Structures and stability of isomers of [Si,N,N,P] system

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Abstract Some stationary points on the potential energy surface of [Si, N, N, P] system were located at the B3LYP/6-311G(d) and QCISD(t)/6-311+G(2df)(single-point) levels of theory, while the isomerization, structures, and stability of these obtained isomers were suggested. The computed results indicate that only four-membered ring isomer SiNPN(E1, 2A") isomer, which possesses butterfly-like structure and Si-P cross bonding, is kinetically stable in all optimized isomers. Other isomers may be considered as kinetically unstable towards isomerization or dissociation because of the corresponding smaller reaction barriers. Furthermore, the present paper also proposes electronic and geometric structures, vibrational frequencies and the corresponding vibrational modes, dipole moments, and rotational constants of isomer E1. To make use of the computed results, we can clearly know that the reaction pathway via an intermediate E3 (SiNPN) is the most favorable channel producing isomer E1 from fragments SiN ( 2Π) and PN (1Σ), which have been well characterized in space, and thus, isomer E1 can be considered as a candidate for interstellar observation. The reaction enthalpy of SiN ( 2Π) + PN(1Σ) → E1 and the standard enthalpy of formation of isomer E1 are 215.25 and 457.99 kJ/mol, respectively, at 298.15 K.

Keywords: potential energy surface, [Si,N,N,P] system, isomerization, kinetic stability.

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Recently, silicon- and nitrogen-containing small molecules, such as SiN, SiC, SiC2, and NP, which have been identified in interstellar medium⁴, and well characterized for the formation, structures, spectra, and reactivity using theoretical and experimental methods⁵–⁸, have attracted more attentions because of their potential importance in chemical kinetics, interstellar chemistry, astrophysics, and material science. The systems with three, four, and five atoms, for example, Si2N, SiN2, Si2P, SiP2, Si3N, SiN3, Si2N2, Si2P2, N2P2, and SiN₄, have been also given sufficient recognition by theoretical and experimental chemists because of the experimental identification and theoretical studies⁹–¹⁴ of a lot of CN and CP bearing clusters and the important implications of phosphors- and nitrogen-doped Si-based materials and clusters in material science¹⁵, and much structural information about multiple bonding was predicted in many unsaturated systems¹⁶–¹⁹. The corresponding structures and stability of some isomers in many analogues containing nitrogen and phosphors atoms have very obvious discrepancy, resulting from the distinctness of chemical properties of nitrogen and phosphors elements, especially their respective bonding nature. For example, thermodynamically and kinetically the most stable two isomers in Si₂P₂ system are butterfly-like PPSi(Si)(C₂v)

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and planar rhombic SiPSiP(D$_{2h}$)\textsuperscript{(13)}, which shows obvious Si-Si and Si-P bondings. But for Si$_2$N$_2$ system, all isomers with higher stability, SiNNSi, SiNSiN, and SiSiNN, possess linear configurations\textsuperscript{(19)}, and the N-N and Si-N interaction are incarnated. The revelation for these bonding features not only increases the understanding for the structural manner of complex compounds with coordinating centers of (SiP)$_n$ and (SiN)$_n$\textsuperscript{(21)}, but also provides available knowledge for cognizing the chemical properties and Si-N and Si-P bonding patterns of nitrogen- and phosphors-doped silicon-semiconductor materials as well as their Chemical Vapor Deposition (CVD) processes\textsuperscript{(22)}. We select [Si,N,N,P] system as our research goal for better understanding for multiple bond characters of Si-N, Si-P, and N-P, also for finding the differentia and resemblance of bonding nature between tetramotic radical, containing silicon, nitrogen, and phosphors simultaneity, and species, including only silicon and nitrogen or silicon and phosphors, as well as for providing available theoretical data for the study of the nature of relevant clusters and materials. Furthermore, because diatomic molecules SiN and PN have been identified in dense interstellar cloud\textsuperscript{(1–3)}, it is very possible to form dimer or trimer from SiN and PN monomers. Considering the suggestion of experimental observation for four-atom clusters Si$_2$N$_2$\textsuperscript{(19)} and N$_2$P$_2$\textsuperscript{(20)}, we can reasonably think that the [Si,N,N,P] isomer should be considered as objects for interstellar exploration. Accordingly, the present paper will study the structural properties and stability of [Si,N,N,P] system as well as their theoretical spectra, and provide some theoretical knowledge for future experimental work.

1 Computational

All geometric optimizations were performed using density function method. The geometric structures of isomers, transition states, and molecular fragments were computed at the B3LYP/6-311G(d) level of theory, while frequency analysis method was employed to identify the nature of all obtained stationary points. The structural parameters and zero-point energies used in present paper were obtained at the B3LYP/6-311G (d) level of theory. For obtaining more believable energies, QCISD(t) method, which requires a quadratic configuration interaction calculation including single and double substitutions with a triples contribution to the energy added, were employed to compute single-point energies using B3LYP/6-311 G(d)-computed geometries with 6-311+G(2df) basis set. The energies at the QCISD(t)/6-311+G(2df)//B3LYP/6-311G(d) level of theory with zero-point vibrational energy included were used on the potential energy surface in present paper. Intrinsic reaction coordinate (IRC) calculations were carried out at the B3LYP/6-311G(d) level. Some relevant properties of isomers were computed using G2 and QCISD(t) methods directly. All computational works were performed by employing Gaussian98 quantum chemistry program codes running on the SGI/Origin300 server and SGI/Fuel workstation.

2 Results and discussion

2.1 Isomers of [Si,N,N,P] system

Eleven isomers, which are shown in fig. 1, were located on the potential energy surface of [Si,N,N,P] system. Based on their structural features, we can classify them into four types as nonlinear chain isomers E3, E4, and E10, linear isomers E5 and E8, three-membered ring isomers E7, E9, and E11, and four-membered cyclic isomers E1, E2, and E6. The ordering of thermodynamical stability of the eleven isomers is E1 (0.00 kJ/mol) > E2 (3.71 kJ/mol) > E3 (13.78 kJ/mol) > E4 (43.89 kJ/mol) > E5 (66.30 kJ/mol) > E6 (98.35 kJ/mol) > E7 (111.61 kJ/mol) > E8 (158.22 kJ/mol) > E9 (175.92 kJ/mol) > E10 (176.46 kJ/mol) > E11 (194.52 kJ/mol).

Isomers E1 and E6 possess SiNPN four-membered ring with electronic states $^2$A" and $^2$A’, respectively. Their corresponding electronic configurations are [core]…(15A’)\textsuperscript{(2)} (16A’)\textsuperscript{(2)} (6A")\textsuperscript{(2)} and [core] … (15A’)\textsuperscript{(2)} (6A")\textsuperscript{(2)} (16A’), which can be formed from the splittings of planar four-membered saddle points E1* and E6*, which possess $^2$B\textsubscript{2} ((core)…(12A\textsubscript{1})\textsuperscript{(2)} (1A\textsubscript{2})\textsuperscript{(2)} (6B\textsubscript{2}) and $^2$B\textsubscript{1} ((core)…(12A\textsubscript{1})\textsuperscript{(2)} (1A\textsubscript{2})\textsuperscript{(2)} (4B\textsubscript{1})) states, along the imaginary vibrational frequencies appearing at −109.8 cm\textsuperscript{−1} (B\textsubscript{2} symmetry) and −176.1 cm\textsuperscript{−1} (B\textsubscript{1} symmetry), respectively. Isomer E1 is the global point of the potential energy surface of [Si,N,N,P] system.
and is thermodynamically the most stable structure, which is very similar to the configuration of the most stable Si$_2$P$_2$ isomer.

If we constrain E1 and E6 as planar structures in the optimizations, two saddle points (E1* and E6*) can be located, which are higher in energy than E1 and E6 by 30.43 and 7.79 kJ/mol, respectively. Obviously, the difference of energy between E1 and E1*, namely planarity energy, is higher than that between E6 and E6*. This results from more energy required in the process E1 $\rightarrow$ E1* along with the stretching of cross-bonding Si-P and lower energy required in the process E6 $\rightarrow$ E6* since no crossing bond formed. For E1 and E6, their corresponding $^2$A$'$ and $^2$A$''$ states are very high in energy, and the wave functions described the two states are unstable at the QCISD(t)/6-311G(d) level of theory, which can easily cause orbital exchanges leading to the formation of $^2$A$''$ and $^2$A$'$ states, respectively.

Isomer E2, whose energy is 3.71 kJ/mol above the species E1, is a planar four-membered ring structure with $^2$A$_1$ electronic state, C$_{2v}$ symmetry, and Si-P cross bonding. Furthermore, we can also obtain other three stationary points of E2 with different states, $^2$A$_2$ (E2*), $^2$B$_1$ (E2**), and $^2$B$_2$ (E2***), as shown in fig. 1. Frequency analyses indicate $^2$A$_2$ and $^2$B$_2$ states to be two one-level saddle points. The energy of $^2$B$_1$ state is unstable because of easy transition to $^2$A$_1$ state at the QCISD(t)/6-311G(d) level of theory via orbital exchange. And thus, in the four structures of E2, only $^2$A$_1$ state is stable.

The computational results indicate that the lowest two structures in energy are E1 and E2 on the potential energy surface of [Si,N,N,P] system, which is obviously different from that of SiN$_3$\cite{16}, which is isovalent electron system with [Si,N,N,P]. The two isomers with the lower energies in SiN$_3$ are nonlinear chain SiNNN and NSiNN, but the four-membered cyclic SiNNN species possesses lower stability because of higher relative energy with respect to SiNNN and NSiNN\cite{16}. We can also find that SiPNN(E4), one of phosphors analogues of species SiNNN, is higher in energy than E1 by 43.89 kJ/mol.
In the search of linear SiNPN and SiPNN, two saddle points with $^2\Sigma$ state (SiNPN, $r_{SN} = 0.15946$ nm, $r_{NP} = 0.17655$ nm, $r_{PN} = 0.15946$ nm) and $^2\Sigma$ state (SiPNN, $r_{SP} = 0.21157$ nm, $r_{PN} = 0.16295$ nm, $r_{PN} = 0.11485$ nm) were located, and the former can split into two states, $^2A'$ and $^2A''$, along the direction of imaginary vibration frequency appearing at $-556.4$ cm$^{-1}$. The $^2A'$ state SiNPN (E3) lies 13.78 kJ/mol above E1. The E3* with $^2A''$ state is higher in energy than 2000 kJ/mol, and considering sized spin contamination in computations ($\langle s^2 \rangle = 2.23$), we can propose the state to be an unstable stationary point. Furthermore, a nonlinear isomer E4 (2A') with SiPNN connectivity and almost collinear PNN chain was located along with the imaginary vibration direction of linear SiPNN (2Π). In SiNNN, the angle SiNN is 158.76°, but the angle SiP in species SiPNN is only 97.34°, which results from the different interactions of electrons in SiNNN and SiPNN. In SiNNN, single electron resides mainly on the Si atom (0.88 e), and the Si-N bond length of 0.17069 nm proposes it to be a normal single bond by comparing with experimental the Si-N bond length of 0.17778 nm in NH$_2$PH$_2$, indicating that it is a somewhat weak single bond.

2.2 Stability and isomerization of [Si,N,N,P] isomers

The located eighteen transition states on the potential energy surface of [Si,N,N,P] system are presented in fig. 2, while the isomerization pathways and possible fragment dissociation channels are plotted in fig. 3. From figs. 2 and 3, we can find that the ring-closed processes dominate the interconversions of [Si,N,N,P] isomers, such as E3→E1, E8→E2, E5→E7, E8→E11, and E10→E2, accompanied by some hackneyed isomerization patterns, for examples, group exchange, atom shift, structural relaxation, and the rupture and formation of multiple bonds.

Based on fig. 3, we can know that isomers E1 and E3 reside in a deeper potential well, and the reaction rate from E3 to E1 via transition state TS1/3 should be quick because of lower reaction barrier of 22.43 kJ/mol. The $\Delta G$ of reaction E1→E3 computed at the G2 level and at one standard atmospheric pressure and 298.15 K can make us estimate the equilibrium ratio value of 0.054 for E3/E1, which suggests that in the equilibrium system of E1→E3 at 298.15 K, the main component should be isomer E1. The experimental identification for isomer E3 at low and ac-
Fig. 2. Structures of located transition states on the potential energy surface of [Si,N,N,P] system. Bond distances are in nanometers and bond angles in degrees.

Fig. 3. Isomerization and dissociation pathways of [Si,N,N,P] isomers at the QCISD(t)/6-311+G(2df)//B3LYP/6-311G(d) level with zero-point vibrational energy correction.
customed temperature is almost impossible. For isomer $E_2$, there are three isomerization pathways, from $E_2$ to $E_9$, $E_8$, and $E_{10}$ via transition states $TS_{2/9}$, $TS_{2/8}$, and $TS_{2/10}$ with initial reaction barriers of 213.63, 239.29, and 176.14 kJ/mol, respectively. Isomer $E_2$ difficultly isomerizes into other species under thermodynamical conditions because of higher initial reaction barriers mentioned above. But considering similar geometries and thermodynamical stability between $E_2$ and $E_1$, the easier rearrangement reactions are expected to happen. Unfortunately, no such interconversion transition state was located despite of a lot of work paid. Therefore, potential energy surface scanning technology was employed to study the possible reaction channels, and the results are shown in fig. 4. A structural relaxation pathway, i.e. from $E_1$ to $E_1^*$ along the reaction coordinate followed by the relaxation process to $E_2$, was selected in computations. The computed results show that the energy of system increases with the increasing of dihedral angle $SiNNP$. While the geometry was constrained to change into a plane, the energy increases by 30.43 kJ/mol (corresponding to planarity energy). Subsequently, with the lowering of Si-P bond length, the energy continues to increase to the highest energy value followed by the decreasing. And at last, the structure is converted into $E_2$. Because the highest energy value is only 45.82 kJ/mol above $E_2$, species $E_2$ is very easy to isomerize into $E_1$ along the studied pathway, and thus, $E_2$ is kinetically unstable and almost impossible to observe in experiments.

At the B3LYP/6-311G(d) level with zero-point energy correction, the barrier height of reaction from $E_6$ to $E_1$ via $TS_{1/6}$ is 7.47 kJ/mol, but surprisingly, the value is $-4.3$ kJ/mol at the QCISD(t)/6-311+G(2df)//B3LYP/6-311G(d) level with zero-point energy included, as shown in fig. 3. The negative barrier results from the single-point correction, and also often occurs in other theoretical computations,[23,24] which indicates the reaction barrier to be very low or close to zero.

The remained isomers can converse or dissociate into other kinetically stable species or fragments, such as $E_4 \rightarrow SiP(^1T_1) + N_2(^3\Sigma_g)$, $E_5 \rightarrow E_4$, $E_7 \rightarrow E_5$, $E_8 \rightarrow E_{10}$, $E_9 \rightarrow E_3$, $E_{10} \rightarrow E_2$, and $E_{11} \rightarrow E_8$ with reaction barriers of 39.18, 74.08, 42.34, 28.61, 34.30, 3.39, and 13.02 kJ/mol, respectively. Considering these lower barriers, we can safely suggest these isomers to be kinetically unstable and very difficult to be observed in experiments.

2.3 Structure and relevant properties of isomer $E_1$

As discussed above, in $[Si,N,N,P]$ system, only isomer $E_1$ possesses higher kinetic stability and can be experimentally characterized. The electronic configuration of isomer $E_1$ with $^2A^\pi$ state is $[core] \cdots (15A')^2(16A')^2(6A'\pi)$. The geometric structures at different levels are listed in table 1, while the vibrational frequencies, rotational constants, and dipole moments are presented in table 2. From table 1, we can know for isomer $E_1$ the $\langle s^2 \rangle$ values are 1.02 and 1.13 at the MP2/6-311G(d) and QCISD(t)/6-311G(d), respectively, which indicate higher spin contamination. But at the B3LYP level, no obvious spin contamination can be found. Thus, the computation at the B3LYP level gave more compellent geometry. The Si-N and Si-P bond lengths in $E_1$ are 0.18200 and 0.24419 nm, respectively. They can be described as somewhat weak single bonds by comparing with normal Si-N and Si-P single bond lengths of 0.172[25] and 0.225 nm[26], respectively. But in $E_1$ the N-P bond length of 0.16578 nm is an intermediate between normal N-P single bond length of 0.17778 nm (in NH$_2$PH$_2$) and normal N-P double bond distance of 0.15580 nm (in HNPH), and in view of the single
electron residing on the two nitrogen atoms (0.56 e, 0.56 e), we can propose isomer $E_1$ as two resonance structures shown in fig. 5(a) or as a delocalization form described in fig. 5(b).

It should be noted that fragments SiP($^2\Pi$) + N$_2$(1$\Sigma_g$) is higher in energy than $E_1$ by only 0.82 kJ/mol, and no transition state for the reaction SiP($^2\Pi$) + N$_2$(1$\Sigma_g$)$\rightarrow E_1$ was located. The required energy for the triple bond rapture in the reaction should be very high because no bonding action was found between two nitrogen atoms of $E_1$. And thus, it is almost impossible to form $E_1$ from fragments SiP($^2\Pi$) + N$_2$(1$\Sigma_g$). But we can consider another pathway of the formation of $E_1$ from fragments SiN($^2\Pi$) + PN(1$\Sigma$), which is higher in energy than $E_1$ by 206.91 kJ/mol and has been well characterized in density interstellar cloud, because the direct products from the initial reactants SiN($^2\Pi$) and PN(1$\Sigma$) is species $E_3$, which is very easy to isomerize into isomer $E_1$. Therefore, $E_1$ can be considered as goal for interstellar observation and experimental synthesis. For the reaction SiN($^2\Pi$) + PN(1$\Sigma$)$\rightarrow E_1$, its reaction enthalpy is 215.25 kJ/mol at the G2 level and 298.15 K. Furthermore, based on the enthalpies of formation of SiN($^2\Pi$) and PN(1$\Sigma$)$^{[27,28]}$, the standard enthalpy of formation of $E_1$, 457.99 kJ/mol, can be obtained.

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