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Structures and Energetics of Si$_3$N$_2$ Clusters

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Aglomerados mistos de silício e nitrogênio com fórmula Si$_3$N$_2$ foram investigados teoricamente com os métodos SCF e MP2. Dos onze pontos estacionários encontrados abaixo de 80 kcal/mol, oito correspondem a mínimos locais (ML); desses, cinco são estados singletos. Quanto aos tripletos, três ML e um estado de transição (ET) foram caracterizados. O mínimo global corresponde a uma estrutura angular com ligações alternadas silício-nitrogênio, que contrasta com as estruturas lineares de outros aglomerados menores de Si/N. Uma estrutura bipiramidal mais alta em energia 41.0 kcal/mol pode ser vista como um padrão natural para um crescimento tridimensional. Em geral, estruturas com mais ligações SiN são preferidas energeticamente em relação àquelas em que as ligações SiSi predominam. Tentativas para se localizar ET que se correlacionam com os canais de dissociação mais baixos não tiveram sucesso devido à complexa e computacionalmente difícil busca. Apesar disso, garante-se a estabilidade termodinâmica das estruturas I, III, IV e V, sendo a energia do canal mais baixo um limite inferior. A energia de atomização da estrutura do mínimo global é de 420.6 kcal/mol (MP2).

Mixed clusters of silicon and nitrogen with formula Si$_3$N$_2$ have been investigated at both SCF and MP2 levels of theory. Of eleven stationary points found below 80 kcal/mol, eight correspond to local minima (LM); of these, five are singlet states. Of the triplets, three LM and one transition state (TS) were characterized. The global minimum corresponds to an angular structure with alternating silicon-nitrogen bonds, in contrast with linear ones for other smaller Si/N clusters. A bipyramidal structure 41.0 kcal/mol high in energy can be seen as a natural pattern for tridimensional growing. In general, structures with more SiN bonds are energetically preferred to those in which the SiSi bonds predominate. Attempts to locate TS correlating with the lowest dissociation channels have been unsuccessful due the complex and computationally demanding search. Despite this fact, the thermodynamic stability for structures **I**, **III**, **IV**, and **V** is guaranteed, being the energy of the lowest channel a lower bound. The atomization energy for the global minimum structure amounts to 420.6 kcal/mol (MP2).

Keywords: silicon nitrides, structure, IR spectra, stability

Introduction

The study of clusters of silicon, and of silicon with other elements has received a great deal of attention recently[1-5]. The development of techniques such as chemical vapor deposition has greatly stimulated the investigation of these new compounds[6]. Other techniques such as neutralization-reionization mass spectrometry has also played a significant role in identifying these species[7,8]. Considering the technological importance of these materials, the understanding of the chemical processes that occur in their preparation would certainly be very much welcome. In this respect, the experience accumulated to date on the structures and energetics of a series of binary species of increasing complexity could also be of great help in formulating models for the reactions occurring in these processes.

In the case of high-performance ceramics, films of silicon nitride (Si$_3$N$_4$) are of great interest as high-temperature materials. The good thermal and mechanical resistance of these substances is due to the highly covalent nature of the Si-N bonds. Their high thermal stability, good resistance to thermal shock and to oxidation enable the use of these materials in high-temperature engines, such as ceramic gas turbine engine and automotive engine components, for example. Another important application of Si$_3$N$_4$ films is in the electronic industry, as an electrical insulator[9].

Three methods are usually employed industrially for the preparation of films of Si$_3$N$_4$: direct nitridation of elemental silicon, carbothermal reduction of silicon dioxide under a nitrogen or ammonia atmosphere, and the ammonolyses of SiCl$_4$ or SiH$_4$[10,11]. Understanding the mechanisms of the reactions involved in these methods is of great importance to allow the control and the optimization of the chemical and physical processes. The control of the deposition rate is

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essential to have a material with high quality, that is, with a very uniform film deposited and a well-defined composition.

The study of mixed clusters of silicon and nitrogen is an area not very much explored theoretically. A knowledge of the stability and the structural properties of the various possible species is certainly an important step that can help determine the composition and the possible reactions that occur in gas phase and that leads to the formation of Si_3N_4. The small number of studies so far contrasts sharply with those already carried out for clusters of silicon[12-14], and silicon with carbon[15-18].

Concerning the compounds of silicon and nitrogen, the simplest species SiN was investigated experimentally by Ito *et al.*[19], Elhanine *et al.*[20], and Naulin *et al.*[21], and by theoretical *ab initio* methods by Bruna *et al.*[22], Chong[23], Cai *et al.*[24], and Borin[25]. The triatomic molecule SiNN was first observed experimentally by Lembke *et al.*[26] with the technique of electron spin resonance (ESR); in this experiment the SiNN molecules were trapped in neon, argon and nitrogen matrices. On the basis of the neon matrix spectra, they proposed a linear structure ($^3\Sigma^-$) for this species. Theoretical studies were carried out using conventional approaches[27] like HF, CISD and CASSCF, and the main conclusion from these studies was that SiNN is a van der Waals type molecule, with a weak interaction between the silicon atom and the nitrogen molecule in a linear arrangement. The disagreement between these results and experimental studies motivated the use of more sophisticated methodologies like coupled cluster with single and double excitations (CCSD), and with a quasi-perturbative estimate of the contributions of connected triple excitations (CCSD(T))[28], and multi-reference configuration interaction (MRCI)[29], and also of the density functional theory (DFT)[30-32]. These approaches predicted the existence of a tight structure, with a better agreement of the theoretical harmonic frequencies with experiment, being the best result the one obtained with the coupled cluster methodology. In our investigation of this system[33], we have performed a high-level calculation with the CCSD(T) method and an extended basis set (cc-pVQZ). One of our main conclusions was that the values of the experimental frequencies were probably wrongly interpreted, possibly because of interactions between the molecule and the matrix. We have also shown that the agreement between the other theoretical studies and the "experimental" frequencies was fortuitous.

The first experimental evidence about the existence of the triatomic species Si_2N was presented by Iraqi *et al.*[7] using the technique of neutralization-reionization mass spectrometry. A tentative hypothesis that its most stable form would probably show a cyclic geometry was also proposed. The first theoretical calculation of geometries and frequencies of some possible Si_2N structures was carried out by Goldberg *et al.*[8] at the HF and MP2 levels of theory, with the 6-311+G* basis set. A more complete study was reported by Ornellas and Iwata[34], where various isomers were analyzed using different levels of theories (HF, MP2, MP4 and CSD(T)), and basis set (DZP, cc-pVTZ-f and cc-pVTZ). In that work, three thermodynamically stable isomers were found, with the global minimum corresponding to a symmetric linear structure (SiNSi). To explain the theoretical prediction of the infrared spectra of the most stable structure, the Renner-Teller effect was invoked, and an estimate of the Renner parameter was made.

The molecule Si_3N was studied for the first time by Goldberg *et alli*[8]. Collisional-activation and neutralization-reionization mass spectrometry, and theoretical methods were used to describe the neutral, cationic and anionic Si_3N. The methodologies used to optimize the geometries were restricted to the HF and MP2 levels of theory with the 6-311+G* basis set. In a recent work, Gingerich *et al.*[35] have determined the thermal parameters of Si_3N using Knudsen effusion mass spectrometry.

The silicon analog of cyanogen, the species Si_2N_2, is also experimentally unknown. This molecule was extensively studied theoretically in our group where various stationary points were analyzed with increasing levels of correlation treatment (HF, MP2, MP4 and CSD(T))[36]. The existence of thermodynamically stable isomers was predicted, with the global minimum corresponding to a linear symmetric SiNNSi structure. A comparison of the effects of each methodology on the determination of the geometric parameters, vibrational frequencies, and relative energies was also carried out in that study.

This work reports a further step in our investigation of mixed compounds of silicon and nitrogen. Here, we have extended this series of investigations of silicon and nitrogen compounds to a larger cluster of molecular formula Si_3N_2, yet unknown experimentally, and characterized the properties of possible structures for the first time. Together with the results of our previous studies, we expect that besides the set of structural and energetic data about the various new species it can also provide insights on the processes of formation and growing of silicon-nitrogen clusters. In the long run, after further investigations of still larger members of this series, we also hope to develop a model of the interaction between a nitrogen atom or molecule with a silicon surface or cluster, and therefore contribute to the formulation and understanding of the mechanisms of formation of Si_3N_4 films. Besides, it is also our hope that the present results can motivate the experimental identification of these new compounds in interstellar space, as well as in the laboratory.

Methodology

Various structures with molecular formula Si$_3$N$_2$ were first analyzed at the Hartree-Fock (HF) level using the restricted formalism (RHF) for closed shell species and the unrestricted (UHF) one for open shell systems. Geometrical parameters and vibrational frequencies, within the harmonic oscillator approximation, were also determined. The values of these frequencies allowed the assignment of the nature of the stationary points determined in the geometry optimization step, that is, to know if they corresponded to minima, transition states or a higher order saddle points in the potential energy surface. The importance of correlation effects on the structures, relative stability, and frequencies was investigated at the second-order Møller-Plesset perturbation (MP2) level of theory, with the core electrons being frozen in all calculations. Molecular orbitals (MO) were constructed using McLean and Chandler's[37] (13s,9p) set of primitive Gaussians contracted to [6s,5p], and augmented with two sets of d-type polarization functions with exponents 0.553 and 0.158 for silicon, and the 6-311G(d) (α_d=0.913) set of Krishnan $et\ al.$[38] for nitrogen. This basis set can be symbolized as (13s,9p,2d)/[6s,5p,2d] for silicon and (11s,5p,1d)/[4s,3p,1d] for nitrogen, corresponding to a total of 137 contracted Gaussians functions for Si$_3$N$_2$. Concerning the UHF wavefunction, it is worth-recalling that it does not describe a pure spin state and usually contains contributions from higher multiplicities. The amount of spin contamination can be usually inferred from the expectation value of the operator $\hat{S}^2$, $<\hat{S}^2>$. Also, by including a certain amount of static correlation, the UHF energy is generally lower than its ROHF counterpart. At the MP2 level, since a large part of the electron correlation is recovered, the net effect of an unrestricted MP2 (UMP2) calculation is an increase in the energy due to spin contamination[39]. All calculations reported in this work were performed with the Gaussian-94 package[40].

Results and Discussion

Structures and energetics of Si$_3$N$_2$ species

Initially, using the HF methodology, the potential energy surface of several atomic arrangements with linear, planar and three-dimensional geometries was analyzed in the search of stationary points. Many of these possibilities represent very unstable species and are located very high energetically. The set of the most representative structures investigated are shown in Figures 1 and 2, which also contain the relative energies between the stationary points, the geometrical parameters at the SCF and MP2 levels, and the energy of the most stable structure determined with both methodologies. In Table 1 are presented the infrared frequencies calculated in the harmonic approximation at both SCF and MP2 levels of theory.

For the discussion that follows, it is convenient to establish a relative standard to which we can refer when discussing the types of bonds involved in the various structures. In this work, we will be using the bond distance between atoms in well-known compounds as a standard to infer the single, double, or triple character of the bonds. In the case of bonds between two silicon atoms, we have disilane as a reference for a standard single bond (2.34 Å)[41], and Si$_2$ for a double (2.25 Å)[42]. Between silicon and nitrogen, H$_3$Si-NH$_2$ illustrates a typical single bond (1.72 Å)[43,44] and H$_2$Si=NH is a model for a double bond (1.58 Å)[45]; finally, between two nitrogens, N$_2$ is a standard for a triple bond (1.098 Å)[46], diazene HN=NH for a double bond (1.252 Å)[47-49], and H$_2$N-NH$_2$ for a single bond (1.414 Å)[50].

The isomer with the lowest energy corresponds to structure **I** in Figure 1; it is predicted to be the global minimum with both methodologies, as can be seen by the positive definiteness of the frequencies values in Table 1. This structure shows only silicon-nitrogen bonds, with the Si-N central distances typical of a single bond, while the terminal ones are comparable to double bonds. As one can see in Figure 1, the difference between the SCF and MP2 geometrical parameters is small, with the bonds lengths increasing by about 0.04 Å in going from SCF to MP2. It is interesting to point out that a Mulliken population analysis predicts a relatively ionic structure with the nitrogen atoms negatively charged with one unit of charge each, and compensating for this relatively large charge, the central and the terminal silicon atoms acquire a positive charge of about 0.8 and 0.6 units of charge, respectively. Despite the positive definiteness of all frequencies, we note that the small values of 59 (a$_1$) and 94 (b$_2$) cm^{-1} for ω_1 and ω_2, respectively, imply the existence of very shallow potential wells, which could certainly lead to molecular rearrangement or dissociation if enough energy is concentrated on these modes. This species is most likely to be found at low temperatures, trapped in matrices; its most intense (708 km/mol) infrared absorption line calculated at the MP2 level occurs at 1285 cm^{-1} (antisymmetric SiN stretching).

Close to isomer **I**, we have found another planar structure (^{1}A$_1$, **II**) that is to be associated with a transition state at both SCF and MP2 levels of theory. This structure is located at 16.61 kcal/mol (MP2) above **I**, and exhibits a relatively long SiN bond length (2.00 Å), and a standard SiN single bond (1.72 Å). An analysis of the normal modes shows that the frequency values of 416, 867 and 992 cm^{-1} can be neatly
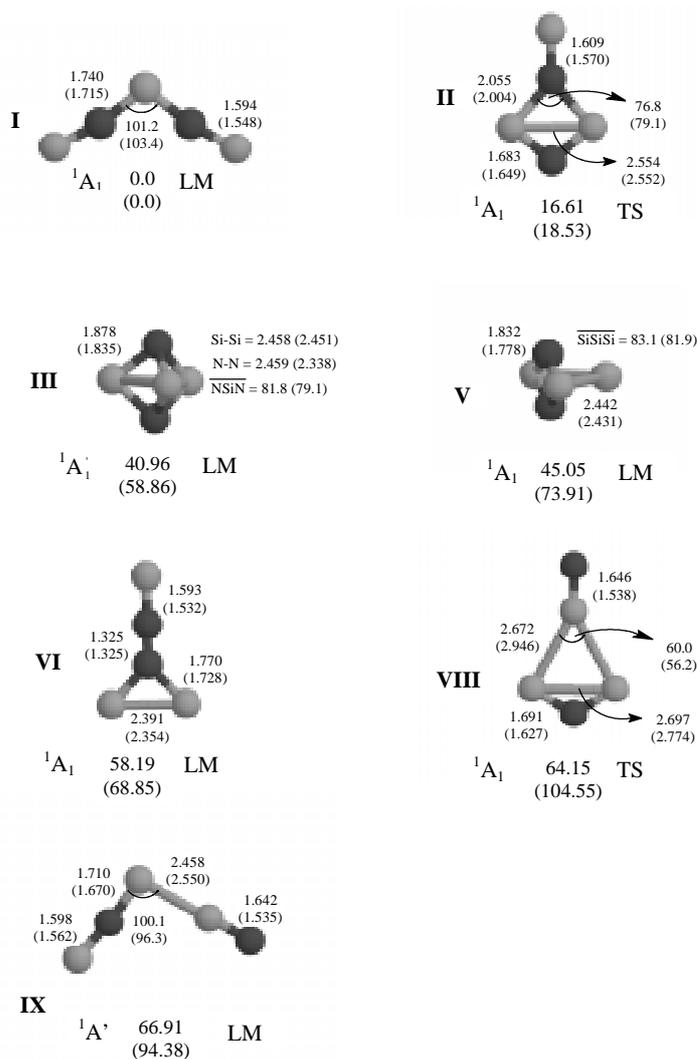
Figure 1. Theoretical stationary points geometries (Å, degrees) and relative energies (kcal/mol) for singlet states of species with formula Si_3N_2. The numbers in parentheses refer to SCF values. E(MP2) = -976.342604 a.v.; E(SCF) = -975.744471 a.v.
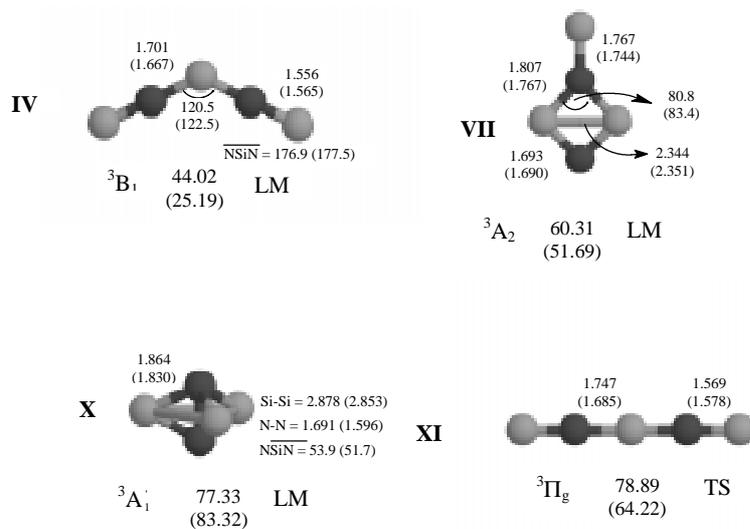
Figure 2. Theoretical stationary points geometries (Å, degrees) and relative energies (kcal/mol) for triplet states of species with formula Si_3N_2. The numbers in parentheses refer to SCF values.

Table 1. Calculated harmonic vibrational frequencies (in cm^{-1}) and $\langle\hat{S}^2\rangle$ values for various clusters of Si$_3$N$_2$ at the MP2 and SCF (in parentheses) levels of theory.

Structure		$\langle\hat{S}^2\rangle$	ω_1		ω_2		ω_3		ω_4		ω_5		ω_6		ω_7		ω_8		ω_9		ω_{10}	
I	($^1A_1$)	0.00	59 (73)	a_1	94 (155)	b_1	103 (156)	a_2	155 (179)	b_2	323 (378)	a_1	556 (621)	b_2	565 (627)	a_1	1285 (1443)	b_2	1303 (1487)	a_1		
II	($^1A_1$)	0.00	171i (126i)	b_2	74 (131)	b_1	138 (154)	b_2	225 (275)	b_1	298 (344)	a_1	416 (470)	a_1	867 (965)	a_1	992 (1098)	b_2	1152 (1295)	a_1		
III	($^1A'_1$)	0.00	262 (251)	e''	262 (251)	e''	406 (433)	e'	406 (433)	e'	590 (631)	a_1'	592 (707)	a_2''	593 (697)	e'	593 (697)	e'	764 (957)	a_1		
IV	($^3B_2$)	2.16 (2.17)	57 (66)	a_1	151 (164)	b_2	184 (234)	a_2	191 (243)	b_1	326 (347)	a_1	504 (560)	a_1	661 (717)	b_2	1474 (1253)	a_1	1948 (925)	b_2		
V	($^1A_1$)	0.00	255 (280)	a_1	277 (258)	b_2	374 (275)	b_1	481 (546)	a_1	526 (527)	b_2	535 (602)	a_1	703 (689)	a_2	751 (882)	a_1	808 (856)	b_1		
VI	($^1A_1$)	0.00	122 (138)	b_2	151 (179)	b_1	334 (381)	a_1	391 (422)	b_2	425 (468)	b_1	505 (568)	a_1	776 (852)	b_2	942 (1103)	a_1	1426 (1663)	a_1		
VII	($^3A_2$)	2.08 (2.08)	113 (155)	b_1	126 (162)	b_2	259 (317)	b_1	403 (437)	a_1	463 (313i)	b_2	573 (618)	a_1	836 (646)	b_2	993 (1096)	a_1	1037 (864)	a_1		
VIII	($^1A_1$)	0.00	46i (65i)	b_2	62 (36)	b_1	203 (153)	a_1	211 (38)	b_2	222 (217)	b_1	393 (305)	a_1	801 (900)	a_1	961 (1179)	b_2	1137 (1384)	a_1		
IX	($^1A'$)	0.00	59 (45)	a'	96 (41)	a''	170 (140)	a'	225 (170)	a''	301 (219)	a'	502 (358)	a'	613 (650)	a'	968 (1393)	a'	1304 (1453)	a'		
X	($^3A_1'$)	2.04 (2.05)	318 (196i)	e'	318 (196i)	e'	459 (456)	a_2''	480 (541)	a_1'	524 (508)	e''	524 (508)	e''	763 (890)	a_1'	782 (729)	e'	782 (729)	e'		
XI	($^3\Pi_g$)	2.16 (2.21)	727i (890i)	π_u	43 (25)	π_u	52 (63)	π_u	86 (192)	π_g	157 (129)	π_g	289 (375)	σ_g	358 (382)	π_u	530 (486i)	σ_u	1504 (1142)	σ_g	2449 (718)	σ_u

correlated with the SiNSi vibrations, while 1152 cm^{-1} is close to that of the stretching of SiN. An internal reaction coordinate (IRC) evaluation has shown however that structure **II** corresponds to a transition state connecting two equivalents forms of **I**. It is not unlikely that a matrix can bring stabilization to this species, allowing therefore the observation of some of the vibrational frequencies.

Next, **III** is the first three-dimensional structure, and shows a trigonal bipyramidal geometry. At the SCF level, it is found at 58.86 kcal/mol above **I**, and corresponds to the third most stable isomer, whereas at the MP2 level it is second in energy, located at 40.96 kcal/mol above the global minimum **I**. Both methodologies predict it to be a local minimum with practically identical geometries, the largest difference being the distance between the two nitrogens, that increased 0.12 Å in going from SCF (2.34 Å) to MP2 (2.46 Å). The Si-N and Si-Si bonds lengths are about 0.1 Å longer than typical single bonds. This interesting cage-like structure is similar to the geometry of the global minimum of Si_5[12], and in the study of Si_3C_2 isomers, Froudakis *et al.*[51] have also found an analogous structure corresponding to the second most stable isomer.

Structure **IV** corresponds to the lowest lying triplet state ($^3B_1$) and is a local minimum at both SCF and MP2 levels of theory, with a geometry similar to **I**. At the SCF level, it is the second most stable isomer (25.19 kcal/mol), but the MP2 calculation places it higher in energy (44.02 kcal/mol), being now the third isomer in stability. The changes in the geometric parameters are small in going from the SCF to the MP2 approaches. The internal Si-N bonds increased by about 0.03 Å, while the terminal bonds and the angles remained practically unaltered relative to the SCF results. Compared to the singlet structure (**I**), both distances have shrunk by 0.04 Å (MP2). Similarly to **I**, the frequency $\omega_1(a_1)$ turned out to be small, whereas for $\omega_2(b_1)$ and $\omega_3(a_2)$ significant increases of about 100 and 80 cm^{-1} occurred. For this structure, therefore, despite the positive values of the frequencies, multiphoton absorption by the a_1 mode (57 cm^{-1}) is expected to lead to a molecular rearrangement or dissociation. Observation of this species in a matrix is also a possibility open. If this isolation is viable, then the larger value of the $\omega_2(b_2)$ frequency (1948 cm^{-1}) would allow one to differentiate the spectrum of **IV** from that of the singlet analogue **I**. Relative to the first dissociation channel, structure **I** is stable by 54.2 kcal/mol.

As a starting structure leading to the three-dimensional isomer **V**, we have used a silicon atom approaching the two nitrogens in a dibridged structure similar to the low-lying one found in Si_2N_2 by Ornellas and Iwata.[6] At both SCF and MP2 levels of theory, the optimization process showed a convergence of the initial dibridged structure to

a planar one, with a small increase in the Si-N bond, and the formation of a weak Si-Si single bond of the planar silicons with the out of plane one, which is about 0.1 Å greater than a typical single bond. With both methodologies, this structure corresponds to a local minimum, with the MP2 result indicating a much more stable structure than the SCF one. Energetically, structure **V** is only about 4.0 kcal/mol above **III**, and similarly to **III** its frequency values are certainly indicative of a tight structure. Note also that the Si – Si bond distances are about the same in structures **III** and **V**, and in fact they differ only in the shifting of the nitrogen atoms from above the central region of the triangular silicon moiety to the peripheral region. We also note that the energy difference between structures **IV** and **V**, 1.1 kcal/mol, is too small for one to have a definite assignment of the relative energetic position of these two isomers, since basis set extension could reverse this order. However, the two sets of vibrational frequencies are quite distinct and there should be no problem in identifying either species if isolated.

The planar isomer **VI** corresponds also to local minimum structure. It shows the interesting feature of being the first planar structure with a cyclic fragment. The Si-Si and Si-N bonds distances in the ring are of the order of magnitude of typical single bond distances, and the N-N bond length (1.325 Å) lies between that representative of a N-N double bond as in diazene (1.252 Å), and that of a single bond as in hydrazine (1.414 Å); the terminal Si-N bond distance (1.593 Å) is very close to that of a standard Si-N double bond of 1.58 Å as in $H_2Si=NH$. Concerning the relative energies, the MP2 result indicates a structure about 10 kcal/mol more stable than the SCF one, and 58.2 kcal/mol above the global minimum.

Isomer **VII** corresponds to a triplet state ($^3A_2$) and is another representative of a stable cyclic planar structure. At the MP2 level of theory it lies 2.1 kcal/mol higher than **VI**. We note that the relative order of stability of **VI** and **VII** is dependent on the level of calculation, since at the SCF level **VII** corresponds to a lower lying transition state. Here, although the HF calculation is variational, the static correlation present in the UHF wavefunction overstabilizes structure **VII** relative to **VI**. On the other hand, spin contamination causes the UMP2 expansion to converge much more slowly than the RMP2 one. A combination of these factors is certainly responsible for structure **VI** being more stable than **VII** by just 2.1 kcal/mol, a value however too small to definitely set their relative order. Basis set extension and proper account of both static and dynamic correlation might reverse their stabilities. As to its geometry, the Si-Si bond distance in **VII** (2.34 Å) is typical of singly bonded silicons. The Si-N bond distances in the ring are

slightly shorter than typical Si-N single bonds (1.72 Å) for the nitrogen with connectivity two, and slightly longer for the other nitrogen triply connected. It is relevant to point out that we have been unable to locate a stable singlet analogue of **VII**. The closest we could get is structure **II** that turned out to correspond to a transition state.

In the case of structure **VIII**, the stabilization gained in going from SCF to MP2 was very significant. At the SCF level, it is located at 104.55 kcal/mol above the most stable isomer, while with the MP2 approach this difference lowered to 64.15 kcal/mol. However, in both cases this structure corresponds to a transition state, with the optimized geometries corresponding basically to a SiNSi angular group interacting with SiN through the silicons. Notice that when the nitrogen approaches the two silicons as in **II**, a much lower stationary point is located, which however is also associated with a saddle point.

In the case of the asymmetric structure **IX**, the MP2 result is again indicative of a more stable structure than the SCF one; both methodologies predict the existence of a local minimum, being the MP2 result 66.9 kcal/mol high in energy relative to **I**, compared with 94.4 kcal/mol from the SCF result. Notice also that in **IX** the Si-Si bond distance (2.45 Å) is a little bit longer than a standard Si-Si single bond distance (2.34 Å). Similarly to **I**, structure **IX** has a very low (59 cm^{-1}) ω_1(a') frequency which can also lead to molecular rearrangement or dissociation if appropriately excited.

A three-dimensional cage-like structure (**X**) similar to **III** but corresponding to a triplet state was also found; it is much less stable than **III**, with a relative stability of 83.32 and 77.33 kcal/mol at the SCF and MP2 levels, respectively. About the nature of the stationary point, the SCF result implies a second order saddle point, while at the MP2 level it corresponds to a local minimum. Concerning this change, as one shifts form SCF to MP2, it is worth-noting that being the imaginary frequency as well as the other frequencies not so small, this change in stability can only be attributed to a more pronounced dynamic correlation effect recovered by the MP2 calculation. The Si-N distance is about the same as that in **III** and indicative of a single bond. In **X**, one finds a shorter N-N distance (1.69 Å) by about 0.8 Å and a longer Si-Si distance (2.08 Å) by about 0.4 Å relative to **III**, resulting in a more compressed structure when compared with **III**.

Concerning the linear structures, the most stable one (**XI**) involves only SiN bonds, and corresponds to a triplet state. At the SCF level, the stationary state is a second order saddle point, while the MP2 calculation predicts it to be a transition state 78.9 kcal/mol above **I**. No singlets stationary points were found. Various possible linear arrangements have been additionally tested, and, with the exception of

XI, all of them are very unstable, with energies above 100 kcal/mol relative to **I**, and corresponding to first or higher order saddle points.

As one can see from these results, the most stable isomers show a preference to forming structures with the largest possible number of Si-N bonds; the formation of the weaker Si-Si bond is clearly avoided. The fact that structures with Si-Si bonds are less stable than those involving N-N or Si-N bonds was already pointed out in previous work.[34,36] In the case of Si$_2$N, it corresponds to a linear symmetric geometry, and for Si$_2$N$_2$, we have two terminal silicons connected to the nitrogens in a linear symmetric structure. In the case of Si$_3$N$_2$, we have not found any linear isomer with a low energy; the most stable structure corresponds to a planar angular symmetric structure with only Si-N bonds.

Comparisons with Si$_5$ and Si$_3$C$_2$

Concerning the three-dimensional structures, the results for the cage-like isomer **III** have a certain similarity with those for the Si$_3$C$_2$ clusters investigated by Froudakis *et al.*[51] Working at the MP2/DZ2P level of theory, they have also found that the second most stable isomer has a cage-like geometry similar to **III**. For Si$_3$C$_2$, this isomer is only 19.9 kcal/mol higher than the lower energy structure, while in the Si$_3$N$_2$ case the difference is about twice as large. Chemical bonds between the two carbon atoms and between the carbons and silicons are present in Si$_3$C$_2$, with no bonds at all between the silicon atoms. In the case of **III**, the nitrogen atoms are kept very far apart from each other, with the distance between the silicon atoms only a little greater than a typical single bond, and the SiN bonds typical of single bonds. The most stable structure found by Froudakis *et al.* corresponds to a planar pentagon, with one carbon atom adjacent to the other. The stability of this structure was attributed to the greater number of Si-C bonds and the existence of a strong C-C bond, leading to a great stabilization, despite the existence of two Si-Si bonds. In the case of the silicon-nitride isomer **III**, the same rationale can be invoked to justify the stability of this isomer. The search for a similar structure among the Si$_3$N$_2$ isomers resulted in a very unstable species located at more than 110 kcal/mol (SCF) above the global minimum. We also note that **III** is similar to the most stable isomer of Si$_5$. On the basis of previous work[34,36] and also on the evidence discussed above, one can conclude that the number of Si-Si bonds in silicon-nitrogen molecules is a critical factor governing their stability, more than in the silicon-carbon clusters. For the species investigated so far the most stable structures have the least possible number of Si-Si bonds.

Stability trends in the Si_xN_y series and dissociation channels

As already pointed out, for the silicon-nitrogen molecules SiN_2, Si_2N and Si_2N_2 the most stable structure corresponds to a linear geometry. In the case of Si_3N_2, this linear trend is broken and the most stable isomer prefers an angular planar geometry. This behavior is somehow not unexpected because of the preference of silicon to make three-dimensional bonds when compared with carbon. In fact, the tight structure **III,** about 41 kcal/mol above **I**, can certainly be viewed also as a "seed" for three-dimensional growing, especially at high temperatures. Based on this trend, it is very likely that with an increase in the number of silicon atoms, there will be a preference to the generation of three-dimensional structures, as is the case of Si_5.

Energetically next to **III**, structure **V** is also tridimensional, but with the nitrogens symmetrically positioned above the edge of the silicons plane. Attempts to find a transition state correlating **III** and **V** have been fruitless.

Structures **I**, **III**, and **V**, associated with singlet states, are all energetically lower than the first dissociation channel $Si_3(^1A_1) + N_2(^1\Sigma^+)$ by 54.2, 41.0, and 45.1 kcal/mol, respectively, and structure **IV**, associated with a triplet, is also below the first triplet dissociation channel, $Si_3(^3B_2) + N_2(^1\Sigma^+)$ by 55.8 kcal/mol. We also note that first triplet state local minimum (**IV**) correlates with the linear transition state (**XI**) as determined by an IRC calculation. Since the various possible dissociation channels lie quite high in energy, as depicted in Figure 3, one can certainly expect these species to be thermodynamically stable.

With respect to the correlation of these structures with the various dissociation channels, the search in a 9-dimensional hypersurface for transition states (TS) connecting the manifold of local minima with these channels turned out to be very disappointing. To move on this complex hypersurface is very demanding computationally, making the location of first order saddle points very difficult. Of the three TS structures found for energies up to 80 kcal/mol above the global minimum,
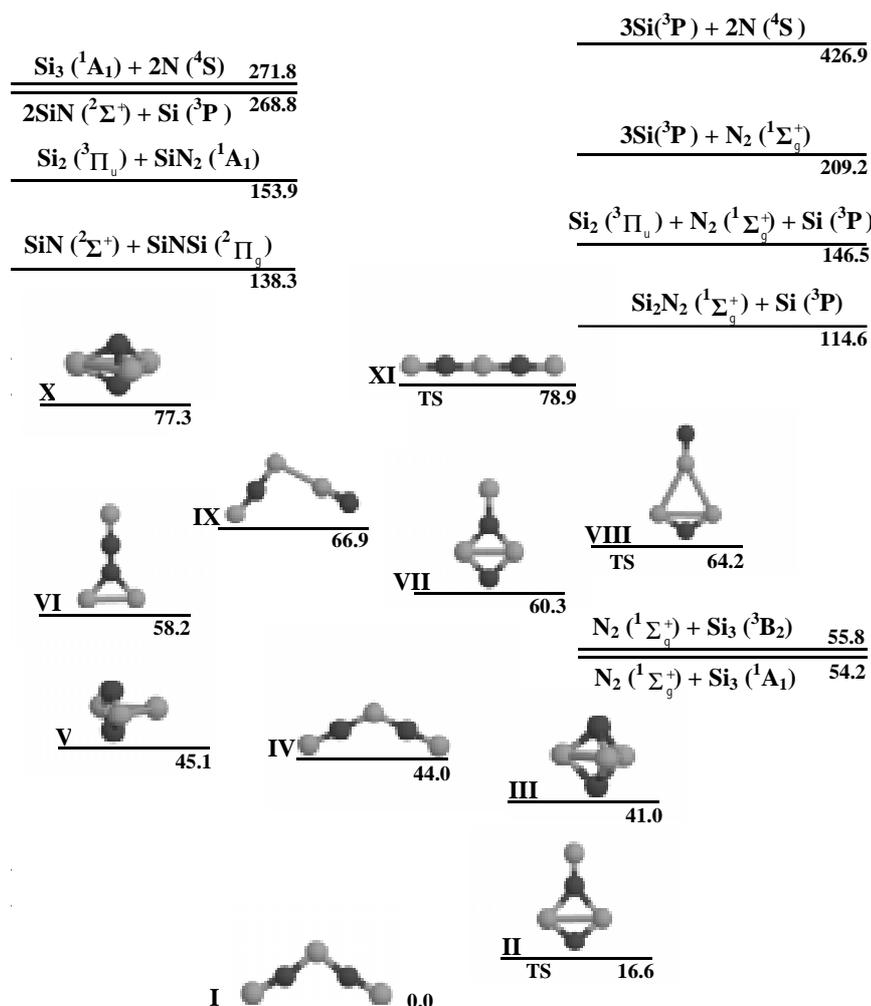
Figure 3. Relative energies (kcal/mol) of stationary point structures of Si_3N_2 and dissociation channels. The numbers in parentheses refer to SCF values. 1 cal = 4.18 J.

structures **II** and **XI**, as mentioned before, connect two equivalent structures of **I** and **IV**, respectively. Various attempts have been made through IRC calculations to locate local minima correlating with the transition structure **VIII**, but due to the flatness of the potential energy surface in the neighborhood of the saddle point, as reflected in the very low vibrational frequencies, the automatic search with varying values of the stepsize parameter always returned to the original stationary point after a few steps.

These difficulties thus prevented us from presently estimating energetic barriers for interconversions and dissociation energies. However, atomization energies can be easily estimated from Figure 3 and Tables 1 and 2, being that of structure **I** equal to 420.6 kcal/mol, including the zero-energy correction.

Conclusions

This study has characterized the structures of several clusters of molecular formula Si_3N_2 and established a relative scale of stability between the various species and also relative to the different possibilities of dissociation of the molecules. Contrary to trends in previous studies, an angular structure was found as the global minimum; a bipyramidal structure about 41.0 kcal/mol higher in energy is the next local minimum and resembles the tridimensional structure of Si_5. Linear structures are very unstable. A few transition state structures have been found and correlated with local minima, but for others it turned out to be very difficult to follow the motion to a local minimum via an IRC calculation. Transition states correlating minima and dissociation channels have also been very difficult to locate in this 9-dimensional hypersurface, however, various species have been found to be thermodynamically stable, being the energy of the lowest dissociation channel a lower bound to the dissociation energy.

Acknowledgements

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