Computational Study on the Structures of the [H, Si, N, C, O] Isomers: Possible Species of Interstellar Interest

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Ab initio methods have been used to study the lowest lying [H, Si, N, C, O] isomers, which are of astrochemical interest. Over 20 [H, Si, N, C, O] isomers in the $^1A'$ electronic state have been investigated at the MP2/aug-cc-pVTZ level of theory. Of these, the seven lowest isomers have been further investigated using different levels of theory, including B3LYP and QCISD(T). It has been found that the relative energies of the isomers in their ground electronic state ($^1A'$) are very dependent on the level of theory used with either the *cis*-HOSiCN or *cis*-HOSiNC isomers being the lowest in energy. Overall, the four lowest isomers are within 6 kcal/mol of each other, and a further three isomers are less than 15 kcal/mol higher in energy than the lowest lying isomer, including HSiNCO, which has recently been detected spectroscopically. Natural bond analysis has been carried out on the ground electronic states of the seven lowest lying isomers to examine their electronic structure. The enthalpies of formation of the seven lowest isomers have also been evaluated using the G3MP2 and G3B3 multilevel methods and show that the isomers are relatively thermodynamically stable. The structures and energies of lowest lying $^1A''$ and $^3A''$ electronic states of these isomers have also been investigated and show that for most of the isomers the optimized structures in these excited electronic states correspond to a transition state structure.

Introduction

There has been considerable interest in the chemistry of organosilicon compounds over the last 30 years. This interest stems from that fact that organosilicon radicals play an important role in a number of chemical deposition methods used by the semiconductor industry. However, much interest in organosilicon compounds is also due to the fact that a number of silicon containing species have been detected in the interstellar medium. The cosmic abundance of silicon is thought to be only slightly lower than those of carbon, nitrogen, and oxygen.[1] Unfortunately, due to the limitation of accurate spectroscopic data, the number of detected silicon containing molecules is far fewer than those containing carbon, nitrogen, and oxygen. To date, approximately 10 silicon containing species have been detected in space, including SiO, SiC, SiC_2, cyclic-SiC_3, and just recently SiCN and SiNC.[2−5] To help in the search for new silicon containing species, a number of groups have carried out theoretical and experimental studies to obtain spectroscopic parameters to aid in the detection of these species in the interstellar medium.[6−17] One of these investigations led to two new species, HSiCN and HSiNC, being observed in the laboratory. Both of these species were regarded as being very strong candidates for detection in the interstellar medium due to fact that similar species had already been observed in space (e.g., SiCN). In this work, Sanz et al. used a high-voltage electric discharge source coupled to a molecular beam Fourier transform microwave spectrometer to study the HSiCN and HSiNC isomers. They obtained rotational constants for a number of different isotopomers of each isomer allowing the elucidation of both their structures. They found that both HSiCN and HSiNC have C_s symmetry with the H−Si−X (X = C or N) angle being ∼95°.[18]

Dover and Evans have recently carried out laser-induced fluorescence spectroscopy on the $\tilde{A}^1A''$ electronic state of HSiNC and found that upon excitation the H−Si−N angle increases by ∼20°, giving rise to the observation of forbidden transitions as a result of axis-switching.[19] This work also examined a number of vibrational states in both the excited and ground electronic states. Further work was pursued on analogous systems resulting in the observation of the $\tilde{A}^1A''$ electronic state of HSiNCO.[20] HSiNCO has the same potential of being found in the interstellar medium as HSiCN and HSiNC because the cosmic abundance of oxygen is only slightly less than carbon and nitrogen.[1] To date, there have been no previous studies on HSiNCO or on any of its isomers. This paper aims to look at possible isomers of [H, Si, N, C, O] using *ab initio* methods to investigate their stability and to evaluate their spectroscopic constants to aid in the detection of these species both in the laboratory and in space.

Theoretical Methods

For the most part calculations were carried out using the Gaussian 03 suite of programs.[21] The geometries of the different isomers were fully optimized at different levels of theory using the augmented triple-ζ correlated consistent basis set (aug-cc-pVTZ) of Dunning et al.[22−24] The methods used include, the hybrid density functional method B3LYP,[25] the second-order Møller−Plesset method (MP2)[26−29] and the quadratic configuration interaction method including singles and doubles, QCISD.[30] Further single-point calculations were carried out using QCISD(T), with the molecular structure fixed to the QCISD optimized structure.[30] For accurate relative energies and evaluation of thermodynamic properties the G3B3 and G3MP2 multilevel methods, as implemented in Gaussian 03, were used.[31,32] Harmonic vibrational frequencies were calculated at the MP2 and B3LYP levels of theory to check if the optimized

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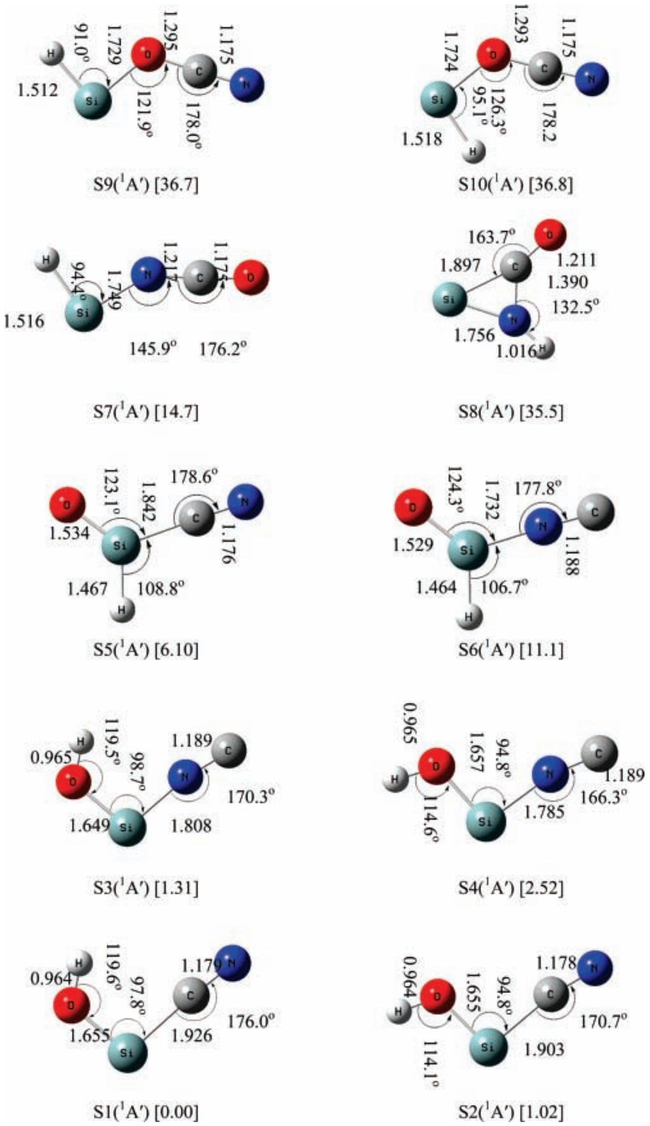
structures were true minima. The MP2, QCISD, and QCISD(T) calculations were carried out using both full electron correlation (i.e., including the core electrons [Full]) and the standard frozen core method (FC). As the difference in the zero-point energy (ZPE) between MP2(FC) and MP2(Full) was small, the MP2 energies were corrected using the MP2(FC) ZPE. For the QCISD calculations the vibrational frequencies and zero-point energies were evaluated using the aug-cc-pVDZ basis set.[22−24] Multiconfiguration SCF (MC-SCF) calculations were carried out as implemented in the MOLPRO suite of programs using the aug-cc-pVTZ basis set with (9,3) active orbitals and (11,6) closed orbitals.[33] CIS calculations were carried out as implemented in the Gaussian 03 suite of programs. For the Gaussian 03 calculations a "tight" optimization and SCF convergence was employed, and for the B3LYP calculations an "ultrafinegrid" was used. Natural bond analysis (NBO 5.0) was carried out at the B3LYP/aug-cc-pVTZ level of theory using the NWChem suite of programs.[34] Calculations were carried out on two computer clusters: the system managed by the EPSRC National Service for Computational Chemistry Software[35] and the University of Leicester Mathematical Modeling Centre's supercomputer, which was purchased through the HEFCE Science Research Investment Fund. The visualization software MOLDEN[36] and GaussView[37] were used throughout this work.

Results and Discussion

A series of calculations were carried out on a number of different isomeric forms of [H, Si, N, C, O]. The optimized geometries and vibrational frequencies of over 20 different isomers were calculated at the MP2(FC) level of theory. Figure 1 shows the 10 lowest [H, Si, N, C, O] isomers in the $\tilde{X}^1A'$ electronic state using the MP2(FC) level theory. For each isomer the electronic configuration of the singlet species is $15a'^2\ 3a''^2$. As can be seen from Figure 1, the five lowest isomers (S1−S5) are all within approximately 6 kcal/mol of each other. At the MP2(FC) level of theory the lowest isomer (S1) was found to be *cis*-HOSiCN, and the *trans* form of this isomer (S2) lies 1.02 kcal/mol higher in energy. Isomers S3 and S4 are the isocyanide analogues to species S1 and S2. The next two isomers are HSi(O)CN (S5) and HSi(O)NC (S6), which are the silicon analogues to formyl cyanide and formyl isocyanide and are 6.10 and 11.1 kcal/mol higher in energy than isomer S1.[38−40] Isomer S7 is the isocyanate analogue to HSiNC and is 14.7 kcal/mol higher in energy than the S1 isomer. It was found that the corresponding cyanate species (HSiCNO) is significantly higher in energy (~88 kcal/mol) than the HSiNCO isomer, which is similar to that seen for HNCO/HCNO (0.0/70.1 kcal/mol)[41,42] and CH_3NCO/CH_3CNO (0.0/54.9 kcal/mol).[43] The S8 isomer is a cyclic system with the oxygen double bonded to the carbon and the hydrogen bonded to the nitrogen and is 35.5 kcal/mol higher in energy than the S1 isomer. The next two isomers, S9 and S10, which are cyanatosilylene and isocyanatosilylene, are found to be 36.7 and 36.8 kcal/mol higher in energy than the S1 isomer. All of these isomers gave non-imaginary vibrational frequencies indicating that their optimized structures are true minima.



S9(^{1}A′) [36.7] S10(^{1}A′) [36.8]

S7(^{1}A′) [14.7] S8(^{1}A′) [35.5]

S5(^{1}A′) [6.10] S6(^{1}A′) [11.1]

S3(^{1}A′) [1.31] S4(^{1}A′) [2.52]

S1(^{1}A′) [0.00] S2(^{1}A′) [1.02]

Figure 1. MP2(FC)/aug-cc-pVTZ optimized geometries (bond lengths in Å; bond angles in degrees) of the 10 lowest [H, Si, N, C, O] isomers in the $^1A'$ electronic state. All energies (kcal/mol) are relative to the lowest energy isomer (S1).

Further calculations were carried out using different levels of theory to check if the MP2(FC) calculations gave the correct ordering of the seven lowest isomers. To look at the influence that core electrons have on the relative energies of the found isomers, the MP2 calculations were re-run with inclusion of the core electrons [MP2(Full)]. Higher level calculations were carried out on the lowest seven isomers at the QCISD and QCISD(T) level of theory, and to test the reliability of DFT methods, the B3LYP hybrid functional was also employed. For each calculation the geometries were re-optimized and where possible the harmonic vibrational frequencies evaluated. In the case of the QCISD(T) calculations the geometry was re-optimized at the QCISD level of theory and a single-point calculation at this geometry was carried out. The QCISD/QCISD(T) calculations were also carried out with the inclusion of core electrons. Table 1 shows the relative energy differences between the seven lowest isomers found at each level of theory. The results in Table 1 show there is some confusion with regard to the ordering of the lowest lying isomers. Both the B3LYP and QCISD(T) results indicate that the S3 isomer is the lowest in energy with the S4 isomer, the *trans* form of S3, being the second lowest in energy. The relative energy difference between the S1−S2 and the S3−S4 isomers is consistent from one level of theory to the next. The other main difference can be seen in the energy of the S5 isomer, which is predicted to change significantly with the inclusion of triple excitations, whereas for the analogous isocyanide isomer (S6) the predicted relative energy is fairly consistent from one level of theory to the next. The B3LYP calculations predict the separation between isomers

TABLE 1: Energies of the Lowest Seven [H, Si, N, C, O] Isomers (kcal/mol)[a]

isomer	B3LYP	MP2[b]	QCISD(T)[c]	G3B3	G3MP2
S1	0.0	0.0 (0.0)	0.0 (0.0)	0.0	0.0
S2	1.1	1.0 (1.1)	1.1 (1.2)	1.2	1.1
S3	−2.5	1.3 (0.15)	−1.6 (−2.8)	−1.6	−2.4
S4	−1.2	2.5 (1.4)	−0.4 (−1.5)	−0.2	−1.2
S5	6.9	6.1 (5.9)	10.0 (9.6)	7.6	7.7
S6	10.6	11.1 (9.8)	11.0 (9.5)	8.6	7.7
S7	10.7	14.7 (12.2)	13.8 (11.2)	12.4	12.5

[a] All energies are relative to isomer S1 (as in Figure 1). All energies have been ZPE corrected. [b] Numbers in parentheses are the MP2 values with inclusion of the core electrons [MP2(Full)]. [c] Zero-point energy calculated at the QCISD level of theory with an aug-cc-pVDZ basis set. Number in parentheses are the QCISD(T) values with inclusion of the core electrons.

S6 and S7 as only 0.1 kcal/mol, whereas other methods predict a much larger separation.

The inclusion of the core electrons is important, especially for the lowest four isomers. The MP2(Full) calculations agree with the MP2(FC) calculations with isomer S1 being the lowest in energy; however, the second lowest isomer was determined to be the *cis*-HOSiNC isomer (S3), which is predicted to be only 0.15 kcal/mol higher in energy than isomer S1. The MP2(Full) calculations also predict the third and fourth lowest isomers to be S2 and S4 with a separation of only 0.3 kcal/mol. For the other isomers the MP2(Full) calculations give smaller relative energies than the MP2(FC) calculations but predict the same order. Similar calculations have also been carried out using QCISD/QCISD(T). At this level of theory the inclusion of core electrons also greatly affects the relative energies of the isomers. For isomers S1 to S4 the separation is similar to that found using B3LYP; however, for isomers S5 and S6 the predicted energy difference is only 0.1 kcal/mol. The inclusion of the core electrons has resulted in isomer S6 becoming slightly more energetically stable than isomer S5. The inclusion of core electrons at the QCISD/QCISD(T) level of theory has resulted in the relative energy of isomer S7 to drop from 13.8 to 11.2 kcal/mol.

The G3MP2 and G3B3 multilevel methods were carried out on the lowest seven isomers in their ground electronic state to determine more accurate relative energies.[31,32] As can be seen from Table 1 the G3B3 and G3MP2 results agree fairly well with the QCISD(T) results. Both methods show that isomer S3 is the lowest lying isomer and not isomer S1, as found at the MP2 level of theory.

In recent years there has been a lot of work on comparing the differences in bonding and reactivities of carbon- and silicon-containing compounds. Looking at the [H, C_2, N, O] isomers, it is found that HC(O)CN (0.0 kcal/mol) is the most stable isomer followed by HC(O)NC (12.0 kcal/mol), HNCCO (31.2 kcal/mol), HOCCN (45.0 kcal/mol), and HCCNO (81.0 kcal/mol) using B3LYP with a 6-311++G(d, p) basis set.[44] The ordering of the carbon based isomers is in complete contrast to the silicon containing species. It is interesting to note that to date the isocyanate analogue, HCNCO, has yet to be investigated as a potential [H, C_2, N, O] isomer.

HOSiCN/HOSiNC. As can be seen from Figure 1 the geometry of these silanols shows a short O−H bond length, which is analogous to that observed for light alcohols and is similar to that predicted for alkylsilanols.[45] The average Si−O bond length is 1.654 Å, which is much shorter than the covalent radii sum (1.87 Å) and is similar to that seen in other silanols. The C−N/N−C bond lengths are similar to those observed in SiCN/NC and HSiCN/NC and are longer than the average CN/NC bond.[6,8,18] The two most interesting structural aspects of these species are the O−Si−X (X = C or N) and Si−O−H angles. The O−Si−X angle is small, ∼90°, and is similar to the H−Si−X angle found in HSiNC/CN (∼95°),[6,8,18] whereas the Si−O−H angle is in line with that observed for the alkylsilanols (∼120°) and is 10° larger than the alcohol analogues.[46] Going from the *cis* to the *trans* forms results in a shortening of the Si−X (X = C or N) bond length by ∼0.02 Å, and the Si−C−N/Si−N−C angle decreases by up to 6°.

Natural Bond Analysis: (*cis*/*trans*)-HOSiCN. Natural bond analysis (NBA) on HOSiCN indicates that the C−N bond is triple in nature with the Si−O bond being a double bond, whereas the bonding between Si−C and O−H is single in nature. The bonding of Si−O is counteracted slightly by population of antibonding MOs and results in the Si−O bond length being 0.1 Å longer than the diatomic SiO, which is regarded to be double bonded.[47] The NBA also indicates the presence of three lone pairs situated on the Si, O, and N. The Si lone pair has s character (*cis*, $sp^{0.24}$ (19.2%); *trans*, $sp^{0.24}$ (19.4%)). For O and N the lone pairs are, to a fair extent, hybridized: for O (p_z) *cis*, $sp^{1.83}$ (64.4%), and *trans*, $sp^{1.53}$(60.2%); for N *cis*, $sp^{0.92}$ (47.8%), and *trans*, $sp^{0.91}$ (47.5%). The bonding between Si−O is almost pure p in character on the silicon atom (*cis*, $sp^{7.25}$ (86.8%); *trans*, $sp^{7.73}$ (87.6%)), whereas the bonding between Si−C is again almost pure p in character on the silicon atom (*cis*, $sp^{9.97}$ (89.7%); *trans*, $sp^{8.86}$ (88.6%)). The almost pure p character of these MOs explains the relatively small O−Si−C angle seen in both isomers. No additional resonance structures are thought to contribute to the structural characteristics of these isomers.

Natural Bond Analysis: (*cis*/*trans*)-HOSiNC. The NBA on HOSiNC indicates that the N−C bond is triple in nature, the bonding between Si−N and O−H bonds are single in nature, whereas, like HO−SiCN, the Si−O is considered a double bond. The NBA indicates the presence of three lone pairs situated on the Si, O, and C. The Si lone pair has s character (*cis*, $sp^{0.23}$ (18.8%); *trans*, $sp^{0.23}$(18.9%)), whereas for O and C the lone pairs are hybridized to a fair extent: for O (p_z) *cis*, $sp^{1.84}$ (64.6%), and *trans*, $sp^{1.51}$ (60.0%); for C *cis*, $sp^{0.45}$ (31.1%), and *trans*, $sp^{0.45}$ (31.2%). The bonding between Si−O is almost pure p in character on silicon atom (*cis*, $sp^{7.33}$ (86.9%); *trans*, $sp^{7.87}$ (87.7%)), whereas the bonding between Si−N again is almost pure p in character on the silicon atom (*cis*, $sp^{9.61}$ (89.8%); *trans*, $sp^{8.35}$ (88.6%)). As seen for HO−SiCN, the almost pure p character of these MOs explains the relatively small O−Si−N angle as seen in both isomers. Again, there is thought to be no additional resonance structures that will contribute to the structural characteristics of these isomers.

Isomerization. For the *cis* and *trans* forms of HOSiCN and HOSiNC, calculations were performed on both species to determine the potential of rotation of the hydrogen about the oxygen atom. Figure 2 shows the potentials for both HOSiCN and HOSiNC. The potentials were generated by changing the HOSiC/HOSiN dihedral angle, while relaxing the rest of the structure at the MP2(Full) level of theory using the aug-cc-pVTZ basis set. For each species a total of 20 points were calculated along the potential energy surface. From Figure 2 it can be seen that both potentials have a double minimum at $\theta = 0$ and 180° corresponding to the *cis* and *trans* forms, respectively; θ is the dihedral angle between H−O−Si−C/N. In both cases the *trans* form is higher in energy by ∼0.3 kcal/mol, which is opposite to the trend found for formic,

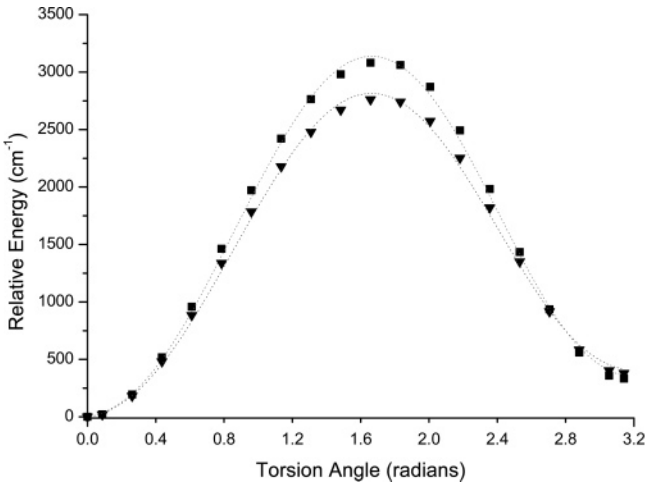


Figure 2. *Cis* to *trans* isomerization of HOSiCN (■) and HOSiNC (▼).

thiolformic, thionformic, and dithioformic acids.[48] The potentials have been fitted using the function of Torro-Labbe et al.:[48,49]

$$V(\theta) = \frac{1}{2}\Delta V^{\circ}(1 - \cos\theta) + \frac{1}{4}(k_t + k_c)(1 - \cos^2\theta) + \frac{1}{4}(k_t - k_c - \Delta V^{\circ})(1 - \cos^2\theta)\cos\theta \quad (1)$$

The results from the fits are shown in Table 2 and are compared against the results found for formic, thiolformic, thionformic, and dithioformic acids using the same method.[48] It can be seen that HOSiCN and HOSiNC have similar, although lower, barrier heights than thiolformic and dithioformic acids. The values of k_c and k_t are slightly different from those of thiolformic and dithioformic acids with the k_c force constant larger than k_t. These force constants indicate that for the *trans* form there is a repulsive interaction between the hydrogen and the silicon and oxygen atoms. Furthermore, the natural bond analysis shows some delocalization between the O−H and Si−C units, which could further stabilize the *cis* form over the *trans* form. The parameters α and $\Delta V^{\ddagger}$ are the angle in which the potential is at a maximum and the barrier height, respectively. For HO−SiCN $\alpha = 95.4°$ and $\Delta V^{\ddagger} = 3169$ cm^{-1}, and for HO−SiNC $\alpha = 95.3°$ and $\Delta V^{\ddagger} = 2841.3$ cm^{-1}. On isomerization the Si−C/N bond length decreases by ∼0.02 Å going from the *trans* to the *cis* form, which is most likely the result of delocalization between H−O and Si−C/N.

Vibrational Frequencies. Vibrational frequencies have been calculated for all the species at the B3LYP and MP2(FC) levels of theory. Table 3 shows the ground electronic state unscaled vibrational frequencies for *cis*/*trans*-HOSiCN and *cis*/*trans*-HOSiNC. There is good agreement between the B3LYP and MP2(FC) results except for the C−N stretching mode where there is a ∼200 cm^{-1} difference. The rotational constants at the equilibrium geometry are also given for each species in Table 3. At the MP2(Full) level of theory the dipole moments (μ_x/μ_y) of *cis*/*trans*-HOSiCN are 1.66/1.36 and 2.71/4.82 Debye, respectively, and for *cis/trans*-HOSiNC they are 1.70/1.21 and 2.57/3.51 Debye, respectively. The dipole moments for all these species are sufficiently high enough that detection using microwave spectroscopy should be possible.

Excited Electronic State. Calculations were carried out on the $\tilde{A}^1A''$ excited state for *cis*/*trans*-HOSiCN and *cis*/*trans*-HOSiNC at the MP2(FC) and B3LYP levels of theory. For each species an optimized structure was determined (see Figure 3), which shows that the H−O−Si angle opens up to ∼115°. This increase in the H−O−Si angle is expected as electron density is being transferred to the out-of-plane p_z orbital on the silicon. Both the MP2(FC) and B3LYP vibrational frequency calculations give an imaginary frequency for the H−O−Si out-of-plane bending mode for both isomers and indicates the optimized structures are most likely transition state structures. The nature of these transition states needs to be explored further.

HSiNCO. The ground electronic state structure of HSiNCO (see Figure 1) is analogous to HSiCN and HSiNC with the H−Si−X angle being approximately 95°. The small H−Si−X (X = C or N) angle is also seen for the analogous halogen species HSiX (X = F, Cl, Br, I) where the H−Si−X angles are 97.6°, 102.8°, 102.9°, and 102.7°, respectively.[50−52] The Si−H bond length of 1.516 Å is similar to that observed for HSiNC (1.526 Å); however, it is ∼0.03 Å longer than the Si−H bond in H_3SiNCO.[18,53] Table 4 compares the N═C and C═O bond distances against other molecules containing an isocyanate group. From Table 4 it can seen that in most cases the N═C bond is longer than the C═O bond. The question of linearity or nonlinearity of the N═C═O bond has been of much interest for several decades. The natural bond analysis proposes three resonance structures with the N═C═O form being the most probable, and $^{+}$N═C−O^{-} and $^{-}$N−C═O^{+} being the other minor forms. It is therefore possible that the N═C═O group is in fact nonlinear based on the proposed resonance structures. However, in most of the early microwave spectroscopy and electron diffraction studies the N═C═O group was assumed to be linear. Only in a few cases has the N═C═O angle actually been determined and is usually found to be nonlinear. For the microwave studies it has been found that fixing the N═C═O group to being linear typically gives a poor fit to the observed frequencies. However, fits have been improved by using increasingly complex Hamiltonians, which incorporate bending and rotational terms. The results from the electron diffraction and microwave work are heavily dependent on the model used to fit the experimental data and are therefore open to much debate. In comparison, *ab initio* studies on species containing the NCO group have typically found the N═C═O angle to be less than 180°, with the average angle being between 172° and 178°.[50−52] For HSiNCO the N═C═O angle is found to range from 174.7° to 177.5°.

The variation in the bond angle of the atom adjacent to the isocyanate group has also been of much interest. It can be seen from Table 4 the X−N═C angles can range from being linear to 120°. In the case of X = Si it has been put forward that this range in angles is a result of the $p_\pi - d_\pi$ character of the bonding involving the available 3d orbitals of silicon.[54] It has also been suggested that there is a good correlation between the variation of the X−N═C angle and the r(X−N) bond length. It is found that, as the X−N═C angle decreases, the double bond character of the X−N bond also seems to decrease.[54] By this argument, the Si−N bond in HSiNCO would be more likely a single bond, which is in agreement with that found by the natural bond analysis (see below). On average, the X−N═C angle when X = Si seems to be larger than those when X = C. Furthermore, the Si−N═C angle for HSiNC is 169.3°, which is substantially higher than HSiNCO (145.9°) and would indicate that for HSiNC the Si−N bond is more double bond in character.[18]

Vibrational frequencies and rotational constants for HSiNCO in its ground electronic state were also calculated and are given in Table 3. The dipole moments (μ_x/μ_y) at the MP2(Full) level of theory were calculated to be −1.49/0.20 Debye, respectively. Again, the dipole moments are sufficiently high enough that

TABLE 2: Isomerization Parameters for HO−SiNC and HO−SiCN[a]

parameters	HOSiCN	HO−SiNC	HO−OCH[b]	HS−OCH[b]	HO−SCH[b]	HS−SCH[b]
k_c	18.63	15.93	15.08	15.41	16.63	17.17
k_t	15.23	13.92	27.24	20.40	30.79	25.45
V_1	−278.17	−278.59				
V_2	−1480.45	−1304.99				
V_3	97.08	69.91				
ΔV^0	362.2	417.4	2098.60	495.6	2236.7	611.0
α_0	95.42	95.29	98.2	92.0	93.0	92.0
$\Delta V^\ddagger$	3169.04	2841.28	4768.5	3379.7	5162.9	4037.0

[a] k_c and k_t (force constants) in kcal mol^{-1} rad^{-2}, V_1, V_2, V_3, ΔV_0, and $\Delta V^\ddagger$ in cm^{-1}, and α_0 in degrees. [b] Reference 48.

TABLE 3: Harmonic Vibrational Frequencies[a] (cm^{-1})[a] [Intensities (KM/mol)] and Rotational Constants (GHz) of the Seven Lowest [H, Si, N, C, O] Isomers in the ^{1}A′ State at the B3LYP and MP2(FC) Levels of Theory

species	frequencies (infrared intensity)	rotational constants (*A*, *B*, *C*)
cis-HOSiCN	135.9 (14), 183.9 (19), 384.8 (10), 518.3 (118), 551.2 (138), 803.9 (235), 895.5 (42), 2259 (48), 3816.4 (81)	194.293, 3.738, 3.135
cis-HOSiCN[b]	131.2 (14), 189.4 (19), 387.5 (10), 527.5 (123), 563.8 (138), 816.6 (232), 906.8 (41), 2073.5 (87), 3828.5 (101)	190.331, 3.756, 3.137
trans-HOSiCN	154.3 (2), 194.9 (0.4), 385.2 (0.5), 551.3 (140), 559.6 (81), 851.3 (233), 878.6 (52), 2266.3 (51), 3833.8 (140)	206.697, 3.718, 3.151
trans-HOSiCN[b]	149.1 (2), 199.5 (0.5), 382.7 (0.1), 562.5 (141), 578.1 (76), 863.5 (235), 890.4 (47), 2085.4 (91), 3834.3 (157)	202.381, 3.731, 3.150
cis-HOSiNC	136.9 (8), 139.5 (8), 351.5 (22), 530.0 (139), 576.0 (143), 793.3 (254), 894.1 (59), 2110.6 (386), 3807.5 (69)	210.356, 4169, 3.479
cis-HOSiNC[b]	126.2 (10), 134.8 (10), 353.4 (23), 539.1 (139), 574.1 (159), 803.9 (248), 910.0 (63), 2042.5 (293), 3821.0 (92)	203.705, 4.192, 3.477
trans-HOSiNC	146.6 (1), 150.0 (0), 363.1 (2), 524.1 (80), 613.6 (183), 844.8 (272), 860.3 (31), 2117.4 (413), 3839.1 (130)	221.349, 4.167, 3.507
trans-HOSiNC[b]	138.6 (1), 143.7 (0.1), 361.0 (2), 541.6 (79), 615.5 (199), 854.4 (244), 877.0 (56), 2050.5 (310), 3839.5 (153)	215.215, 4.187, 3.505
HSi(O)CN	167.5 (28), 228.1 (6), 387.6 (13), 556.3 (37), 604.0 (97), 847.9 (65), 1237.4 (89), 2293.3 (39), 2300.6 (58)	32.245, 3.387, 3.065
HSi(O)CN[b]	159.3 (25), 223.9 (6), 372.7 (14), 565.0 (36), 610.1 (94), 859.1 (73), 1201.0 (58), 2107.6 (84), 2347.3 (44)	31.881, 3.338, 3.022
HSi(O)NC	140.4 (13), 162.4 (1), 357.7 (38), 556.1 (43), 682.0 (125), 854.4 (65), 1250.4 (118), 2133.9 (455), 2312.7 (34)	33.975, 3.784, 3.405
HSi(O)NC[b]	134.2 (14), 151.1 (1), 347.8 (33), 567.0 (42), 675.1 (141), 863.1 (72), 1223.4 (92), 2080.3 (361), 2367.6 (34)	33.973, 3.726, 3.357
HSiNCO	103.9 (1), 147.0 (0.1), 569.0 (73), 625.2 (52), 652.9 (24), 869.7 (84), 1452.7 (31), 2002.3 (368), 2330.8 (1619)	134.174, 2.687, 2.635
HSiNCO[b]	103.5 (2), 159.2 (0.5), 569.1 (63), 638.4 (17), 643.9 (72), 885.5 (88), 1412.7 (62), 2097.1 (370), 2323.3 (1528)	101.827, 2.736, 2.665

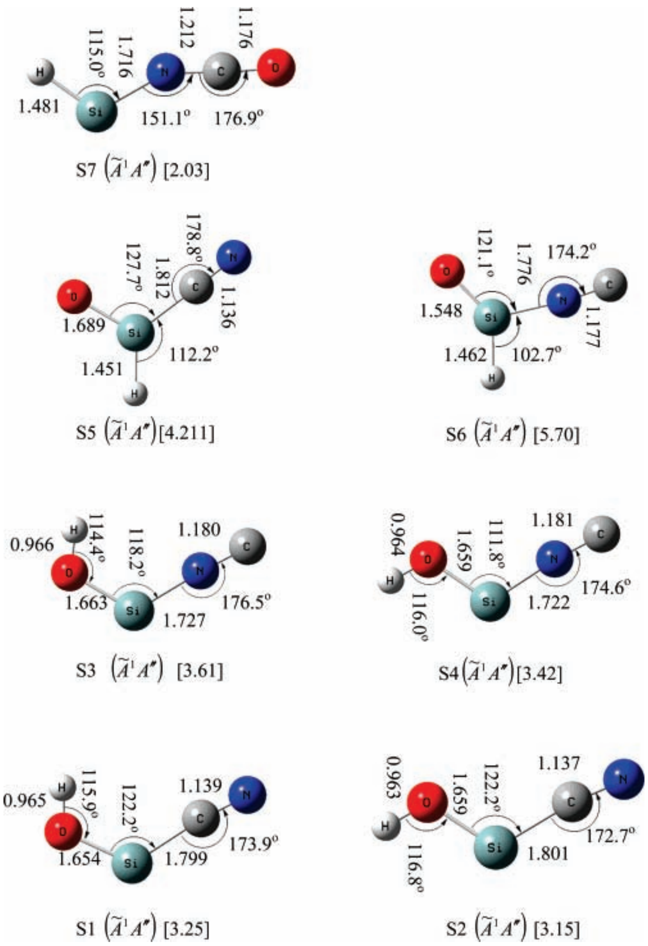
[a] Unscaled frequencies. [b] MP2(FC) calculations.

the rotational spectrum of HSiNCO should be observable using standard microwave spectroscopy techniques.

Natural Bond Analysis. The NBA shows the Si−H and Si−N bonds are single in nature. On the oxygen the LP is mainly s in character with sp$^{0.63}$ (p character 38.5%), which is different from that seen in the HO−SiCN/NC isomers where the oxygen LP was situated out-of-plane and was mainly p in character. The bonding between Si−H and Si−N is mainly p in character with sp$^{8.41}$ (88.4%) and sp$^{7.59}$ (86.9%) which, as seen in the HO−SiCN/NC isomers, explains the small H−Si−N bond angle of 95°.

Excited Electronic State. Dover and Evans have recently performed laser-induced fluorescence and dispersed fluorescence experiments on HSiNCO in the $\tilde{A}^1A''$ electronic state.[20] Table 5 shows calculations carried out on the $\tilde{A}^1A''$ state of HSiNCO. It shows that, on excitation, the H−Si−N angle increases significantly. This large increase in the bond angle is due to electron density being transferred from the Si−H molecular orbital to the out-of-plane p_z orbital on the silicon. This can be seen in Figure 4, which gives a three-dimensional representation of the HOMO orbital (using natural bond analysis) in both the ground electronic state ($\tilde{X}^1A'$) and the $\tilde{A}^1A''$ excited electronic state of HSiNCO at the B3LYP level of theory. All levels of theory predict that on excitation the H−Si−N angle increases from ∼94° to ∼115°. Similar increases are seen for the analogous halogen species HSiX (X = F, Cl, Br, I) where on excitation the H−Si−X angles are 115.3°, 116.1°, 116.6°, and 116.2°, respectively.[50−52] For all but the MC-SCF calculations the Si−H and Si−N bonds decrease by ∼0.04 Å, and the Si−N−C angle increases from ∼146° to ∼151°.

The excitation transition frequencies calculated using B3LYP, MP2(FC), MP2(Full), and QCISD(T) levels of theory are significantly lower than the observed value of ∼20 000 cm^{-1}.[20] On the other hand, the MC-SCF transition frequency is in reasonable agreement with the observed value, although slightly higher. Obviously, this particular excitation involves more than one configuration, which standard methods are not able to describe correctly. Similar discrepancies in the excitation energy have been found for the halogen species (HSiX; X = F, Cl, Br), where similar B3LYP and MP2 calculations underestimated the transition energy by ∼4000 cm^{-1}. CIS calculations on HSiNCO show the lowest lying $^1A''$ state is located around ∼20 000 cm^{-1}, which is in very good agreement with the experimental results. This state is predicted to have an oscillator strength of $f = 0.04$, and results from 15a′ → 4a″ and 15a′ → 5a″ excitations. The CIS calculations also predict two $^1A'$ states at ∼50 000 cm^{-1} (vertical excitation energies) with oscillator strengths of $f \sim 0.12$.



S7 ($\tilde{A}^1A''$) [2.03]

S5 ($\tilde{A}^1A''$)[4.211]

S6 ($\tilde{A}^1A''$) [5.70]

S3 ($\tilde{A}^1A''$) [3.61]

S4($\tilde{A}^1A''$)[3.42]

S1 ($\tilde{A}^1A''$) [3.25]

S2 ($\tilde{A}^1A''$) [3.15]

Figure 3. MP2(FC)/aug-cc-pVTZ optimized geometries of the $^1A''$ excited state of the seven lowest [H, Si, N, C, O] isomers (bond lengths in Å; bond angles in degrees). All energies (eV) are relative to their corresponding $^1A'$ isomers as in Figure 1.

HSi(O)CN and HSi(O)NC. The fifth and sixth lowest isomers are HSi(O)CN and HSi(O)NC, which are analogous to formyl cyanide and formyl isocyanide.[14] For both isomers the Si−H bond length is ~1.47 Å, which is smaller than that found in HSiNCO and is similar to that observed for H_3SiNCO.[55,56] The Si−X (X = C and N) bond length decreases by 0.1 Å going from C to N, which is seen in the other isomers. The Si−O bond length is ~1.52 Å, which is much shorter than the ~1.65 Å observed in HO−SiCN/NC and is similar to the 1.51 Å bond length observed for the diatomic SiO, which indicates that this is a double bond.[47] In going from CN to NC, the C−N bond length increases by 0.02 Å, again this is similar to the trend seen in HO−SiCN/NC. The H−Si−C angle of 109.1° with the O−Si−C angle of 122.8° indicates that some sp^2 hybridization is occurring on Si, resulting in the ~120° angles. The dipole moments (μ_x/μ_y) in the ground state for HSi(O)CN and HSi(O)NC are −2.55/1.78 and −2.61/1.62 Debye, respectively, and are sufficiently high that these species should be observable using standard microwave spectroscopy techniques. Table 3 shows the vibrational frequencies and rotational constants for these species. Excited state calculations on these species at the MP2(FC) level of theory show that the first $^1A''$ state of HSi(O)CN is located around ~25 000 cm^{-1}, whereas for HSi(O)NC the transition energy is predicted to be shifted to the blue and is ~28 000 cm^{-1}. On excitation, there is a significant change in the geometry with the Si−O bond increasing by more than 0.1 Å and the C−N bond decreasing by 0.04 Å. However, the biggest change is in the C−Si−O angle, which decreases by ~15°, whereas the C−Si−H angle increases by ~20°. This is a result of electron density being shifted into an out-of-plane orbital on the silicon. Upon excitation, both isomers give an imaginary frequency for the out-of-plane Si−H wag, which indicates the optimized structures are transition state structures. The nature of these transition states needs to be explored further.

Natural Bond Analysis. For HSi(O)CN the NBA assigns the C−N bond as a triple bond and the Si−O bond as a double bond. It gives three lone pairs, one on the nitrogen and two on the oxygen. The LP on nitrogen is substantially hybridized with $sp^{0.88}$ (46.8%). On the oxygen the first LP is mainly s in character ($sp^{0.57}$ (36.2%)), and the other lone pair is mainly p in character and is similar to the out-of-plane LP seen for HO−SiCN/NC. The bonding contributions from Si for the Si−H, Si−C, and Si−O bonds show a fair amount of hybridization, 65.5%, 70.7%, and 61%, respectively, which would explain the slightly larger H−Si−C and O−Si−C angles seen than in the other isomers. For HSi(O)NC the bonding is very similar to that seen for HSi(O)CN, except there is now a lone pair on the carbon that, like the lone pair on the nitrogen in HSi(O)CN, is substantially hybridized, $sp^{0.43}$ (30.2%).

Enthaplies of Formation. To get some understanding of how the chemical structure of the isomers relate to their reactivity, the enthalpies of formation for some of the isomers were evaluated. Table 6 shows the enthalpy of formation at 0 and 298 K of the seven lowest isomers using the G3MP2 and G3B3 multilevel methods. The enthalpies were calculated using the method of Curtiss et al. where the theoretical enthalpies were calculated by subtracting the calculated atomization energies from the known enthalpies of formation of the isolated atoms.[57] To calculate the enthalpy of formation at 0 K, eq 2 was employed:

$$\Delta H^\circ_{f,0}(M) = E(M) + \mathrm{ZPE}(M) - \sum_{z}^{\text{atoms}} E(X_z) + \sum_{z}^{\text{atoms}} \Delta H^\circ_{f,0}(X_z) \quad (2)$$

and for the enthalpy of formation at 298 K eq 3 was used:

$$\Delta H^\circ_{f,298}(M) = E(M) + \mathrm{ZPE}(M) + [H_{298}(M) - H_0(M)] - \sum_{z}^{\text{atoms}} \{E(X_z) + [H_{298}(X_z) - H_0(X_z)]\} + \sum_{z}^{\text{atoms}} \Delta H^\circ_{f,298}(X_z) \quad (3)$$

In eq 3, $H_{298}(M)$ and $H_0(M)$ were taken from the theoretical calculations, and the values of $H_{298} - H_0$, $\Delta H^\circ_{f,0}$, and $\Delta H^\circ_{f,298}$ for the atoms were taken from the JANAF tables.[58]

The enthalpies of formation of the seven lowest isomers are similar to those of silane (8.2 kcal/mol, 298 K) and disilane (19.1 kcal/mol, 298 K).[59] If we compare the enthalpies of formation against those from other transient species, then we see that the generation and detection of the [H, Si, N, C, O] isomers is, from a thermodynamic standpoint, highly possible. For instance, the enthalpy of formation of HNCO (298 K) has been estimated to be −27 kcal/mol, and for the other isomers HOCN, HCNO, and HONC the $\Delta H^0_f(298K)$ are 3.1, 40.9, and 56.4 kcal/mol, respectively.[60] Furthermore, work on NCO has estimated that its enthalpy of formation is around 30.3 kcal/mol.[61] If we compare the results against some recently studied silicon containing transient species, we see that SiCH ($\Delta H^0_f(298K)$ = 123.1 kcal/mol), $H_2Si{=}CH_2$ ($\Delta H^0_f(298K)$ = 43.0 kcal/mol), SiC ($\Delta H^0_f(298K)$ = 178.6 kcal/mol), SiC_2

TABLE 4: Bond Distances (Å) and Angles (Degrees) for Molecules Containing the Isocyanate Group

compound	r(N=C)	r(C=O)	∠(N=C=O)	∠(X−N=C)	r(X−N)	ref
HSiNCO	1.217	1.175	176.2	145.9	1.749	this work [MP2(FC)]
HSiNCO	1.203	1.168	177.5	154.1	1.742	this work [B3LYP]
HSiNCO	1.198	1.150	174.7	144.1	1.748	this work [MCSCF]
HNCO	1.2140(24)	1.1664(8)	172.6(27)	123.9(17)	0.9946(64)	MW r_s ref 66
CH_3NCO	1.168(5)	1.202(5)	(180)[b]	140.3(4)	1.450(4)	ED [C_{3v}] ref 67[7]
CH_3CH_2NCO	1.217(5)	1.173(4)	174.1(3)	130.3(21)	1.45.2(9)	ED + MW r_α* ref 68
H_3SiNCO	1.199(12)	1.174(6)	(180)[a,b]	158.9	1.703(9)	MW r_0 ref 55, 56
$(CH_3)_3SiNCO$	1.202(16)	1.176(10)	165.8(36)	156.9(30)	1.74(4)	ED r_a ref 69
F_3SiNCO	1.190[c]	1.168(25)	(180)[b]	160.7(12)	1.648(10)	ED [C_1] ref 70
Cl_3SiNCO	1.219(7)	1.139(8)	(180)[b]	138.0(4)	1.646(8)	ED [C_1] ref 71
ClNCO	1.226(5)	1.162(5)	170.9(5)	118.8(5)	1.705(5)	MW r_s ref 72

[a] Electron diffraction data put this angle at 173.3°.[73] [b] Angle is assumed to 180°. [c] Fixed.

TABLE 5: Bond Distances (Å), Bond Angles (Degrees), Dipole Moments (D), and Transition Energy (cm^{-1}) for the $\tilde{A}^1A''$ State of HSiNCO

parameter	B3LYP	MP2(FC)	MP2(Full)	QCISD[a]	MC-SCF
r(H−Si)	1.499	1.481	1.478	1.482	1.534
r(Si−N)	1.710	1.716	1.696	1.697	1.717
r(N−C)	1.202	1.212	1.203	1.194	1.195
r(C−O)	1.169	1.176	1.173	1.165	1.153
∠(H−Si−N)	113.1	115.0	115.5	115.1	114.1
∠(Si−N−C)	156.9	151.1	163.0	165.6	150.8
∠(N−C−O)	177.8	176.9	178.0	178.5	177.3
μ_x	−1.70	−1.65	−1.70	−1.83	−2.03
μ_y	−0.05	−0.14	−0.04	−0.10	0.08
T_0	14485	16342	16355	15313 14659[b]	21700

[a] ZPE correction taken from a QCISD/aug-cc-pVDZ calculation. [b] QCISD(T) value.

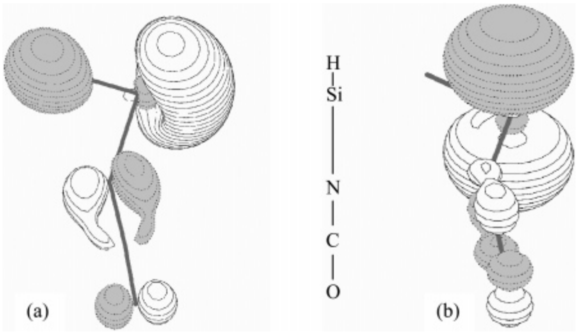


Figure 4. Three-dimensional representations of the HOMO of HSiNCO in the (a) ground electronic state ($^1A'$) and (b) the lowest $^1A''$ electronic state.

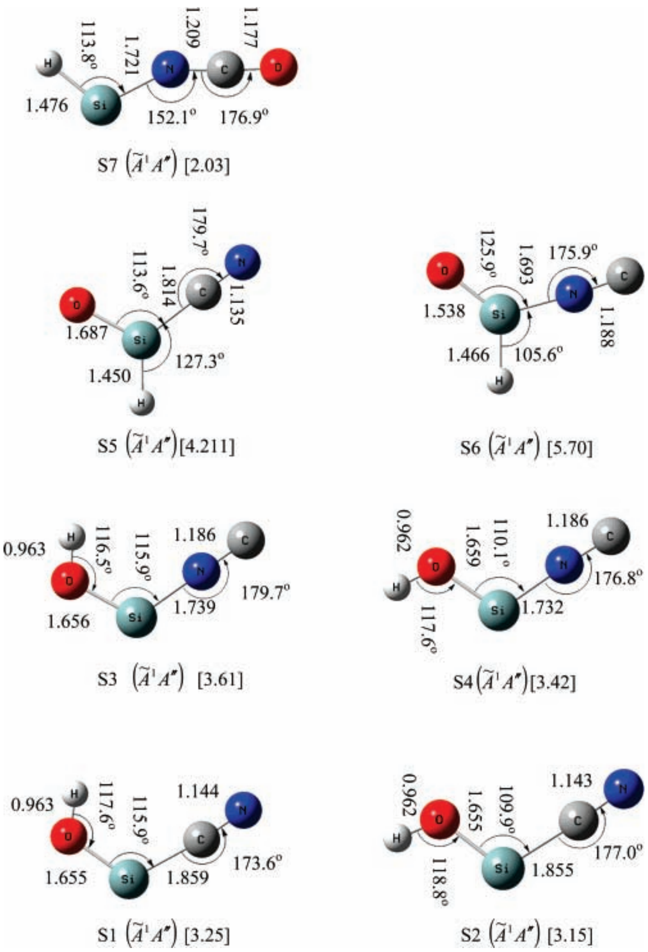
TABLE 6: Enthalpies of Formation (kcal/mol) at 0 and 298 K of the Seven Lowest $^1A'$ Isomers

	$\Delta_f H^0$ [G3MP2]		$\Delta_f H^0$ [G3B3]	
isomer	0 K	298 K	0 K	298 K
cis-HOSiCN	7.84	11.14	6.93	10.26
trans-HOSiCN	8.92	12.18	8.14	11.42
cis-HOSiNC	5.40	8.78	5.35	8.74
trans-HOSiNC	6.64	10.00	6.72	10.08
HSi(O)CN	15.55	18.71	14.53	17.72
HSi(O)NC	15.55	18.79	15.55	18.82
HSiNCO	20.36	23.63	19.28	22.56

($\Delta H_f^0(298K)$ = 149.1 kcal/mol), and $SiCH_2$ ($\Delta H_f^0(298K)$ = 74.6 kcal/mol).[62] Work by Flores has estimated the $\Delta H_f^0(298K)$ of SiCN, SiNC, HSiCN, and HSiNC to be 103.6, 106.3, 85.1, and 87.4 kcal/mol, respectively.[8,63] Of these species, SiC_2, SiC, SiCN, and SiNC have already been observed in the interstellar medium. Overall, if the correct generation technique is employed (i.e., photolysis, pyrolysis, laser ablation, or electric discharge) in conjunction with the right precursor, then the spectroscopic detection of some of the proposed [H, Si, N, C, O] isomers is highly feasible.

Triplet States. Calculations were carried out on the $^3A''$ state of the seven lowest [H, Si, C, N, O] isomers at the MP2 and B3LYP level of theory. The $^3A''$ state was found to be the lowest lying triplet state for each species with the $^3A'$ state being substantially higher in energy. Figure 5 shows the structures of the $^3A''$ state of each isomer and their energies relative to their $^1A'$ isomer as given in Figure 1 at the MP2(FC) level of theory. In all cases the electronic configuration of the triplet species was $14a'^2 15a'^1 3a''^2 4a''^1$. Both the MP2(FC) and B3LYP calculations gave very similar structures and relative energies. At the MP2(FC) level of theory the isomers T1−T5 (see Figure 5) had one imaginary frequency (the out-of-plane Si−H wag), which mostly likely indicates that these are transition state structures. At this level of theory isomers T6 and T7 did not give any imaginary vibrational frequencies. However, at the B3LYP level of theory isomer T6 had one imaginary frequency (the out-of-plane Si−H wag). The nature of these transition states needs to be further explored. The inclusion of core electrons [MP2(Full)] results in a slight contraction of all bond lengths and only small shifts in the bond angles from the MP2(FC) calculations. The biggest differences were seen for the T7 isomer (HSiNCO) where the inclusion of the core electrons caused the Si−N−C angle to increase from 152.1° to 166.6° with the Si−N bond length decreasing from 1.721 to 1.701 Å. The predicted transition frequencies were very similar to those found with MP2(FC).

It has been found that the lowest energy electronic excited state of simple polyatomic inorganic anions is a triplet state.[64,65] For inorganic species, the cyanate ion (CNO^-) exhibits distinct phosphorescence at ∼415 nm. The vibrational structure observed with this phosphorescence indicates that it originates with the NCO^- ion. Work by Rabalais et al. showed that the organic isocyanates CH_3NCO, C_6H_5NCO, and CH_3CH_2NCO also exhibit phosphorescence spectra.[64,65] For these species the phosphorescence spectra resulted from a $^3A'-^1A'$ transition. For HSiNCO the frequency for the $^3A''-^1A'$ transition at the MP2-



S7 $(\tilde{A}^1A'')$ [2.03]

S5 $(\tilde{A}^1A'')$[4.211]

S6 $(\tilde{A}^1A'')$ [5.70]

S3 $(\tilde{A}^1A'')$ [3.61]

S4$(\tilde{A}^1A'')$[3.42]

S1 $(\tilde{A}^1A'')$ [3.25]

S2 $(\tilde{A}^1A'')$ [3.15]

Figure 5. MP2(FC)/aug-cc-pVTZ optimized geometries of the lowest $^3A''$ electronic states of the seven main [H, Si, C, N, O] isomers (bond lengths in Å; bond angles in degrees). All energies (eV) are relative to their corresponding $^1A'$ isomers as in Figure 1.

(FC) level of theory is ∼11 000 cm^{-1}, and the frequency for $^3A'$–$^1A'$ transitions is ∼40 000 cm^{-1}. It is of interest to see whether the HSiNCO species follows the same trend as the alkyl isocyanates and phosphoresces. Work is currently underway to investigate this process.

Conclusion

In this work we have looked at a number of [H, Si, N, C, O] isomers in different electronic states. This is the first ever study on these species. We have shown that the identity of the lowest energy isomer in the ground electronic state is strongly dependent on the level of theory used. In brief, the B3LYP and QCISD(T) methods give the *cis*-HOSiNC isomer as being the lowest energy isomer, and the MP2(FC) and MP2(Full) methods give the *cis*-HOSiCN isomer as being the lowest. The corresponding *trans* isomers are situated ∼1.0 kcal/mol above their *cis* analogues. Overall, the lowest four isomers are situated within approximately 6.0 kcal/mol of one another. Three other isomers were predicted to be between 6.0 and 15.0 kcal/mol above the lowest energy isomer. We have found that the inclusion of core electrons does have a significant impact on the structure and relative energies of the isomers studied. One of main reasons for this paper was to collect data to aid in the detection of these species spectroscopically. To do this, we have calculated vibrational frequencies and equilibrium rotational constants of the seven lowest isomers in their ground electronic state. For each of these isomers we have also determined the structure and transition energy of the first $^1A''$ electronic state. For all but the HSiNCO isomer, vibrational analysis indicates the first $^1A''$ excited state of the isomers is in fact a transition state. We have also determined the enthalpy of formation of the seven lowest isomers using the G3B3 and G3MP2 multilevel methods and have found that, for the most part, the species are relatively thermodynamically stable with the enthalpies of formation comparable to that of silane and disilane. Finally, we have looked at the lowest lying triplet state ($^3A''$) of the seven main isomers. Vibrational analysis has shown that for all but HSiNCO the optimized structure is most likely a transition state. It is thought the isomers investigated in this work should be observable in their ground electronic state using spectroscopic techniques, in particular, microwave spectroscopy. Given that these species are fairly thermodynamically stable, it is reasonable to assume that the species studied in this work may also be present in the interstellar medium.

Acknowledgment. We thank the EPSRC National Service for Computational Chemistry Software for the time on the Magellan computer cluster.

Supporting Information Available: Raw energies of the isomers studied at the B3LYP, MP2, QCISD, QCISD(T), MCSCF, G3MP2, and G3B3 levels of theory. Vibrational frequencies and mode descriptions for the seven lowest lying isomers at the B3LYP and MP2 levels of theory in the $^1A'$, $^1A''$, and $^3A''$ electronic states. Raw data from the isomerization analysis. Structures of all the isomers studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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