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Theoretical Study on Structures and Stability of Si_2P_2 Isomers

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The structures, energetics, spectroscopies, and isomerization of possible low-lying Si_2P_2 isomers in both singlet and triplet states are theoretically investigated at the B3LYP/6-311G(d) and CCSD(T)/6-311+G(2df) (single-point) levels. At the final CCSD(T)/6-311+G(2df)//B3LYP/6-311G(d) level, the lowest energy isomer is a singlet butterfly-like SiPSiP structure ^{1}1 with P−P cross bonding followed by a singlet rhombic SiPSiP isomer ^{1}2 with Si−Si cross bonding, whereas the cyanogen analogue PSiSiP ^{1}5 is the highest lying of all the singlet isomers. The singlet potential energy surface of Si_2P_2 indicates that the rhombic isomer ^{1}2 is kinetically much more stable than the butterfly-like isomer ^{1}1, although isomer ^{1}2 is 3.2 kcal/mol higher in energy than isomer ^{1}1, while other isomers are kinetically unstable toward isomerization to isomer ^{1}1 or ^{1}2. It is also shown that the triplet Si_2P_2 isomers are energetically higher than all the single species except ^{1}5. Furthermore, for the most relevant singlet Si_2P_2 isomers and interconversion transition states, the relative energies obtained at the B3LYP/6-311G(d) level are in excellent agreement with the values calculated at the single-point CCSD(T)/6-311+G(2df) level within 2 kcal/mol. Finally, the structural, energetic and kinetic similarities and discrepancies between the isomers of Si_2P_2 and other analogous molecules C_2N_2, Si_2N_2 and C_2P_2 are compared and analyzed.

1. Introduction

Recently, the chemistry of silicon−phosphorus bonding has received much interest, though compared with other aspects of silicon chemistry the attention is still very little. Many examples concerning Si−P bonding can been found in various fields such as inorganic, organic, and organometallic chemistry.[1] Up to now, a number of silicon−phosphorus containing species have been prepared and characterized.[2] Most of these Si−P species involve coordinated organic functional groups, hydrogen or metallic atoms. Many computational studies have been performed on the hydrogenated species with Si−P bonding.[3] In addition to, and possibly more importantly, Si−P bonding is relevant to the chemical vapor decomposition (CVD) of phosphorus-doped silicon for semiconducting materials.[4]

It is known that the isolated pure Si_n and P_n clusters have long been the subject of numerous experimental and theoretical studies (see ref 5 for Si_n, ref 6 for P_n, and references therein). However, no experimental studies on the synthesis or characterization of pure mixed gas-phase silicon−phosphorus clusters Si_mP_n with no coordinated atoms or functional groups have been reported, despite that the crystal composition $Si_{12}P_5$[4e−g] has been found in Si−P containing alloys. Theoretically, to our best knowledge, only the species SiP,[7] SiP_2,[8] Si_2P[9], and $Si_{24}P_4$[10] have been studied using ab initio or semiempirical methods. In sharp contrast, other mixed Si_mX_n clusters (X = C, O, N, etc.) (see ref 11 for X = C, ref 12 for X = O, and ref 13 for X = N, and references therein) have been extensively investigated. In addition to the intrinsic value of predicting the structures and spectroscopies for future experimental observation, studies of these mixed clusters may provide helpful information for understanding the interaction of contaminating atoms such as C, O, N, and P with the silicon clusters and may also help us to gain deeper insights into the nature of bonding and the growth mechanism of these clusters. Therefore, a study of Si−P containing species Si_mP_n with larger size than SiP, SiP_2, and Si_2P may be very useful to understand and enrich the Si−P chemistry related to the silicon-based materials.

In this paper, we choose the tetraatomic species Si_2P_2 for our study. Formally, Si_2P_2 is the intermediate of the other two tetraatomic clusters Si_4 and P_4. It has been well established that the ground state of Si_4[5] is a planar structure while that of P_4[6] is tetrahedral. A study of Si_2P_2 may then be suitable for elucidating the bonding similarities and differences between Si and P elements. Also, although the naked Si_2P_2 cluster is still experimentally unknown, it has already been detected as a unit in several compounds either with interesting SiPSiP butterfly-like or planar rhombic structures which are coordinated by organic functional groups, hydrogen or metal atoms.[2g] Principally, we may expect that such four-membered ring analogous structures also exist for the naked Si_2P_2 cluster. However, caution must be taken because it is not always the case when the stationary properties, energetics, and kinetic stability between the naked and coordinated clusters are compared. For example, cyclic CCPP trapezoidal structures have long been detected as a building unit in organophosphorus compounds.[14] Yet, it is not a minimum isomer at all for the naked C_2P_2 cluster.[15] Thus, without carrying out ab initio calculations, it is not quite safe enough for us to "predict" the structural, energetic and kinetic properties of Si_2P_2. Furthermore, our theoretical investigation on the structural, energetic and kinetic properties of Si_2P_2 is of fundamental importance because Si_2P_2 is chemically isovalent and analogous to the molecules C_2N_2, Si_2N_2, and C_2P_2. The well-known molecule C_2N_2 (see ref 16 and references therein) has been attracting rather extensive experimental and theoretical consideration. Four linear isomers NCCN, CNCN, CNNC, and CCNN as well as a NNC three-membered ring isomer have been theoretically found to be local minima on potential energy surface, and all except the nonlinear form have been calculated

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to be kinetically very stable. The former three linear isomers have already been synthesized or detected in the laboratory, and the first isomer NCCN has even been detected in interstellar space. The molecule Si_2N_2 has received theoretical investigation very recently.[13] Two linear isomers SiNNSi and SiNSiN, one butterfly-like SiNSiN isomer, and one SiNN three-membered ring isomer have been located as stationary points, whereas the linear NSiSiN and SiSiNN isomers are not minima on potential energy surface. It should be pointed out that the butterfly-like SiNSiN isomer is the second low-lying isomer following the lowest energy isomer SiNNSi. In our very recent theoretical study on C_2P_2,[15] seven isomers have been located as local minima among which the lowest lying isomer is a cyanogen-like structure PCCP and the second low-lying isomer is a rhombic CPCP form with C−C cross bonding. However, the linear isomers CPCP and CPPC are not minima. It can be readily seen that from C_2N_2 to Si_2N_2 and C_2P_2, the structural forms and energetic order of isomers vary much. Because Si and P are of the same group as C and N, respectively, it is very natural for us to ask what will be the structural, energetic and kinetic properties as well as the bonding nature for the molecule Si_2P_2. Are the properties of Si_2P_2 close to or different from those of C_2N_2, C_2P_2, or Si_2N_2? Without detailed ab initio calculations on the whole potential energy surface of Si_2P_2, it is surely difficult to answer this question.

On the other hand, our theoretical investigation aims to provide a theoretical prediction for future possible astrophysical detection of the molecule Si_2P_2. Up to now, the small silicon-containing and phosphorus-containing molecules such as SiC, SiC_2 (ring), SiC_3 (ring), SiC_4, SiN, SiO, CP, and PN have been detected in interstellar space.[17] However, the species containing both Si and P atoms (even the simplest SiP radical) have not been detected yet.

In this paper, an attempt is made to investigate the structures, energetics and kinetic stability of possible low-lying Si_2P_2 isomers so as to provide some instructive information for their future laboratory and interstellar detection. Also with the calculated results, we hope to understand the structural, energetic, and kinetic stability discrepancies between Si_2P_2 and its isovalent species such as C_2N_2, Si_2N_2, and C_2P_2.

2. Computational Methods

All calculations are carried out with Gaussian 98 program package. The optimized geometries and vibrational frequencies of the singlet and triplet Si_2P_2 isomers and their interconversion transition states are obtained at the B3LYP/6-311G(d) level. To obtain more reliable energetics, single-point calculations are further performed at the CCSD(T)/6-311+G(2df) level for all singlet and some triplet species. Furthermore, to test whether the transition states connect the correct isomers, the intrinsic reaction coordinate (IRC) calculations are carried out at the B3LYP/6-311G(d) level.

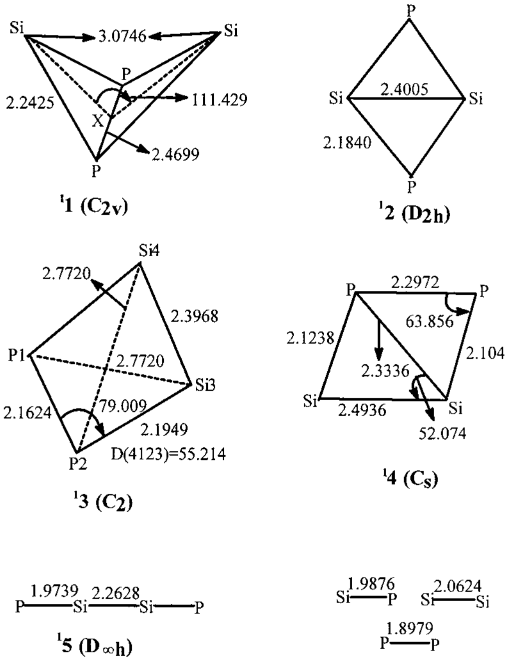


Figure 1. Optimized geometries of singlet Si_2P_2 isomers and dissociation products. Bond lengths are in angstroms and angles in degrees. The symbol “X” denotes the dummy atom.

TABLE 1: Harmonic Vibrational Frequencies (in cm^{-1}) and Infrared Intensities in Km/Mol (in parentheses) of Si_2P_2 Isomers at the B3LYP/6-311G(d) Level

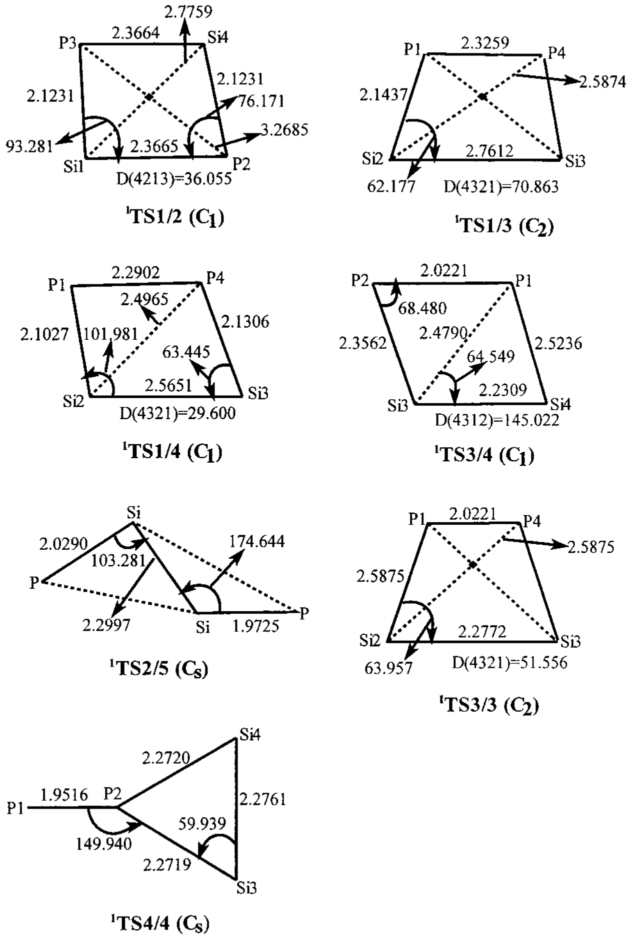
species	frequencies
$^{1}1$	209 (0) 287 (0) 297 (7) 423 (7) 492 (42) 517 (6)
$^{1}2$	202 (3) 257 (0) 320 (0) 395 (0) 511 (0) 569 (25)
$^{1}3$	220 (1) 248 (10) 299 (1) 433 (1) 495 (4) 538 (4)
$^{1}4$	125 (0) 184 (0) 313 (1) 332 (11) 545 (9) 581 (2)
$^{1}5$	46 (1) 80 (0) 278 (0) 723 (0) 774 (0)
^{1}TS1/2	309i (1) 241 (0) 300 (1) 337 (0) 519 (0) 534 (1)
^{1}TS1/3	217i (0) 251 (2) 267 (18) 349 (1) 554 (21) 564 (8)
^{1}TS1/4	169i (2) 216 (2) 262 (6) 346 (0) 526 (18) 573 (1)
^{1}TS3/4	342i (11) 191 (7) 233 (3) 351 (2) 474 (12) 608 (3)
^{1}TS2/5	128i (7) 75 (0) 75 (0) 323 (0) 642 (3) 750 (11)
^{1}TS3/3	445i (0) 253 (14) 261 (0) 294 (3) 503 (10) 633 (1)
^{1}TS4/4	218i (13) 121 (5) 169 (3) 296 (1) 475 (4) 681 (7)
$^{3}1$	124 (1) 231 (2) 364 (3) 366 (0) 395 (2) 497 (0)
$^{3}2$	172 (3) 290 (2) 321 (0) 394 (0) 438 (1) 475 (2)
$^{3}3$	177 (0) 202 (0) 268 (4) 302 (6) 423 (4) 539 (5)
$^{3}4$	169 (1) 294 (1) 315 (7) 385 (1) 440 (5) 493 (5)
$^{3}4$*	186 (5) 290 (1) 304 (2) 399 (1) 455 (10) 642 (175)
$^{3}4$**	182 (1) 319 (9) 347 (30) 369 (17) 416 (13) 488 (8)
$^{3}5$	31 (1) 44 (1) 124 (0) 323 (0) 505 (49) 606 (0)
$^{3}6$	37 (1) 91 (1) 292 (4) 414 (28) 435 (9) 565 (15)
$^{3}7$	83 (1) 104 (1) 299 (0) 406 (5) 449 (18) 592 (32)
3TS1/1	111i (3) 194 (3) 376 (0) 400 (0) 404 (1) 491 (0)
3TS1/6	175i (5) 81 (2) 276 (3) 365 (7) 414 (43) 531 (20)
3TS2/7	208i (5) 71 (1) 211 (5) 327 (3) 488 (6) 597 (2)
3TS3/4	200i (4) 273 (6) 304 (10) 338 (3) 444 (13) 506 (4)
3TS4/4	256i (3) 208 (3) 354 (5) 403 (13) 456 (0) 50 (1)
3TS(4/4)′	448i (33) 85 (1) 280 (90) 362 (11) 408 (2) 472 (21)
3TS4**/4**	172i (0) 188 (2) 251 (0) 391 (0) 523 (0) 557 (11)
3TS4/6	126i (1) 129 (1) 249 (7) 372 (20) 418 (22) 518 (34)
3TS4/7	165i (1) 85 (0) 278 (1) 333 (2) 456 (7) 540 (12)
3TS5/7	52i (1) 48 (0) 122 (1) 325 (0) 540 (1) 626 (48)

3. Results and Discussions

For such a small tetraatomic molecule Si_2P_2, it is feasible to search for all possible isomeric forms on potential energy surface in both singlet and triplet states. We have performed geometrical surveys on nearly all possible isomers including linear, three-membered ring, four-membered ring, and closed tetrahedral-like structures followed by vibrational analysis to confirm whether the obtained structure is a local minimum or not. Five singlet and nine triplet isomers are found as local minima with all real frequencies. Other structures either possess imaginary frequencies or collapse to the minimum isomers. For simplicity, we list only the calculated results of the minimum isomers. For various Si_2P_2 isomers and their interconversion transition states, the harmonic vibrational frequencies are presented in Table 1, while the total and relative energies are given in Table 2. The detailed geometries of the five singlet Si_2P_2 isomers and their interconversion transition states are summarized in Figures 1 and 2, respectively, while those of the nine triplet isomers and transition states are shown in Figures 3 and 4, respectively.

TABLE 2: Total (a.u.) and Relative (kcal/mol) Energies of Si_2P_2 Isomers and Interconversion Transition States at the B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311+G(2df) Levels

species	B3LYP/6-311G(d)	CCSD(T)/6-311+G(2df)//B3LYP/6-311G(d)
^{1}1	−1261.7505758 (0.0)	−1259.8956166 (0.0)
^{1}2	−1261.7464450 (2.6)	−1259.8905042 (3.2)
^{1}3	−1261.7410479 (6.0)	−1259.8864082 (5.8)
^{1}4	−1261.7203968 (18.9)	−1259.8637001 (20.0)
^{1}5	−1261.6771442 (46.1)	−1259.8046421 (57.1)
Si_2+P_2	−1261.5937662 (98.4)	−1259.7312640 (103.1)
2SiP	−1261.5986992 (95.3)	−1259.7218280 (109.1)
^{1}TS1/2	−1261.7094509 (25.8)	−1259.8524167 (27.1)
^{1}TS1/3	−1261.7296198 (13.2)	−1259.8766030 (11.9)
^{1}TS1/4	−1261.7148135 (22.4)	−1259.8568062 (24.4)
^{1}TS3/4	−1261.6909944 (37.4)	−1259.8360525 (37.4)
^{1}TS2/5	−1261.6676324 (52.0)	−1259.7980886 (61.2)
^{1}TS3/3	−1261.7008132 (31.2)	−1259.8496957 (28.8)
^{1}TS4/4	−1261.6759296 (46.8)	−1259.8131680 (51.7)
^{3}1	−1261.7070510 (27.3)	−1259.8466743 (30.7)
^{3}2	−1261.7246655 (16.3)	−1259.8617729 (21.2)
^{3}3	−1261.7074682 (27.1)	−1259.8547964 (25.6)
^{3}4	−1261.7131193 (23.5)	−1259.8514598 (27.7)
^{3}4*	−1261.6886226 (38.9)	−1259.8261106 (43.6)
^{3}4**	−1261.6737789 (48.2)	−1259.8177378 (48.9)
^{3}5	−1259.6517576 (62.0)	−1259.7692559 (79.3)
^{3}6	−1261.6848882 (41.2)	−1259.8133031 (51.7)
^{3}7	−1261.6942087 (35.4)	−1259.8220777 (46.1)
^{3}TS1/1	−1261.7052260 (28.5)	
^{3}TS1/6	−1261.6781678 (45.4)	−1259.8085587 (54.6)
^{3}TS2/7	−1261.6748254 (47.5)	
^{3}TS3/4	−1261.6989409 (32.4)	
^{3}TS4/4	−1261.7004204 (31.5)	
^{3}TS(4/4)′	−1261.6777119 (45.7)	
^{3}TS4**/4**	−1261.6617413 (55.7)	
^{3}TS4/6	−1261.6783415 (45.3)	−1259.8097089 (53.9)
^{3}TS4/7	−1261.6828418 (42.5)	
^{3}TS5/7	−1261.6498280 (63.2)	



^{1}TS1/2 (C_1) ^{1}TS1/3 (C_2)

^{1}TS1/4 (C_1) ^{1}TS3/4 (C_1)

^{1}TS2/5 (C_s) ^{1}TS3/3 (C_2)

^{1}TS4/4 (C_s)

Figure 2. Optimized geometries of singlet Si_2P_2 interconversion transition states. Bond lengths are in angstroms and angles in degrees.

Furthermore, a schematic potential energy surface (PES) showing the isomerization between the singlet and triplet Si_2P_2 isomers is plotted in Figure 5. In section 3.1, the structural, energetic and isomerization features of singlet Si_2P_2 isomers are described, and in section 3.2, the corresponding properties of triplet Si_2P_2 isomers are described. Finally, a comparison is made between Si_2P_2 and three analogous molecules C_2N_2, Si_2N_2 and C_2P_2 in section 3.3.

3.1. Singlet PES of Si_2P_2. *A. Isomers.* There are five singlet Si_2P_2 isomers identified as local minima. Note that in this paper, the number at the top left corner is referred to as the spin state (1 for singlet and 3 for triplet state). For example, the symbol ^{1}1 means isomer 1 in singlet state. The lowest lying isomer ^{1}1 is a C_{2v}-symmetrized butterfly-like SiPSiP form with P−P cross bonding. The bond length of four identical peripheral Si−P bonds is 2.2425 Å, which is very close to the experimental value 2.25 Å[2b] of the normal Si−P single bond. The transannular P−P bond length is 2.4690 Å slightly longer than the normal P−P single bond 2.21 Å.[18] The most intense vibrational band of isomer ^{1}1 is 492 cm^{-1}.

Isomer ^{1}2 of Si_2P_2 is a rhombic form with a planar SiPSiP four-membered ring. It contains a transannular Si−Si bond with the bond length 2.4005 Å which is very close to the normal Si−Si single bond 2.34 Å.[19] The four identical peripheral SiP bonds of 2.1840 Å are roughly the intermediate between the normal Si−P single bond 2.25 Å[2b] and normal Si═P double bond 2.09 Å.[2s] As a result, the four SiP bonds display strong π bonding character. The situation is a little different from the butterfly-like isomer 1 where the four peripheral SiP bonds are all single-bonded. Actually, the rhombic isomer ^{1}2 may be described as a four-π-electron, four-center (4πe-4c) system. The characteristic vibrational band of isomer ^{1}2 is 569 cm^{-1}.

Isomer ^{1}3 with C_2 symmetry may be considered as a folded SiSiPP trapezoidal structure along either of the two identical cross SiP bonds. The bond length of two identical peripheral SiP bonds is 2.1949 Å, which is about 0.06 Å shorter than the normal Si−P single bond 2.25 Å[2b] and is about 0.10 Å longer than the normal Si═P double bond 2.09 Å.[2s] Also, the peripheral PP bond (2.1624 Å) is 0.05 Å shorter than normal P−P single bond (2.21 Å[18]) and is 0.15 Å longer than normal P═P double bond (2.01 Å[18]). This indicates that the two SiP bonds and one PP bond possess certain π-bonding characters. However, the peripheral SiSi bond length 2.3968 Å is about 0.06 Å longer than the normal Si−Si single bond length 2.34 Å,[19] indicating that the π electrons contribute little to the Si−Si bonding of isomer ^{1}3. Then, we may consider the peripheral Si−Si bond as the weakest bond of isomer ^{1}3 and the cleavage of Si−Si bond may first take place during isomerization or dissociation of isomer ^{1}3. The bond distance between a set of diagonal Si and P atoms is 2.7720 Å (about 0.52 Å longer than normal Si−P single bond), indicating that the two identical cross SiP bonding of isomer ^{1}3 is rather weak and almost nonbonding. The strongest infrared vibrational frequency of isomer ^{1}3 is 248 cm^{-1}. The other two vibration bands at 538 and 495 cm^{-1} are about half as strong.

Isomer ^{1}4 is a C_s-symmetrized form with a distorted SiSiPP trapezoidal structure. A set of Si and P atoms forms a bridge SiP bond across the four-membered ring. The bridge SiP bond length 2.3336 Å is slightly longer than the normal Si−P single bond length 2.25 Å.[2b] The two peripheral SiP bond lengths

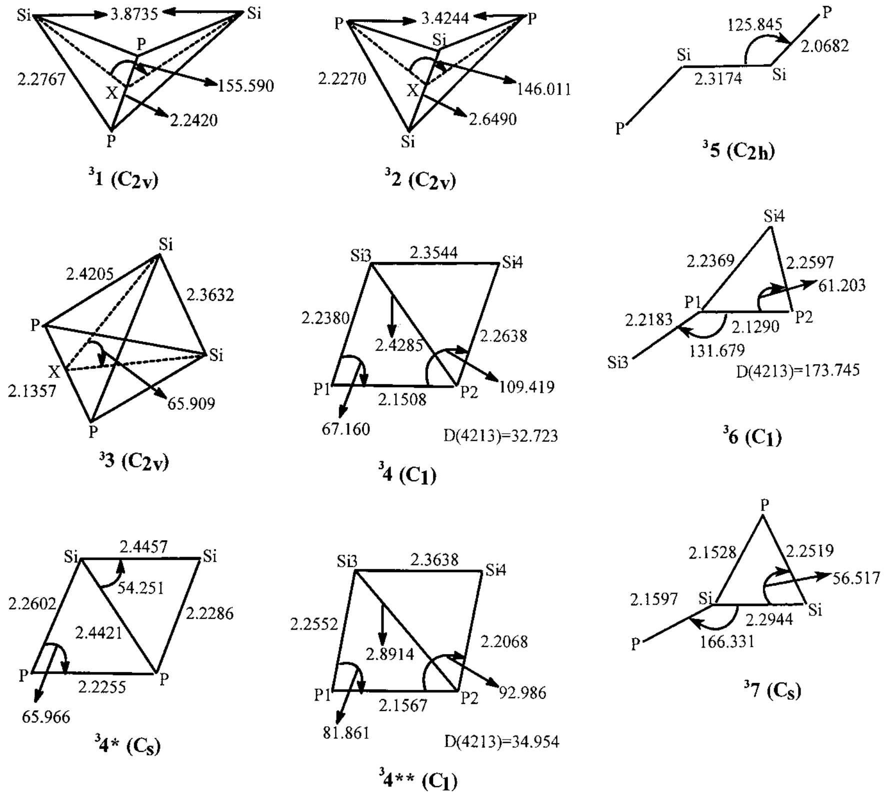


Figure 3. Optimized geometries of triplet Si_2P_2 isomers. Bond lengths are in angstroms and angles in degrees. The symbol "X" denotes the dummy atom.

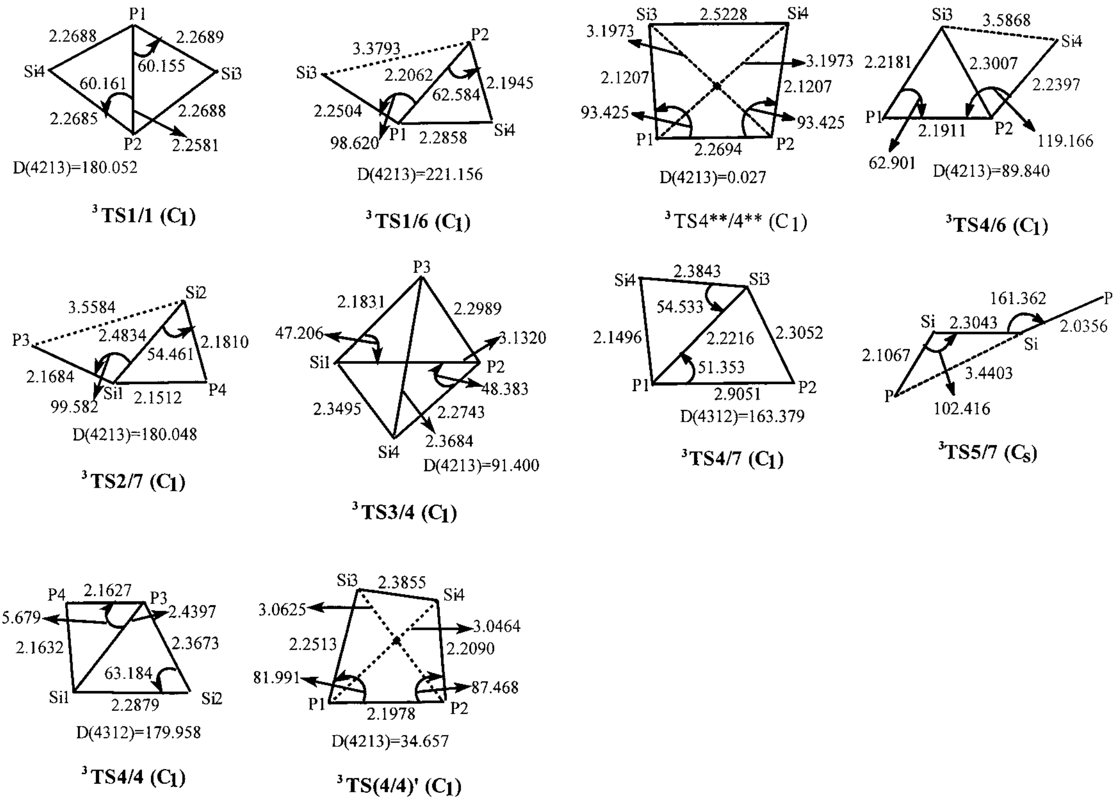


Figure 4. Optimized geometries of triplet Si_2P_2 interconversion transition states. Bond lengths are in angstroms and angles in degrees.

2.1238 and 2.1045 Å are close to the normal Si=P double bond length 2.09 Å.[2s] The bond length of PP bond is 2.2972 Å and is a typical single bond compared to the experimental value 2.21 Å.[18] However, the peripheral SiSi bond length 2.4936 Å is about 0.15 Å longer than the normal Si−Si single bond 2.34 Å,[19] though it is still single-bonding. Thus compared to other bonding of isomer ^{1}4, the peripheral Si−Si single bond is the weakest and may be easier to be broken. There are two vibrational bands 549 and 332 cm^{-1} with almost equal infrared intensities for isomer ^{1}4.

Isomer ^{1}5, a formal analogue of the well-known cyanogen NCCN, has a linear PSiSiP structure with P≡Si triple bonding

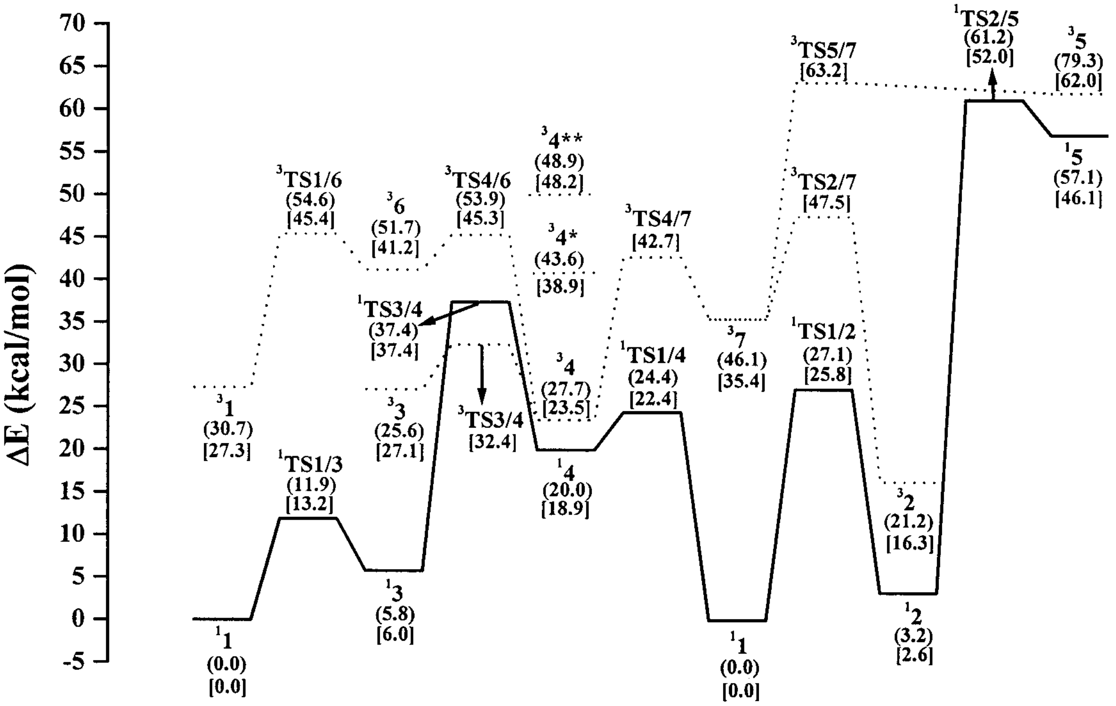


Figure 5. Schematic potential energy surface (solid lines for singlet and dotted for triplet) of Si_2P_2 at the CCSD(T)/6-311+G(2df)//B3LYP/6-311G(d) level. The values in ( ) and [ ] are at the CCSD(T)/6-311+G(2df)//B3LYP/6-311G(d) and B3LYP/6-311G(d) levels, respectively.

as indicated by the natural bond orbital analysis. The bond length of two identical terminal SiP triple bonds is 1.9739 Å. This value is very close to that of the SiP radical 1.9876 Å and is about 0.12 Å shorter than the normal Si=P value.[2s] The central SiSi bond is just single bonding because the bond length 2.2628 Å is about 0.08 Å shorter than the normal Si−Si single bond 2.34 Å.[19] Thus, isomer ^{1}5 may be considered as a structure formed by two SiP radicals via a Si−Si central single bond. However, as will be discussed in section 3.3, the bonding between PSiSiP and NCCN is actually quite different. Frequency calculations show that isomer ^{1}5 has no strong infrared vibrational bands.

From Table 2 we can easily see that of the five Si_2P_2 isomers, the butterfly-like isomer ^{1}1 is the lowest lying followed by the rhombic isomer ^{1}2, whereas the cyanogen-like linear isomer ^{1}5 lies the highest. At the final single-point CCSD(T)/6-311+G-(2df) level, the thermodynamical order of the five Si_2P_2 isomers is isomer ^{1}1 (0.0) > isomer ^{1}2 (3.2) > isomer ^{1}3 (5.8) > isomer ^{1}4 (20.0) > isomer ^{1}5 (57.1). It is interesting to note that the B3LYP/6-311G(d) relative energies of the isomers ^{1}1 (0.0), ^{1}2 (2.6), ^{1}3 (6.0), and ^{1}4 (18.9) are rather close to the single-point CCSD(T)/6-311+G(2df) values within the limit 1.1 kcal/mol. The predicted thermodynamical stability of the linear isomer ^{1}5 (46.1) at the B3LYP/6-311G(d) level is much higher than that at the CCSD(T)/6-311+G(2df) level. Notice that the values in parentheses in kcal/mol are relative energies of Si_2P_2 isomers with reference to the lowest lying isomer ^{1}1.

B. Isomerization. In addition to the thermodynamical stability of singlet Si_2P_2 isomers discussed in section 3.1 A, the kinetic stability of these isomers may be of particular interest. The kinetic stability of an isomer is usually governed by its isomerization and dissociation barriers. The larger the barrier, the higher kinetic stability of the isomer. In this section, we shall discuss the isomerization and dissociation between the five singlet Si_2P_2 isomers and fragment products by means of the potential energy surface as shown in Figure 5. As shown in Figure 2, there are altogether seven transition states: ^{1}TS1/2, ^{1}TS1/3, ^{1}TS1/4, ^{1}TS2/5, ^{1}TS3/4, ^{1}TS3/3, and ^{1}TS4/4. Note that ^{1}TSm/n is referred to as the singlet transition state connecting the singlet isomers ^{1}m and ^{1}n where m and n are Arabic numbers.

From Figure 5, we can see that the five singlet Si_2P_2 isomers can directly or indirectly be converted to each other. The thermodynamically most stable butterfly-like isomer ^{1}1 can isomerize to the rhombic isomer ^{1}2, folded trapezoidal isomer ^{1}3, and distorted trapezoidal isomer ^{1}4 via the transition states ^{1}TS1/2, ^{1}TS1/3, and ^{1}TS1/4, respectively. The corresponding conversion barriers are then 27.1 (^{1}1→^{1}2), 11.9 (^{1}1→^{1}3), and 24.4 (^{1}1→^{1}4) kcal/mol. Isomer ^{1}2 may isomerize to the lowest energy isomer ^{1}1 or to the highest energy isomer PSiSiP ^{1}5 with the respective barriers 23.9 (^{1}2→^{1}1) and 58 (^{1}2→^{1}5) kcal/mol. Interestingly, although the energy gap between the two low-lying isomers ^{1}1 and ^{1}2 is only 3.2 kcal/mol, large barriers separate them from conversion to each other. This is understandable because concerted bond cleavage and formation process of either of the Si−Si and P−P cross bonds must be involved between the isomers ^{1}1 and ^{1}2. The conversion barriers of isomer ^{1}3 are 6.1 (^{1}3→^{1}1) and 31.6 (^{1}3→^{1}4) kcal/mol. Isomer ^{1}4 may take two isomerization pathways to the isomers 1 and 4 with respective barriers 4.4 (4→1) and 17.4 (4→3) kcal/mol. For the linear isomer ^{1}5 with the highest energy, we only locate one isomerization pathway from ^{1}5 to ^{1}2 via ^{1}TS2/5 with the barrier 4.1 kcal/mol. Simply from the structural features of the five singlet Si_2P_2 isomers, we preliminarily expect that there are transition states between the isomers ^{1}2 and ^{1}3, ^{1}2 and ^{1}4, ^{1}4 and ^{1}5. However, despite numerous attempts, such transition states cannot be obtained. Furthermore, we can easily see from Table 2 that the two dissociation products, i.e., two doublet SiP radicals and two singlet molecules Si_2 and P_2, lie high above isomer 1 at 109.1 and 103.1 kcal/mol, respectively. It is worthy of note that for the most important transition states ^{1}TS1/2, ^{1}TS1/3, ^{1}TS1/4, and ^{1}TS3/4, the B3LYP/6-311G(d) relative energies are very close to the single-point CCSD(T)/6-311+G-(2df) values, within 2 kcal/mol. Also, though the relative energies for ^{1}TS2/5 and ^{1}5 at the CCSD(T)/6-311+G(2df) level are about 11.0 and 9.2 kcal/mol higher than those at the B3LYP/

6-311G(d) level, the barriers for 5→2 conversion at the two levels are very close (4.1 and 6.9 kcal/mol, respectively). The transition states ^{1}TS3/3 and ^{1}TS4/4 are associated with the interexchange of the isomers ^{1}3 and ^{1}4, i.e., ^{1}TS3/3 corresponds to the interexchange of either of the two Si-atoms or of the two P-atoms within isomer ^{1}3 (cSi1Si3P4P1↔cSi1Si3P1P4 in Figure 2), while ^{1}TS4/4 corresponds to the wagging of the PSiSi three-membered ring along the PP bond within isomer ^{1}4 (cP1P2-Si4Si3↔cP1P2Si3Si4 conversion in Figure 2).

Now let us discuss the kinetic stability of the five singlet Si_2P_2 isomers. The lowest isomerization or dissociation barriers usually determine the kinetic stability of an isomer. Since the relative energies of the two products 2SiP and Si_2+P_2 are much larger than those of the Si_2P_2 isomers and the corresponding isomerization states, the isomerization barriers mainly govern the kinetic stability of these isomers. From Figure 5, we can obtain the kinetic stability order of the five singlet Si_2P_2 isomers as isomer ^{1}2 (23.9 for ^{1}2→^{1}1) > isomer ^{1}1 (11.9 for ^{1}1→^{1}3) > isomer ^{1}3 (6.1 for ^{1}3→^{1}1) > isomer ^{1}4 (4.4 for ^{1}4→^{1}1) > isomer ^{1}5 (4.1 for ^{1}5→^{1}2). Notice that the values in parentheses denote the isomerization barrier in kcal/mol of the Si_2P_2 isomers. It should be noted that although the butterfly-like isomer ^{1}1 is thermodynamically more stable than the second low-lying rhombic isomer ^{1}2 by 3.2 kcal/mol, the kinetic stability of isomer ^{1}1 is nearly half of that of isomer ^{1}2. The remaining isomers ^{1}3, ^{1}4, and ^{1}5 are kinetically even much less stable since they can easily be converted to the lower lying isomer ^{1}1 or ^{1}2. Therefore, from the theoretical viewpoint, the rhombic isomer may be the best candidate for future experimental detection. The high kinetic stability of isomer ^{1}2 relative to other isomers may be ascribed to its delocalized 4π-4c stabilization. Though the kinetic stability of the butterfly-like isomer ^{1}1 is much less than that of isomer ^{1}2, it may also be observable due to its high thermodynamical stability. However, observation of the other isomers seems unlikely.

3.2. Triplet PES of Si_2P_2. By considering the weak π interaction present in bonds between the second row elements, it is desirable to calculate the triplet potential energy surface of Si_2P_2 to see if there exist any triplet isomers energetically lower than the five singlet isomers. At the B3LYP/6-311G(d) level, we obtain nine triplet minimum isomers with their structures depicted in Figure 3. As can be seen in Table 2, the nine triplet species lie considerably higher than all four important singlet isomers ^{1}1, ^{1}2, ^{1}3, and ^{1}4. Thus, we just briefly describe the structural, energetic and stability properties of the triplet isomers.

Isomers. On triplet PES, ^{3}1 and ^{3}2 are two butterfly-like isomers with PP and SiSi cross bonding, respectively. Note that the singlet species ^{1}2 with SiSi cross bonding is a planar structure. Optimization of structure ^{1}3 with C_2 symmetry in the triplet state leads to a closed tetrahedral-like isomer ^{3}3 (such a closed structure does not exist on singlet PES). Interestingly, three cyclic SiSiPP isomers with SiP cross bonding (^{3}4, ^{3}4*, and ^{3}4**) can be found on triplet PES. ^{3}4 and ^{3}4** are distorted trapezoidal structures folded along the SiP cross bond with C_1 symmetry, whereas ^{3}4* is a planar distorted trapezoidal structure. Isomer ^{3}5 is a zigzag-like PSiSiP form with C_{2h} symmetry. The linear-structure-like ^{1}5 has one imaginary frequency. Unlike the singlet PES, there are two three-membered ring isomers on triplet PES. Isomer ^{3}6 possesses the PPSi three-membered ring with an exocyclic PSi bonding, while isomer ^{3}7 possesses the SiSiP three-membered ring with an exocyclic SiP bonding.

The energetic order of the nine triplet isomers can be obtained from Table 2 as isomer ^{3}2 (21.2) > isomer ^{3}3 (25.6) > isomer ^{3}4 (27.7) > isomer ^{3}1 (30.7) > isomer ^{3}4* (43.6) > isomer ^{3}7 (46.1) > isomer ^{3}4** (48.9) > isomer ^{3}6 (51.7) > isomer ^{3}5 (79.3). The values in parentheses are relative energies with respect to the lowest lying isomer ^{1}1 at the CCSD(T)/6-311+G-(2df)//B3LYP/6-311G(d) level. We can easily find that isomer ^{3}5 with SiP multiple bonding (the bond length 2.0682 Å is very close to the normal Si═P value 2.09 Å[2s]) is also the highest energy isomer. On the triplet PES, isomer ^{3}2 with SiSi cross bonding is energetically lower than isomer ^{3}1 with PP cross bonding by 9.5 kcal/mol, just the opposite for the singlet PES. Moreover, the species ^{3}3 and ^{3}4 are both lower in energy than ^{3}1 by 5.1 and 3.0 kcal/mol, respectively. It should be pointed out that the relative energy discrepancies predicted at the two levels are larger for triplet species than for singlet species, as can be seen in Table 2. The large differences are for ^{3}5 (17.3 kcal/mol), ^{3}6 (10.5 kcal/mol), and ^{3}7 (10.7 kcal/mol), while for the other isomers the differences are within 5.0 kcal/mol.

Isomerization. The isomerization pathways of various triplet Si_2P_2 isomers are shown in Figure 5. Ten transition states are located including ^{3}TS1/1, ^{3}TS1/6, ^{3}TS2/7, ^{3}TS3/4, ^{3}TS4/4, ^{3}TS(4/4)′, ^{3}TS4**/4**, ^{3}TS4/6, ^{3}TS4/7, and ^{3}TS5/7. Note that ^{3}TS1/1, ^{3}TS4/4, ^{3}TS(4/4)′, and ^{3}TS4**/4** are associated with the automerization process of the isomers ^{3}1, ^{3}4, and ^{3}4** (these triplet automerization transition states are not shown in Figure 5, yet their structures are described in Figure 4). The species ^{3}TS1/1 correspond to the turning over of ^{3}1 along the PP cross bonding, and ^{3}TS4/4 and ^{3}TS4**/4** correspond to the turning over of ^{3}4 and ^{3}4**, respectively, along the SiP cross bonding. ^{3}TS(4/4)′ corresponds to the wringing between cSi1Si2P3P4 with P3Si1 cross bonding and cSi1Si2P3P4 with P4Si2 cross bonding. No isomerization transition states of ^{3}4* and ^{3}4** can be located.

On the B3LYP/6-311G(d) triplet PES of Si_2P_2, the SiPSiP cyclic species ^{3}1 and ^{3}2 also possess much higher kinetic stability than other triplet species. As shown in Table 2, the relative energies for ^{3}TS1/6 and ^{3}TS4/6 at the CCSD(T)/6-311+G(2df) are larger than those at the B3LYP/6-311G(d) level by about 9.2 and 4.7 kcal/mol, respectively. Yet the barriers for ^{3}1→^{3}6 (18.1, 23.9), ^{3}6→^{3}1 (4.2, 2.9), ^{3}6→^{3}4 (4.1, 2.2), and ^{3}4→^{3}6 (21.8, 26.2) are relatively closer. The values in parentheses are obtained at the B3LYP/6-311G(d) and CCSD(T)/6-311+G(2df) levels, respectively. Due to the computational expense, the energetics of the other triplet transition states are not calculated at the CCSD(T)/6-311+G(2df) level. However, we hope that the conclusion that the triplet species ^{3}1 and ^{3}2 may have higher kinetic stability than other triplet forms will not change.

3.3. Experimental and Astrophysical Implications. From the preceding discussions, we know that the cyclic SiPSiP species with both PP cross bonding (^{1}1, ^{3}1) and SiSi cross bonding (^{1}2, ^{3}2) may possess either high thermodynamical or high kinetic stability. Despite the theoretical stability of the isomers ^{1}1 and ^{1}2, both have not been experimentally characterized heretofore. However, both have been detected as building units in several organic or organometallic compounds.[2g] These units are usually coordinated by the organic functional groups, hydrogen or metal atoms. In one experiment, the X-ray determined structures of the isomer ^{1}1 unit are about r(SiP) = 2.267 Å, r(PP) = 2.342 Å, and r(SiSi) = 3.244 Å. Other experimentally determined values are about r(SiP) = 2.228 Å, r(PP) = 2.384 Å, and r(SiSi) = 3.050 Å. These bond lengths are close to the corresponding values r(SiP) = 2.2425 Å, r(PP) = 2.4690 Å, and r(SiSi) = 3.0746 Å in pure isomer ^{1}1 calculated in the present work. These data indicate that the butterfly-like structure with a P−P cross bond is well retained in such compounds. If the coordinated groups, hydrogen or metal atoms can be effectively removed, the butterfly-like isomer ^{1}1 may then be formed. The experimental values of the isomer ^{1}2 unit are roughly r(SiP) = 2.28 Å and r(SiSi) = 3.07 Å. By comparing with the corresponding bond lengths of pure isomer 2, i.e., r(SiP) = 2.1840 Å and r(SiSi) = 2.4005 Å, we can easily find that a distinct difference is that no cross Si−Si bonding is formed within the coordinated isomer 2. Also different from the situation in pure isomer ^{1}2, the bond length of the four peripheral SiP bond of the coordinated isomer ^{1}2 is very close to the normal Si−P and 2.25 Å.[2b] Thus, the planar SiPSiP four-membered ring bears no π bonding character within the coordinated isomer ^{1}2. A theoretical study on the mixed Si_2P_2 cluster coordinated by hydrogen atoms, i.e., $H_nSi_2P_2$ (n = 2, 4, and 6), is now underway to investigate the influence of substituent groups on the structures, energetics, and kinetic stability of Si_2P_2 skeleton.

Up to now, more than one hundred molecules have been detected in interstellar space among which small silicon or phosphorus containing molecules such as SiC, SiC_2, SiC_3, SiC_4, SiN, SiO, SiO, CP, and PN are included.[17] Unfortunately, the molecules containing both Si and P have not been found. Our calculation may provide a useful basis for future interstellar detection of the two cyclic low-lying Si_2P_2 isomers. Note that the already detected SiC_2 and SiC_3 molecules possess cyclic structures. Because the dipole moments of the isomers ^{1}1 and ^{1}2 calculated at the B3LYP level are rather small, their microwave detection seems unlikely. Yet, both can be identified with the aid of their infrared vibrational frequencies.

3.4. Comparison with Other Molecules. Usually, isovalent or analogous molecules are expected to possess similar chemical properties. Yet, many discrepancies have been disclosed between the first-row and second-row elements (especially between C and Si, N and P). It is then interesting and useful to make comparisons of the structural, energetic, and kinetic properties between Si_2P_2 and other tetraatomic species such as C_2N_2, Si_2N_2, and C_2P_2.

The C_2N_2 molecule has been extensively studied both experimentally and theoretically (see ref 16 and references therein). Theoretical calculations have concluded that there are four kinetically stable linear isomers NCCN, CNCN, CNNC, and CCNN, and one NNC three-membered ring isomer with much lower thermodynamical and kinetic stability. The first three linear isomers have been experimentally characterized, and NCCN has even been detected in interstellar space. For the presently studied Si_2P_2 cluster, among the four supposed linear isomers PSiSiP, SiPSiP, SiPPSi, and SiSiPP, only the isomer PSiSiP ^{1}5, which is analogous to NCCN, is identified as a local minimum and its energy is the highest. Also, PSiSiP ^{1}5 is kinetically quite unstable toward isomerization to the much lower isomer ^{1}2. It should be pointed out that the bonding nature in isomer ^{1}5 is quite different from that in NCCN. It is known that NCCN can be considered as a dimeric isomer formed by two CN radicals through a C−C single bond. Due to the existence of strong delocalization of π electrons (super conjugation), the central C−C bond length is significantly shortened to 1.37 Å. Unfortunately, such an effect does not exist in PSiSiP due to the poor overlap of π orbitals between the second-row elements. As shown in Figure 1, the central SiSi bond 2.3562 Å is characteristic of normal single bonding.

For Si_2P_2, the four-membered ring isomers ^{1}1, ^{1}2, ^{1}3, and ^{1}4 are not only thermodynamically much more stable, but also are kinetically more stable than the linear isomer ^{1}5. However, the analogues of these four-membered ring structures do not exist for C_2N_2. An inspection on the bonding types of the Si_2P_2 and C_2N_2 isomers may help us to understand the large structural and energetic discrepancies. For C_2N_2, all four linear isomers contain conjugate triple bonds (two C≡N bonds in NCCN, CNCN, and CNNC, and one C≡C and one N≡N bond in CCNN), and the highest energy three-membered ring isomer contains N=N and C=C double bonds. The existence of super conjugate effect greatly strengthens the central CC, CN, or NN bonds. As a result, all four linear isomers of C_2N_2 are both thermodynamically and kinetically lower than the nonlinear isomer. Furthermore, the discrepancies can be simply illustrated by the difference between silicon−phosphorus and carbon−nitrogen bonding energies. The respective bonding energies of Si−P, Si=P, and Si≡P are 55, 69, and 86 kcal/mol,[3l] which do not differ very much from each other. Then, two Si−P single bonds are energetically more favored than one Si=P double bond, whereas three Si−P single bonds or one Si−P single and one Si=P double bonds are more favored than one Si≡P triple bond. As a result, the bonding between Si and P favors Si−P single and Si=P double more than Si≡P triple. On the other hand, the bonding energies of C−N, C=N, and C≡N bonds are 70, 147, and 210 kcal/mol, respectively.[20] The strength of a C≡N triple bond is three times that of a C−N single bond and is the sum of one C−N single and C=N double bond strength, while the C=N strength is twice the C−N strength. Therefore, the bonding between C and N favors C≡N triple and C=N double more than C−N single.

Very recently, the analogous Si_2N_2 cluster has been theoretically investigated by Ornellas and Iwata.[13] The lowest lying isomer was found to be a linear CNNC-like structure SiNNSi instead of a NCCN-like structure NSiSiN. Actually, NSiSiN is energetically very high lying. Furthermore, it is not a local minimum at all on PES. Another linear CCNN-like isomer SiSiNN is not a minimum, either. The second low-lying isomer of Si_2N_2 is a rhombic SiNSiN structure. Yet the NN and SiSi bond lengths are much longer than the corresponding normal single bonds. The linear isomer SiNSiN is the third low-lying isomer. However, the two linear isomers NSiSiN and SiSiNN, which are the respective analogues of NCCN and CCNN, are not local minima at all. Also, a SiNN three-membered ring isomer is a minimum following SiNSiN. The calculation by Ornellas and Iwata[13] has indicated that the formation of Si−Si bonding is unfavorable for Si_2N_2. Similar to Si_2N_2, the Si_2P_2 molecule has a butterfly-like SiPSiP structure ^{1}1 and has no CCNN-like isomer SiSiPP. However, unlike Si_2N_2, the Si_2P_2 molecule has a NCCN-like isomer PSiSiP ^{1}5 and has no CNNC-like isomer SiPPSi and no SiPP three-membered ring isomer. Also, there are planar rhombic SiPSiP ^{1}2, folded trapezoidal SiSiPP ^{1}3, and distorted trapezoidal SiSiPP ^{1}4 isomers for Si_2P_2, whereas the analogous structures do not exist for Si_2N_2. Notice that the isomers ^{1}2, ^{1}3, and ^{1}4 contain appreciable amount of Si−Si single bonding. Because the kinetic stability of Si_2N_2 isomers has not been discussed by Ornellas and Iwata,[13] we will make no comparison on such aspects.

In our very recent theoretical study on the potential energy surface of C_2P_2,[15] we have identified seven isomeric forms as local minima on PES involving two linear (PCCP and CCPP), three four-membered ring (rhombic CPCP, butterfly-like CPCP, and folded trapezoidal CCPP), one PPC three-membered ring, and one closed tetrahedral-like structures. The NCCN-like isomer PCCP has the lowest energy and the second low-lying isomer is the rhombic CPCP structure with C−C cross bonding. By inspecting the isomerization of the C_2P_2 isomers, we have also found that the linear isomer PCCP is kinetically the most stable, while the rhombic isomer and the linear isomer CCPP reside in moderate potential wells and may also be kinetically stable. However, other isomers are kinetically much less stable. Compared with C_2P_2 and Si_2P_2 species, the structural similarities are that there are also butterfly-like SiPSiP isomer ^{1}1, rhombic SiPSiP isomer ^{1}2, folded trapezoidal SiSiPP isomer ^{1}3, distorted trapezoidal SiSiPP isomer ^{1}4, and NCCN-like linear PSiSiP isomer ^{1}5 for Si_2P_2 molecule. Also, both C_2P_2 and Si_2P_2 have no CNCN and CNNC analogues. The structural discrepancies are that the three-membered ring isomer and the closed tetrahedral-like isomer cannot be obtained for Si_2P_2. Considering the energetic properties, we can find that for C_2P_2, the NCCN-like isomer PCCP is thermodynamically the most stable and the butterfly-like isomer is the highest lying except for the tetrahedral-like isomer. However, the thermodynamical stability order is completely reversed for Si_2P_2, i.e., the linear PSiSiP is the highest lying and the butterfly-like isomer is the lowest lying. It should be noted that for both C_2P_2 and Si_2P_2 species, the planar rhombic isomer has considerable kinetic stability possibly due to the 4πe-4c stabilization.

4. Conclusions

The potential energy surface of Si_2P_2 in both singlet and triplet states is theoretically investigated by means of the B3LYP/6-311G(d) and single-point CCSD(T)/6-311+G(2df) methods to determine the structures, energetics, vibrational frequencies and kinetic stability of possible low-lying isomers. It is shown that the singlet butterfly-like SiPSiP isomer ^{1}1 with P−P cross bonding is the lowest lying followed by the singlet rhombic SiPSiP isomer ^{1}2 with Si−Si cross bonding at 3.2 kcal/mol, whereas the cyanogen-like isomer PSiSiP ^{1}5 at 57.1 kcal/mol is the highest lying. It is also shown that isomer ^{1}2 is kinetically the most stable followed by isomer ^{1}1 with nearly half the kinetic stability of isomer ^{1}2. Due to the high thermodynamical or kinetic stability, both the isomers ^{1}1 and ^{1}2 may be experimentally observable. The calculated results also show that the B3LYP/6-311G(d) energetics for the singlet PES of Si_2P_2 agree excellently with the single-point CCSD(T)/6-311+G(2df) values, within 2 kcal/mol except for the linear isomer ^{1}5 and related transition states. Finally, the similarities and discrepancies between Si_2P_2 and three analogous molecules C_2N_2, Si_2N_2 and C_2P_2 concerning the structures, energetics, and kinetic stability of various isomers are compared and discussed. We hope our calculations may be useful for future laboratory and interstellar detection of the two cyclic Si_2P_2 isomers ^{1}1 and ^{1}2.

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