31] as well as the isomers of the tetratomics, Si_2N_2,[32] extensively studied in our group at a high level of correlation treatment. Hydrogenated species which arise on the [H, N, N, Si] PES have also been partially described in a previous work by our group.[33] In that study, the restricted open-shell Hartree–Fock (ROHF), the unrestricted Hartree–Fock (UHF), and the multiconfiguration self-consistent field (MCSCF) formalisms using the 6-31G* basis set were used to optimize the geometries and to compute the vibrational harmonic frequencies of the HNNSi molecule. Another viable isomer, the species HSiNN, was approached only with the ROHF method. Although the energy of the optimized HSiNN structure turned out to be about 36 kcal mol^{-1} lower than that of HNNSi, its structure corresponded to that of a loosely bound HSi···NN complex, with the silicon atom 3.009 Å apart from the nitrogen. The dynamic correlation effects via a multireference configuration interaction calculation (MRCI) were also accounted for, but only in the case of HNNSi.

As to the triatomics SiNN, difficulties were encountered in properly describing this species with the HF, MCSCF, and SDCI methodologies, which predicted a very weakly bound complex Si···NN (see Ref. 31 and references therein). On the other hand, the coupled cluster approach with all single and double excitations, and contributions from connected triples (CCSD(T)), predicts a reasonable stable structure for SiNN; this success led us to reexamine the [H, Si, N, N] PES using this latter methodology. In this study, we therefore present new structural, energetics, and vibrational frequency data which we hope can help in the search and identification of the yet unknown species, and also can contribute to a better understanding of the silicon–nitrogen gas phase chemistry in both the laboratory and in interstellar space.

Methodology

As a general strategy, various potential isomeric species were initially investigated at the unrestricted Hartree–Fock (UHF) level. After a complete geometry optimization, the nature of the stationary points on the potential energy surface (PES) were examined through calculations of the vibrational frequencies in the harmonic approximation. The effect of electron correlation on the structures, relative stabilities, and frequencies of the various structures was investigated by second-order Möller–Plesset perturbation theory (MP2), and by the coupled cluster technique with all single and double excitations, and connected triples (CCSD(T)), as implemented in

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the Gaussian-92 series of programs.[34)] Core electrons were kept frozen in the correlated results. Again, frequency computations revealed the nature of the stationary points either as a minimum or as a transition state.

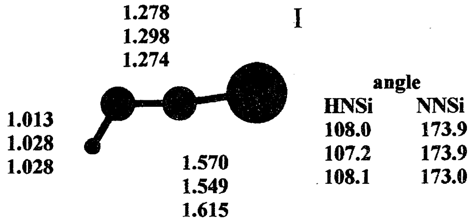
In the expansion of the molecular orbitals (MO), McLean and Chandler[35)] (12s, 9p) set of primitive Gaussians contracted to [6s, 5p] augmented with two sets of *d*-type polarization functions with exponents 0.900 and 0.225 was used for silicon; for nitrogen, the 6-311G(2d) ($\alpha_d = 1.826$ and 0.4565) set of Krishnan et al.,[36)] which was designed to incorporate a substantial part of the electron correlation in MP2 calculations on atomic states, was the choice of work, and the hydrogen basis was the (5s)/[3s] set as also given by Krishnan et alii. These sets comprised a total of 80 contracted functions, which can be symbolized as (11s,5p,2d)/[4s,3p,2d] for nitrogen, and (12s,9p,2d)/[6s,5p,2d] for silicon. We also note that five uncontracted *d*-type functions were employed instead of the usual six second order gaussians. This reduces substantially the number of MO and avoids duplicating the properties of the (s) basis.

Results and Discussion

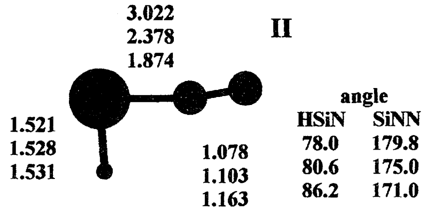
Three major structures (see Fig. 1) associated with the isomers HNNSi (**I**), HSiNN (**II**), and HNSiN (**III**) have been located on the PES. Their optimized geometrical parameters and their energies calculated at the UHF, MP2, and CCSD(T) levels of theory employing the 6-311G(2d) basis set are summarized in Fig. 1 and Table 1, respectively. The harmonic frequencies are given in Tables 2, 3, and 4. All three structures have a C_s symmetry and a $^2A''$ ground state.

An important point to note first is that the species HSiNN (**II**), previously found to be a very weakly bound complex, HSi···NN, as predicted by the ROHF methodology, still maintains this weakly bound complex nature if either the UHF or MP2 approaches are used. However, it does show a structure indicative of a more tightly bound molecule when the calculation is pushed up to a higher level of correlation treatment. The significant bond distance shrinkage from 3.009 Å (ROHF), obtained in a previous study, and the UHF value of 3.022 Å calculated in this study, to 1.874 Å (CCSD-

I



II



III

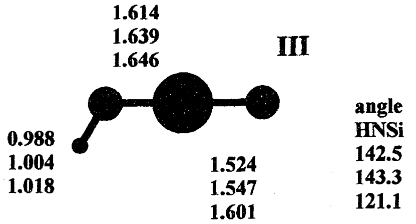


Fig. 1. Optimized distances (in Å) and angles (in degrees) calculated at the SCF, MP2, and CCSD(T) levels of theory with the 6-311G(2d) basis set. From top to bottom, the numerical parameters refer to the SCF, MP2, and CCSD(T) calculations, respectively.

Table 1. Energies (in a.u.) and Relative Energies (in kcal mol^{-1}) in Parenthesis Calculated at Different Levels of Approximation

	UHF	MP2	CCSD(T)
HNNSi (**I**)	−398.362360 (30.65)	−398.778694 (25.10)	−398.833185 (13.63)
HSiNN (**II**)	−398.411229 (0.0)	−398.818696 (0.0)	−308.854909 (0.0)
HNSiN (**II**)	−398.309390 (63.90)	−398.735305 (52.33)	−398.779011 (47.62)

Table 2. Vibrational Frequencies (cm^{-1}), and Intensities (km mol^{-1}) in Parenthesis for the Species HNNSi (**I**)

	Ref. 33		This work		
Mode	UHF	MCSCF	UHF	MP2	CCSD(T)
NH stretch	3531	3577	3523 (0.55)	3360 (0.62)	3316
NN stretch	1298	1291	1272 (365.92)	1353 (1.88)	1261
SiN stretch	809	816	819 (12.20)	902 (208.79)	800
NNH bend	1539	1512	1542 (14.50)	1589 (422.16)	1440
SiNN bend	298	336	298 (26.48)	315 (25.02)	300
Torsion	344	499	337 (13.72)	368 (36.66)	318

Table 3. Vibrational Frequencies (cm^{-1}), and Intensities ($km\ mol^{-1}$) in Parenthesis for the Species HSiNN (**II**)

	Ref. 33	This work	
Mode	RHF	MP2	CCSD(T)
SiH stretch	2157	2014 (259.38)	2045
NN stretch	2764	3197 (53.41)	1690
SiN stretch	59	111 (5.30)	314
HSiN bend	382	662 (25.70)	807
SiNN bend	82	151 (2.21)	443
Torsion	82	160 (0.47)	472

Table 4. Vibrational Frequencies (cm^{-1}), and Intensities ($km\ mol^{-1}$) in Parenthesis for the Species HNSiN (**III**)

	This work		
Mode	UHF	MP2	CCSD(T)
NN stretch	3940 (157.20)	3731 (194.86)	3537
NSiN antisym stretch	1432 (44.67)	1453 (294.50)	1188
NSiN sym stretch	946 (0.78)	1157 (316.11)	933
HNSi bend	273 (175.80)	463 (61.76)	552
NSiN bend	230 (64.70)	193 (211.02)	267
Torsion	232 (110.47)	128 (102.26)	172

(T)), also obtained in the present work, together with the magnitudes of the predicted harmonic vibrational frequencies do support a thermodynamic stability for this system. At the MP2 level, a shorter SiN distance (2.378 Å) is obtained but it is still indicative of a complex structure. Also note that although the SiN distance is about 0.1 Å longer than that of a typical SiN single bond distance, a further decrease is however expected to occur as the size of the basis is extended. This was the case of the molecule SiNN, for which the SiN bond distance calculated at the CCSD(T) level changed from 1.842 (cc-pVTZ-f) to 1.804 (cc-pVTZ), and to 1.788 Å (cc-pVQZ);[31] the notation enclosed in parentheses stands for the correlated consistent basis sets of Dunning and collaborators; also, the termination-f in the first parenthesis implies that we have removed the f-type functions from the original cc-pVTZ sets. We emphasize again that in the case of SiNN conventional approaches (SCF, CASSCF, and SDCI) have failed to predict a stable structure for this system.

At the CCSD(T) level of theory, the isomer HSiNN (**II**) was found to lie 13.63 $kcal\,mol^{-1}$ lower in energy than the species HNNSi (**I**), whereas the equilibrium structure of the molecule HNSiN (**III**) was located at 47.62 $kcal\,mol^{-1}$ above the global minimum **II**. Despite the lower energy of structure **II**, one might expect that its fragmentation into the species N_2 ($^1\Sigma_g^+$) and SiH ($^2\Pi$) is likely to be energetically favoured due to the formation of the very stable N_2 molecule. In effect, 1.82 $kcal\,mol^{-1}$ was computed for the adiabatic dissociation energy; however, when including the zero-point energies, the products were found to be slightly more stable by 0.39 $kcal\,mol^{-1}$. Increasing the length of the SiN bond distance away from its equilibrium value gave no indication of the existence of a barrier height to dissociation, which makes the detection of this molecule likely only at low temperatures or when trapped in matrices. In contrast with the most stable isomer, the next structure in stability, HNNSi (**I**), is expected to require a relatively large energy to separate it into the fragments SiN ($^2\Sigma^+$) and NH ($^3\Sigma^-$). In fact, in this process a nitrogen–nitrogen double bond is broken and an adiabatic dissociation energy of 97.12 $kcal\,mol^{-1}$ is required; the inclusion of zero-point energies increases that value to 99.45 $kcal\,mol^{-1}$. The fragmentation process of structure **III** into diatomic species also leads to the same products as in the case of isomer **I**; however, since its minimum is 33.99 $kcal\,mol^{-1}$ higher than that of structure **I**, the adiabatic dissociation energy for this process turns out to be 63.13 $kcal\,mol^{-1}$; when including the zero-point energies that value changes to 66.58 $kcal\,mol^{-1}$.

A further point to note in Table 1 is that the relative energy between structures **I** and **II** predicted at the MP2 level is about twice as large as that found with the CCSD(T) approach; between structures **I** and **III** the difference is about 5%. Compared to the UHF result, in the MP2 calculation the energy gap is reduced by about 19%. It is also worth pointing out that although the SDCI and CCSD(T) methods are based on a single reference space, the CCSD approach generates a wavefunction that has included not only the single and double excitations relative to the single determinant reference function, but also higher excitations of all orders because of the higher powers of the cluster operators, T_1 and T_2. In addition, the extension (T) symbolizes the inclusion of the effects of connected triple excitations, which are included perturbationally, plus an additional fifth-order singles–triples interaction term. This latter term has been shown to be very relevant in correcting for an overestimation of the connected triples in cases where non-dynamical correlation is important.[37—39] A recent review of the excellent performance of the CCSD(T) approach is also presented in Ref. 39.

Concerning the structures of the two most stable isomers, although they have in common an SiNN skeleton with almost the same bond angle (171°, for **II**, and 173°, for **I**), their bonding nature, as reflected in the bond distances, is however different. In isomer **I**, the CCSD(T) value of 1.615 Å for the SiN bond distance lies very close to that of a Si–N double bond distance (1.58 Å) as in H_2SiNH,[40] whereas in isomer **II** the Si–N bond distance (1.874 Å) is longer than that of a typical Si–N single bond (1.72 Å), as in H_3SiNH_2.[41] Similarly, in isomer **I** the N–N bond distance of 1.274 Å approaches the value of doubly bonded nitrogen atoms, as in N_2H_2 (1.252 Å),[42,43] and in isomer **II** it lies closer to that of a triple bond.

Bonding in these systems is not so easily visualized in terms of the conventional resonance structures involving all fifteen valence electrons. For a single determinant description, all three structures have a common electronic configuration $(^2A'')...(7a')^2(8a')^2(9a')^2(10a')^2(2a'')^2(11a')^2(12a')^2(3a'')^1$. In these molecules, one σ-type electron pair is used to make either the N–H or Si–H bonds; another one can be basically ascribed to the silicon 3s orbital, and two other pairs can be associated with the two nitrogen lone pairs, leaving seven valence electrons to bind the remaining [N, Si, N] skeleton. Of these seven electrons, four are in the plane of the molecule, and three are in a plane perpendicular to the molecular plane (π-type bonds).

In the case of structure **I** (HNNSi), the highest occupied molecular orbital (HOMO) populated by the odd electron is basically Si–N bonding and N–N anti-bonding (3a″); very close in energy lies another Si–N bonding and N–N anti-bonding combination involving the p_x orbitals of these atoms (12a′). The charge densities described by these two orbitals essentially account for the short Si–N distance computed, 1.615 Å. The remaining four electrons are involved in N–N bonds. One is of a p-type (2a″) while the other one basically involves a weak overlap of an sp^2 hybrid on the N connected to the hydrogen with a slightly distorted p_x orbital on the other nitrogen. In fact, a significant portion of the charge density in this latter case can also be interpreted as representing a N lone pair (sp^2 hybrid) in the molecular plane. This sp^2 combination is very clear in the MO composition, and accounts for the 108° N–N–H angle. Orbital 11a′ corresponds practically to the silicon 3s lone pair. Although the structure of the π-electron system in this molecule has a certain resemblance to that of an allyl radical with three electrons in three centers, our numerical results indicate that an odd electron seems to be restricted to the Si–N moiety.

Bonding in structure **II** (HSiNN), besides the obvious difference of the hydrogen atom being connected to the silicon atom rather than to the nitrogen as in **I**, differs from that by a migration of a p-type electron pair from the Si–N moiety to the N–N one; in this way, the single bond character of the computed Si–N bond distance is justified, as well as the much shorter N–N bond distance, now intermediate between that of a double and a triple bond distance. The nature of the HOMO is practically inaltered relative to that of structure **I**; it continues to be Si–N bonding and N–N anti-bonding. The MO associated with the silicon 3s orbital is now higher in energy (12a′), and MO 2a″ and 10a′ are basically N–N localized.

Interestingly, isomer **III** shows a linear N–Si–N arrangement similar to that of the triatomics N–Si–N ($^3\Sigma_g^-$) which, as shown in Ref. 31, exhibited a local minimum at 84.60 kcal mol^{-1} above the global minimum SiNN ($^3\Sigma^-$). Here, as judged by the H–N–Si angle of 121°, one might be led to infer that the two bonds connecting the nitrogen atom to the hydrogen and to the silicon atoms could be rationalized in terms of an sp^2 hybridization on the middle nitrogen atom; a further weak π-type bond with the neighboring silicon would seem to be responsible for an additional shortening of the Si–N bond distance, making it slightly smaller (1.646 Å) than that of a single bond, as in H_3SiNH_2. In this system, the singly occupied MO is basically an anti-bonding combination involving the two N p_z orbitals (with no contribution from Si) and with a major preponderance of the orbital associated with the N connected to the hydrogen atom; MO 12a′ is the counterpart of 3a″, but now lying in the xy plane, and with a major contribution from the terminal N p_x orbital. The NH bond can be clearly associated with orbital 9a′, and an electron pair with orbital 11a′, which is essentially an sp^2 type hybrid lying in the *xy* plane. Orbital 2a″ describes a π-type bond between Si and the terminal N, and orbital 10a′ could not be ascribed to any of the classical bonding pictures. It is important to emphasize also that as judged by the relatively large Mulliken atomic charges (Si = 1.18, N(terminal) = −0.98, N = −0.61, H = 0.42), ionic contributions seem to be playing a role in the bonding of these atoms. One should note also the asymmetry in the two Si–N bonds; that with the terminal nitrogen atom is slightly shorter by about 0.04 Å, which reflects a stronger double bond character.

For the sake of completeness, we have collected in Table 5 the rotational constants and the dipole moment computed with the CCSD(T) and MP2 approaches, respectively, for the three isomers. Since the HSiNN molecule is predicted to be unstable at this level of theory, we have used for this case in particular the geometry optimized at the CCSD(T) level to obtain an estimate of the dipole moment.

We finally consider the harmonic frequencies of the various species, a piece of information of direct relevance to the experimentalists. In the absence of any experimental data for these molecules, a few indirect comparisons are made here with known frequencies of related compounds. We first note the very good agreement of the CCSD(T) prediction of the frequency of the N–H stretching (3316 cm^{-1}) in structure **I** with that of the isolated N–H molecule (3300 cm^{-1});[44] the MP2 result is incidentally also good, and the MCSCF result is overestimated by about 10%. As judged by the frequency associated with the N–N stretching (1262 cm^{-1}, CCSD(T)) in structure **I**, the N–N double bond character in this compound is weaker than that in $H_3CN=NCH_3$ (1580 cm^{-1}).[45] On the other hand, the frequency value of 800 cm^{-1} associated with the Si–N stretching is of similar magnitude to that in singly bonded silicon and nitrogen atoms in H_3SiNH_2 (898 cm^{-1}, HF/3-21G*),[40] a result which contrasts with the relatively short Si–N internuclear distance (1.615 Å), since in this case a distance of about 1.72 Å would be expected for singly bonded atoms. For structure **I**, the MP2 and MCSCF results overshoot the CCSD(T) frequencies by different amounts.

Focusing now our attention on structure **II**, we first note a very good agreement between the Si–H stretching frequency (2045 cm^{-1}, CCSD(T)) and that of the free Si–H species, 2042 cm^{-1}. The N–N and Si–N stretching frequencies (1690 and 314 cm^{-1}, CCSD(T)), and the Si–N–N bending fre-

Table 5. Rotational Constants (GHz), and Dipole Moments (Debye) for the Isomers of $HSiN_2$

	CCSD(T)			MP2
Isomer	A	B	C	μ
HNNSi (**I**)	586.88	5.8300	5.7727	2.512
HSiNN (**II**)	218.74	5.3291	5.2023	0.639[a)]
HNSiN (**III**)	713.82	6.4459	6.3882	2.389

a) Estimated with the CCSD(T) optimized geometry.

quency (443 cm^{-1}, CCSD(T)) are also consistent with those obtained for the non-hydrogenated species Si–N–N: 1898, 326, and 314 cm^{-1}, respectively, (CCSD(T)/cc-pVTZ-f).[31] The frequency value of 807 cm^{-1}, which one might initially guess to be associated with the SiN stretching, in fact corresponds to that of the SiNN bending mode.

In the case of structure **III**, the frequency value of 3537 cm^{-1} corresponds to the NH stretching, whereas the values of 1188 and 933 cm^{-1} can be associated with the antisymmetric and symmetric stretchings of the N–Si–N moiety. The bending mode involving the H–N–Si angle has a frequency of 552 cm^{-1}, and that of the N–Si–N angle, 267 cm^{-1}. Interestingly, the antisymmetric mode (A'') leaves the hydrogen undisplaced on the molecular plane in structure **III** and has a relatively small value of 172 cm^{-1}; in structures **I** and **II** the frequencies of the torsion mode are 318 and 472 cm^{-1}, respectively.

Conclusions

This study has shown that three local minima can be located on the [H, Si, N, N] potential energy surface if the calculation is pushed up to the CCSD(T) level of theory. In contrast with a previous study, we have found the molecule HSiNN to be a stable species, and lower in energy than the molecule HNNSi by 13.63 kcal mol^{-1}; the third isomer was found to be located at 47.62 kcal mol^{-1} above the global minimum. The energetics involved in the dissociation of structure **II** indicates, however, that it is likely to be found only in conditions of very low temperatures or trapped in matrices. Together with other studies in our group on various isomers of the species Si_2N, SiN_2, and Si_2N_2 it is our hope that the present study can provide additional structural, energetics, and vibrational data of relevance to the understanding of the gas phase chemistry of silicon and nitrogen compounds in both the laboratory and in interstellar space.

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