J. Am. Chem. Soc. **1995,** *117,* 7263−7264 7263

Triple Bonds to Silicon. Relative Stabilities and Energy Barriers Separating Silanitriles and Silaisonitriles. An *ab Initio* Study

Yitzhak Apeloig* and Karsten Albrecht

Department of Chemistry
Technion—Israel Institute of Technology
Haifa 32000, Israel

Received February 8, 1995

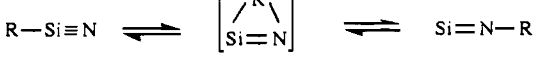
Stable compounds with a double bond to silicon were first synthesized in 1981, and since then they have been studied extensively both experimentally[1a−c] and theoretically.[1d] In contrast, *stable* species with a triply-bonded silicon are still unknown, and only three transient species, HNSi,[2] HSiN,[3] and PhNSi,[4] have been characterized spectroscopically. Of these species only $HSi{\equiv}N$ possesses a formal triple bond while the isomeric silaisonitriles, $HN{=}Si$ and $PhN{=}Si$, can be regarded as having a formal N=Si double bond (i.e., $R{-}N{=}Si{:} \leftrightarrow R{-}N^{+}{\equiv}Si^{-}$). A major difficulty in synthesizing compounds with $Si{\equiv}X$ triple bonds results from the fact that "conventional" triply-bonded isomers (e.g., $HSi{\equiv}SiH$) are generally thermodynamically less stable than isomers having a lower bond order to silicon (e.g., $H_2Si{=}Si{:}$).[1c,d] Similarly, $HSi{\equiv}N$,[2a,5] $H_3CSi{\equiv}N$,[6] and $PhSi{\equiv}N$[6] were calculated to be substantially (i.e., by ca. 55−65 kcal/mol) less stable than the corresponding silaisonitriles. In agreement, early attempts to prepare $HSi{\equiv}N$[2] and $PhSi{\equiv}N$[4] produced instead $HN{=}Si$ and $PhN{=}Si$, which were characterized in argon matrix[2b,4] and in the gas phase.[2a] Only very recently, despite the unfavorable thermodynamics and the low calculated barrier to isomerization, $HSi{\equiv}N$ was characterized at 10 K.[3] In contrast, nitriles are generally more stable than isonitriles, and as the barriers to isomerization are relatively high, both $RC{\equiv}N$ and $RN{=}C$ can be isolated for a variety of R substituents.[7]

Can other silanitriles be prepared and isolated? One possibility to proceed is to design systems where $RSi{\equiv}N$ is more stable than the isomeric $RN{=}Si$ and where relatively large barriers separate the two isomers. To find such systems we have studied, using high-level *ab initio* molecular orbital theory,[8] the effect of various substituents, R, on the relative stability of $RSi{\equiv}N$ and $RN{=}Si$ isomers and on the transition states connecting them (eq 1). On the basis of these calculations, we suggest silanitriles, which are thermodynamically more stable and separated by a significant barrier from the corresponding silaisonitriles, *making both $RSi{\equiv}N$ and $RN{=}Si$ experimentally accessible.*

Table 1. Relative Energies (kcal/mol) of $RN{=}Si$ (Taken as Zero) and $RSi{\equiv}N$ Isomers

R	ΔE^{a}	R	ΔE^{a}
H	52.2 (64.4;[b] 64.2;[c] 59.8;[d] 65.2[e])	NH_2	10.5
Li	39.3	PH_2	43.7
BeH	68.9	OH	−13.2 (−1.8;[b] −3.3;[c] −11.4;[d] −6.5[e])
BH_2	76.2	SH	21.8
CH_3	42.0 (51.5;[b] 49.6;[c] 48.6[d])	F	−34.1 (−31.1;[b] −22.6;[c] −35.5;[d] −26.6[e])
SiH_3	61.2	Cl	−0.5 (8.2;[b] 9.4;[c] −0.4[d])

[a] At MP4/6-311+G**//MP2(fu))/6-31G* (including ZPE). For values in parentheses, see footnotes *b*−*e*. [b] G2. [c] QCISD(T)/6-311G**//QCISD/6-31G*. [d] CASSCF//6-31G*. [e] QCISD(T)/6-311G(2df,p)//QCISD/6-31G*.



(1)

R = H, Li, BeH, BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F, Cl

The geometries of the $RSi{\equiv}N$ and $RN{=}Si$ isomers in eq 1 were fully optimized at MP2(fu)/6-31G*,[9] QCISD/6-31G*,[10] and CASSCF/6-31G*.[11] Comparison of the calculated and experimental stretching frequencies for $HSi{\equiv}N$[3] and $HN{=}Si$[2b] shows that the QCISD/6-31G* and CASSCF/6-31G* frequencies are in reasonable agreement with the experiment whereas the MP2(fu)/6-31G* frequencies are too low.[12] The failure of MP2(fu)/6-31G* is especially apparent for $HSi{\equiv}N$, where the calculated $\nu(Si{-}N)$ of 936 cm^{-1} is even smaller than in $HN{=}SiH_2$ (1038 cm^{-1}), suggesting in $HSi{\equiv}N$ a bond order smaller than 2. Consequently, we assume that energies calculated using QCISD/6-31G* or CASSCF/6-31G* geometries are more reliable than those which use MP2(fu)/6-31G* geometries. Similar conclusions were reached previously for the isoelectronic RCN−RNC system.[13]

The calculated RSiN−RNSi energy differences, ΔE, are strongly dependent on R (Table 1). For most substituents, i.e., R = H, Li, BeH, BH_2, CH_3, SiH_3, PH_2, and SH, ΔE is positive and the silaisonitriles, $RN{=}Si$, are more stable (at MP4/6-311+G**//MP2(fu)/6-31G*, CASSCF//6-31G*, QCISD(T)/6-311G**//QCISD/6-31G*, QCISD(T)/6-311G(2df,p)//QCISD/6-31G*, and G2[13]) than the isomeric silanitriles by 22−76 kcal/mol. For R = NH_2 and Cl, ΔE is significantly smaller (10.5 and −0.5 kcal/mol, respectively). ΔE is in general remarkably smaller for the first-row substituents than for the corresponding second-row substituents, e.g., ΔE for R = CH_3 vs SiH_3, NH_2 vs PH_2, OH vs SH (Table 1). On the other hand, ΔE is negative for R = F and OH. *$FSi{\equiv}N$ and $HOSi{\equiv}N$ are more stable than the corresponding silaisonitriles, $FN{=}Si$ and $HON{=}Si$,* by 26.6 and 6.5 kcal/mol, respectively (QCISD(T)/6-311G(2df,p)//QCISD/6-31G*, Table 1).

---

(1) (a) Patai, S., Pappoport, Z., Eds. *The Chemistry of Organic Silicon Compounds*; John Wiley & Sons: Chichester, **1989**. (b) Raabe, G.; Michl, J. In ref 1a, pp 1015−1142. (c) West, R. *Angew. Chem.* **1987**, *99*, 1231−1241; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201−1211. (d) Apeloig, Y. In fre 1a, pp 57−225.

(2) (a) Goldberg, N.; Iraqi, M.; Hrusak, J.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, 267−270. (b) Ogilvie, J. F.; Cradock, S. *J. Chem. Soc., Chem. Commun.* **1966**, 364−365.

(3) Maier, G.; Glatthaar, J. *Angew. Chem.* **1994**, *106*, 486−488; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 473−475.

(4) (a) Radziszewski, J. G.; Littmann, D.; Balaji, V.; Fabry, L.; Gross, G.; Michl, J. *Organometallics* **1993**, *12*, 4816−4824. (b) Bock, H.; Dammel, R. *Angew. Chem.* **1985**, *97*, 128−129; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 111−112.

(5) Preuss, R.; Buenker, R. J.; Peyerimhoff, S. D. *J. Mol. Struct.* **1978**, *49*, 171−179.

(6) Samy El-Shall, M. *Chem. Phys. Lett.* **1989**, *159*, 21−26.

(7) Rüchardt, C.; Meier, M.; Haaf, K.; Pakusch, J.; Wolber, E. K. A.; Müller, B. *Angew. Chem.* **1991**, *103*, 907−916; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 893−901.

(8) All calculations were carried out using the Gaussian 92 package of programs: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Goperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*, Revision C; Gaussian Inc.: Pittsburgh, 1992.

(9) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281−289.

(10) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968−5975.

(11) Eade, R. H. E.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362−368.

(12) Experimental and calculated $\nu(Si{-}N)$ for HSiN: 1161 cm^{-1} (exptl), 936 cm^{-1} (MP2(fu)/6-31G* corrected by a factor of 0.9427), 1126 cm^{-1} (CASSCF/6-31G*), 1178 cm^{-1} (QCISD/6-31G*). For HNSi: 1198 cm^{-1} (exptl), 1115 cm^{-1} (MP2(fu)/6-31G* corrected by a factor of 0.9427), 1222 cm^{-1} (CASSCF/6-31G*), 1221 cm^{-1} (QCISD/6-31G*).

(13) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221−7230.

0002-7863/95/1517-7263$09.00/0

Table 2. Calculated Barriers (kcal/mol) for the RSi≡N ⇌ RN=Si Isomerization[a]

	RSiN → RNSi				RNSi → RSiN			
R	MP4[b]	G2	QCISD[c]	CASSCF[d]	MP4[b]	G2	QCISD[c]	CASSCF[d]
H	**32.9**	**8.3**	**11.9 (11.4)**	**19.0**	85.1	73.3	76.1 (76.6)	78.9
CH_3	**34.7**	**13.6**	**18.7**	**27.8**	76.6	65.1	68.3	76.4
OH	55.3	37.5	34.2 (35.8)	45.3	**42.1**	**35.7**	**31.1 (29.4)**	**33.8**
F	54.7	46.2	44.3 (49.3)	64.8	**20.6**	**18.5**	**21.8 (22.7)**	**29.3**
Cl	56.5	**19.4**	**26.3**	36.5	**56.0**	27.6	35.7	**36.1**

R	RSiN → RNSi[b]	RNSi → RSiN[b]	R	RSiN → RNSi[b]	RNSi → RSiN[b]
Li	**1.8**	41.1	BeH	**13.2**	82.1
BH_2	**17.3**	93.5	SiH_3	**21.1**	82.3
NH_2	**47.5**	58.0	PH_2	**27.5**	71.2
SH	**42.1**	63.9			

[a] The lower barrier in each case is given in boldface. [b] MP4/6-311+G**//MP2(fu)/6-31G* (including ZPE). [c] QCISD(T)/6-311G**//QCISD/6-31G*, in parentheses QCISD(T)/6-311G(2df,p)//6-31G*. [d] CASSCF//6-31G*.

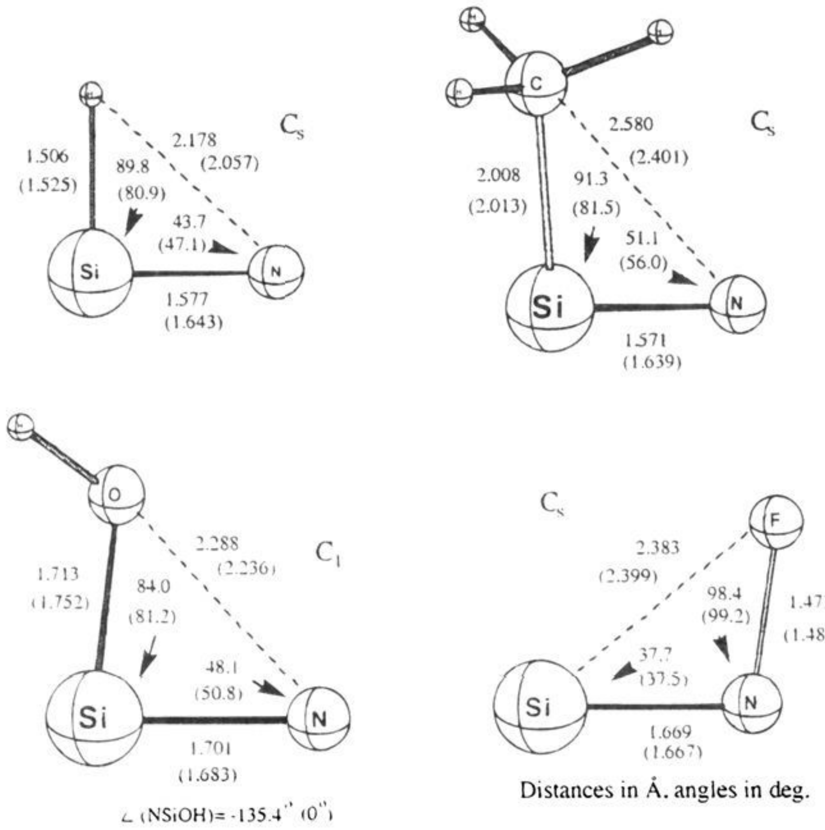


Figure 1. Optimized geometries of MP2(fu)/6-31G* (QCISD/6-31G* values in parentheses) of the transition structures for the RSi≡N ⇌ RN=Si isomerization, for R = H, CH_3, OH, and F.

The effect of R on ΔE can be understood in terms of the R−Si vs R−N bond energies. In general, elements which are more electropositive than Si increase the RSi≡N vs RN=Si energy differences (relative to R = H), while more electronegative elements decrease the gap; ΔE is negative for R = OH and F, where the very strong Si−O and Si−F bond energies (dissociation energies: Si−O, 129 kcal/mol; Si−F, 152 kcal/mol; N−O, 48 kcal/mol; N−F, 68 kcal/mol)[14] override the large (ca. 60−64 kcal/mol) intrinsic preference of HNSi over HSiN.

The transition structures (TS) for the RSiN → RNSi isomerization were determined at the MP2(fu)/6-31G*, CASSCF/6-31G*, and QCISD/6-31G* levels of theory, and four representative cases are shown in Figure 1. For most substituents, i.e., for R = H, Li, BeH, BH_2, CH_3, NH_2, PH_2, SH, OH, and Cl, the TS occurs relatively "early" with respect to RSi≡N along the reaction coordinate. For example, in the TS for the migration of R = H, CH_3, and OH, r(Si··R) = 1.525, 2.013, and 1.752 Å, respectively, compared to r(Si−R) of 1.493, 1.890, and 1.648 Å in the corresponding RSiN (at QCISD/6-31G*). In contrast, for R = F the TS is relatively "late" (Figure 1) with a well-advanced N−F bond of 1.480 Å (compared to 1.346 Å in FNSi) and a long Si··F distance of 2.399 Å (1.603 Å in FSiN).

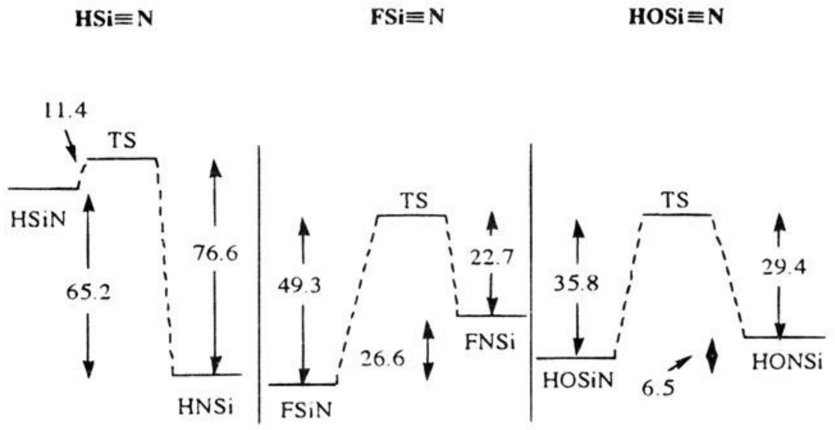


Figure 2. Schematic reaction diagram at QCISD(T)/6-311G(2df,p)//QCISD/6-31G* for the isomerization of HSiN, FSiN, and HOSiN to the corresponding silaisonitriles. Calculated energies are given in kcal/mol.

The calculated isomerization barriers (Table 2) are strongly dependent on the computational level, but in analogy to the minima, we assume that the most reliable barriers are obtained at QCISD(T)/6-311G(2df,p)//QCISD/6-31G*. The activation energy for the RSiN → RNSi isomerization is relatively small for R = H (11.4 kcal/mol), as expected from the Hammond hypothesis for a highly exothermic reaction. For R = F and OH the barrier heights (RNSi → RSiN) are larger, i.e., 22.7 and 29.4 kcal/mol, respectively, suggesting that these rearrangements will be slow even at ambient temperatures (Figure 2). FSi≡N and HOSi≡N are therefore excellent candidates for synthesis, identification, and characterization, and we hope that this study will prompt experimental investigations aimed at this goal.

Acknowledgment. This research was supported by the United States−Israel Binational Science Foundation and the Fund for the Promotion of Research at the Technion. Y.A. acknowledges a Lisa Meitner−Alexander von Humboldt Research Award, and K. A. is grateful to the Minerva Foundation for a postdoctoral scholarship.

Supporting Information Available: MP2(fu)/6-31G* optimized geometries of RSiN and RNSi with R = H, Li, BeH, BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F, Cl and of the transition structures connecting them, data at HF/6-31G*, QCISD/6-31G*, and CASSCF/6-31G* for R = H, CH_3, F, Cl, OH, total energies of all species at MP2(fu)/6-31G* and MP4/6-311+G**//MP2(fu)/6-31G* and for R = H, CH_3, F, Cl, OH also at QCISD(T)/6-311G**//QCISD/6-31G*, G2, and CASSCF//6-31G*, and vibrational spectra of HSiN, HNSi, FSiN, FNSi, HOSiN, and HONSi at MP2(fu)/6-31G*, CASSCF/6-31G*, and QCISD/6-31G* (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9504202

---

[14] (a) Walsh, R. in ref 1a, pp 371−391. (b) Dasent, W. E. *Inorganic Energetics*; Penguin: Harmondsworth, England, 1970.