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Theoretical Study on Structures and Stability of Si_2CP Isomers

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The structures, energetics, spectroscopies, and isomerization of various doublet Si_2CP species are explored theoretically. In contrast to the previously studied SiC_2N and SiC_2P radicals that have linear SiCCN and SiCCP ground states, the title Si_2CP radical has a four-membered-ring form cSiSiPC **1** (0.0 kcal/mol) with Si−C cross-bonding as the ground-state isomer at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE level, similar to the Si_2CN radical. The second low-lying isomer **2** at 11.6 kcal/mol has a SiCSiP four-membered ring with C−P cross-bonding, yet it is kinetically quite unstable toward conversion to **1** with a barrier of 3.5 kcal/mol. In addition, three cyclic species with divalent carbene character, i.e., cSiSiCP **7**, **7′** with C−P cross-bonding and cSiCSiP **8** with Si−Si cross-bonding, are found to possess considerable kinetic stability, although they are energetically high lying at 44.4, 46.5, and 41.4 kcal/mol, respectively. Moreover, a linear isomer SiCSiP **5** at 44.3 kcal/mol also has considerable kinetic stability and predominantly features the interesting cumulenic |Si═C═Si═P|• form with a slight contribution from the silicon−phosphorus triply bonded form |Si═C•−Si≡P|. The silicon−carbon triply bonded form •Si≡C−Si≡P| has negligible contribution. All five isomers are expected to be observable in low-temperature environments. Their bonding nature and possible formation strategies are discussed. For relevant species, the QCISD/6-311G(d) and CCSD(T)/6-311+G(2df) (single-point) calculations are performed to provide more reliable results. The calculated results are compared to those of the analogous C_3N, C_3P, SiC_2N, and Si_2CN radicals with 17 valence electrons. Implications in interstellar space and P-doped SiC vaporization processes are also discussed.

1. Introduction

Silicon and phosphorus chemistries have received considerable attention from various aspects. One of particular interest is their possible role in astrophysical chemistry. Up to now, several silicon- or phosphorus-containing molecules, such as SiC_n ($n = 1-4$), SiN, SiO, SiS, CP, and PN, have been detected in interstellar space.[1] Promisingly, the SiCN radical, which comprises three types of heavy atoms, was recently detected in an astronomical source, and its microwave spectrum was reported in the laboratory.[2] Of particular interest, the ground-state structures of SiC_2[3,4] and SiC_3 are cyclic forms.[5] No cyclic species containing phosphorus have been observed in space up to now. It is thus the present goal to predict novel Si- and P-containing species for potential astrophysical detection. Because carbon is the most abundant element after hydrogen and the inert helium, we focus on the $Si_xC_yP_z$ species.

On the other hand, Si- or P-containing species have been believed to play important roles in materials chemistry. Binary silicon carbides are commonly used in microelectronic and photoelectronic applications.[6] N- or P-doped SiC compounds are generally used as semiconducting materials.[7] Si−P bonds can be found in various fields such as inorganic, organic, and organometallic chemistries.[8] Also, the hydrogenated SiCP ion has been prepared by deposition with properly activated silane−propyne−phosphine mixtures.[9]

In this work, we study the tetraatomic molecule Si_2CP, which belongs to the isoelectronic 17-valence-electron XX′X″Y (X, X′, X″ = C, Si; Y = N, P) series. Extensive experimental and theoretical investigations[10] have shown that C_3N has only linear forms CCCN and CCNC with the dominant valence structures •C≡C−C≡N| and •C≡C−N≡C|, respectively. Both C_3N isomers have been detected in interstellar space.[10a] In addition, the analogues C_3P,[11] SiC_2N,[12] SiC_2P,[13] and Si_2CN[14] have recently received theoretical consideration. The ground state of C_3P is linear CCCP (valence structure |C═C═C═P|•) followed by the four-membered ring cC_3P with C−C cross-bonding, while linear CCPC is not a minimum. For SiC_2N, two linear forms SiCCN (valence structure |Si═C•−C≡N|) and SiCNC (valence structure |Si═C•−N≡C|) and a bent SiNCC were predicted to be observable. Several cyclic forms of C_3P and SiC_2N were also located as minima. For SiC_2P, a linear form SiCCP (valence structure |Si═C═C═P|•) and two four-membered-ring forms, i.e., planar cSiCCP with SiC cross-bonding and rhombic cSiCPC with CC cross-bonding, were predicted to be observable. As for Si_2CN, a four-membered-ring structure with SiC cross-bonding was surprisingly found to be the ground state followed by a close energy and kinetically stable linear SiCNSi isomer. Clearly, there exist some structural, bonding, and energetic discrepancies between C_3N, C_3P, SiC_2N, SiC_2P, and Si_2CN. Naturally we would turn to ask what properties the unknown radical Si_2CP can have.

On the other hand, the present Si_2CP radical is related to the interesting issues of triply bonded or sp-hybridized silicon (−Si≡C−,[15] Si≡P,[16] or ═Si═[17]) chemistry. Because of the reluctance of silicon to form π-bonding, very few such examples are known up to now. It is of interest to wonder whether any isomeric Si_2CP forms with such unique bonding could possess

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TABLE 1: Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (km/mol) (in Parentheses), Dipole Moments (D), and Rotational Constants (GHz) of Doublet Si_2CP Structures at the B3LYP/6-311G(d) Level[a]

species	frequencies (infrared intensity)	dipole moments	rotational constants		
cSiSiPC **1** ($^2A''$)	231 (1), 261 (2), 327 (1), 523 (39), 667 (56), 1084 (13)	0.7503	8.312 40	2.933 82	2.168 47
cSiSiPC **1** ($^2A''$)[b]	256 (2), 258 (3), 348 (1), 533 (35), 692 (57), 1097 (25)	0.7897	8.552 51	2.947 09	2.191 82
cSiCSiP **2** ($^2A''$)	138 (1), 186 (3), 307 (18), 473 (43), 615 (4), 1105 (37)	0.7137			
P-cCSi_2 **3** ($^2A_1$)	130 (3), 340 (3), 383 (5), 402 (4), 524 (1), 1141 (30)	0.4858			
PCSiSi **4** ($^2\Pi$)	18 (1), 28 (0), 213 (6), 245 (2), 374 (17), 674 (3), 1390 (26)	0.6195			
SiCSiP **5** ($^2\Pi$)	66 (0), 73 (1), 163 (21), 190 (19), 409 (1), 680 (12), 1374 (409)	1.6130		1.104 770	
SiCSiP **5** ($^2\Pi$)[b]	57 (1), 62 (2), 121 (20), 164 (21), 493 (0), 1329 (1090), 1737 (2227)	1.6678		1.106 808	
SiCPSi **6** ($^2\Pi$)	18 (1), 37 (4), 166 (3), 200 (5), 412 (3), 666 (31), 1327 (246)	0.1666			
cSiSiCP **7**	156 (15), 276 (6), 320 (8), 436 (3), 590 (7), 788 (13)	2.4068			
cSiSiCP **7′** ($^2A''$)	126 (4), 203 (21), 357 (2), 475 (3), 561 (23), 843 (9)	2.0196	7.004 28	3.776 76	2.453 70
cSiSiCP **7′** ($^2A''$)[b]	198 (7), 214 (7), 372 (0), 506 (11), 575 (16), 853 (13)	2.0514	7.035 15	3.841 25	2.484 62
cSiPSiC($^2B_1$) **8**	77 (77), 271 (0), 433 (1), 503 (4), 599 (0), 723 (0)	1.8848			
cSiPSiC($^2A_1$) **8′**	193 (0), 438 (4), 478 (12), 669 (421), 688 (1), 862 (30)	0.3780			

[a] For the relevant isomers, the QCISD/6-311G(d) values are also included. [b] At the QCISD/6-311G(d) level.

TABLE 2: Total (au) and Relative (kcal/mol) Energies of Si_2CP Isomers and Transition States at B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2df) Levels. for the Relevant Species[a]

species	B3LYP[b]	ΔZPVE/B3LYP[b]	CCSD(T)[c]//B3LYP[b]	total1[e]	QCISD[b]	ΔZPVE/QCISD[b]	CCSD(T)[d]//QCISD[b]	total2[f]
cSiSiPC **1** ($^2A''$)[g]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cSiCSiP **2** ($^2A''$)	10.4	−0.4	12.0	11.6				
P-cCSi_2 **3** ($^2A_1$)	28.6	−0.2	32.9	32.7				
PCSiSi **4** ($^2\Pi$)	36.1	−0.2	41.5	41.3				
SiCSiP **5** ($^2\Pi$)	37.3	−0.2	44.5	44.3	42.9	1.1	44.5	45.6
SiCPSi **6** ($^2\Pi$)	44.1	−0.4	51.1	50.7				
cSiSiCP **7**	50.9	−0.8	45.2	44.4				
cSiSiCP **7′** ($^2A''$)	52.6	−0.8	47.3	46.5	54.1	−0.7	46.6	45.9
cSiPSiC($^2B_1$) **8**	46.7	−0.7	42.1	41.4				
cSiPSiC($^2A_1$) **8′**	53.4	0.3	48.5	48.8				
TS1/2	11.2	−0.5	15.6	15.1	12.5	−0.5	14.9	14.4
TS1/4	37.8	−0.5	45.5	45.0				
TS1/5	60.4	−0.7	70.0	69.3				
TS1/5*	81.8	−1.4	87.2	85.8				
TS1/6	47.3	−0.6	55.0	54.4				
TS1/7′	68.0	−1.1	71.2	70.1				
TS2/8	55.7	−1.0	54.9	53.9				
TS4/7′	63.7	−0.9	65.1	64.2				
TS5/8	56.1	−0.6	54.4	53.8	59.0	−0.7	60.0	59.3
TS7/7′	56.3	−1.0	51.9	50.9				
TS7/7′*	58.5	−1.0	54.4	53.4				
TS7′/8	83.8	−1.4	84.9	83.5				

[a] The values at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) level are also listed. [b] The basis set is 6-311G(d) for B3LYP and QCISD. [c] The basis set is 6-311G(2df) for CCSD(T). [d] The 6-311+G(2df) basis set is used for CCSD(T). [e] At the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE level. [f] At the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level. [g] The total energy of reference isomer **1** at the B3LYP/6-311G(d) level is −958.430 133 9 au, at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d) level is −956.948 544 3 au, at the QCISD/6-311G(d) level is −956.816 284 2 au, and at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) level is −956.951 957 4 au, respectively. The ZPVE values at the B3LYP and QCISD levels are 0.007 044 and 0.007 254 au, respectively.

considerable kinetic stability to allow for detection. To the best of our knowledge, no studies have been reported on Si_2CP. A detailed theoretical study of Si_2CP will promote our understanding of the structural, energetic, and bonding changes among the 17-valence-electron series XX′X″Y (X, X′, X″ = C, Si; Y = N, P). Moreover, since many Si-containing molecules have stable cyclic isomers (such as SiC_2, SiC_3, and Si_2C_2[18]), we wonder whether Si_2CP has stable cyclic forms and even a cyclic ground state to allow laboratory or interstellar identification. Finally, knowledge about the structures, energies, and bonding natures of various Si_2CP isomers may be helpful for understanding the initial step of the growing mechanism during the P-doped SiC vaporization processes.

2. Computational Methods

All computations are carried out using the Gaussian 98 program packages.[19] The optimized geometries and harmonic vibrational frequencies of the local minima and transition states are initially obtained at the B3LYP/6-311G(d) level followed by CCSD(T)/6-311G(2df) single-point calculations using the B3LYP/6-311G(d)-optimized geometries. The B3LYP/6-311G(d) zero-point vibrational energies (ZPVE) are included. To confirm whether the obtained transition states connect the right isomers, the intrinsic reaction coordinate (IRC) calculations are performed at the B3LYP/6-311G(d) level. Furthermore, for the relevant species, higher level QCISD/6-311G(d) (for structures and frequencies) and single-point CCSD(T)/6-311+G(2df) (for energetics) calculations with inclusion of QCISD/6-311G(d) ZPVE are performed. In the context, the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE and CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE methods are generally simplified by CCSD(T)//B3LYP and CCSD(T)//QCISD.

3. Results and Discussion

The results are organized as follows. In section 3.1, we make a rough discussion on the stability of Si_2CP isomers. Then, for

TABLE 3: Relative (kcal/mol) Energies of Dissociation Fragments of the Si_2CP Structures at B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2df) Levels

species	B3LYP[a]	ΔZPVE/ B3LYP[a]	CCSD(T)[b]// B3LYP[a]	total
$SiSi(^3\Pi_g) + CP(^2\Sigma)$[c]	129.9	−1.8	149.4	147.6
$SiSi(^1\Sigma_g) + CP(^2\Sigma)$	143.7	−1.9	161.9	160.0
$SiP(^2\Pi) + SiC(^3\Pi)$	139.4	−2.2	146.0	143.8
$SiP(^2\Pi) + SiC(^1\Sigma)$	166.1	−2.0	160.2	158.2
$C(^3P) + SiSiP(^2\Pi)$	179.2	−2.8	182.9	180.1
$Si(^3P) + SiCP(^2\Pi)$	86.3	−1.2	95.9	94.7
$P(^2D) + SiCSi(^1\Sigma_g)$	110.8	−1.4	116.3	114.9
$P(^4S) + cCSi_2(^3B_2)$	124.8	−2.3	124.4	122.1

[a] The basis set is 6-311G(d) for B3LYP. [b] The basis set is 6-311G(2df) for CCSD(T). [c] The total energies of reference isomer **1** at the B3LYP and single-point energy at CCSD(T) level as well as the ZPVE at the B3LYP level are listed as footnote *g* of Table 2.

the most relevant species, we give a detailed discussion on the structural and bonding properties in section 3.2. In section 3.3, comparisons with the related species are made. The possible relevance of Si_2CP in interstellar space and SiC-vaporization processes are also assessed. Unless otherwise specified, the relative energies are at the CCSD(T)//B3LYP level.

The spectroscopic properties (harmonic frequencies, infrared intensities, dipole moments, and rotational constants) of the Si_2CP species are listed in Table 1. The relative energies of all species are collected in Table 2, and the relative energies of possible dissociation fragments of the Si_2CP structures are collected in Table 3.

3.1. Si_2CP PES. The isomeric search follows the scheme (Figure 1) summarizing the possible atomic arrangements: chainlike [type I formed from (SiSi, CP) and (SiP, SiC) molecule−radical pairs], three-membered ring [type II from SiSiCP and SiPSiC rings], four-membered ring [type III from the perpendicular-like attack between (SiSi, CP) and (SiP, SiC) pairs], all-closed species (type IV), and the branched-chain species (in type V). A total of 10 isomers are located on the doublet potential energy surface (PES). Four isomers possess four-membered-ring structures. The cyclic isomer cSiSiPC **1** with SiC cross-bonding with C_s symmetry is the global minimum on the PES. The cyclic cSiCSiP **2** with CP cross-bonding lies 11.6 kcal/mol higher than cSiSiPC **1**. Interestingly, the two peripheral Si−C bonds as well as the Si−P bonds of **2** are not identical. The isomers cSiSiCP **7** (44.4) and **7′** (46.5) are energetically very close to each other, with each containing an SiP cross-bonding. They differ in the point group symmetry from each other; i.e., **7** has C_1 symmetry whereas **7′** has C_{2v} symmetry. The energy values in parentheses are in kilocalories per mole at the CCSD(T)//B3LYP level. Finally, both C_{2v}-symmetry cSiPSiC **8** (41.4) and **8′** (48.8) with respective $^2B_1$ and $^2A_1$ electronic states have SiSi cross-bonding. The higher energy form **8′** is an excited state of **8** and can only be obtained by orbital switch. **8′** has intrinsic wave function instability toward conversion to **8**.

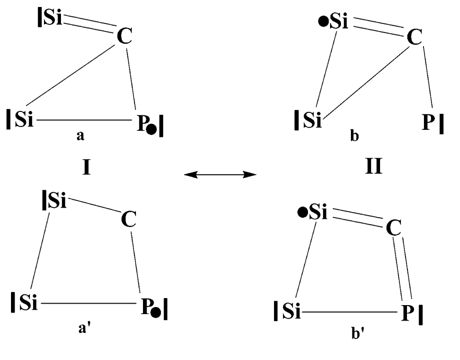
Three isomers have linear structures, i.e., linear SiSiCP **4**($^2\Pi$) (41.3), SiCSiP **5**($^2\Pi$) (44.3), and SiCPSi **6**($^2\Pi$) (50.7). The species CSiPSi and CSiSiP of type I in Figure 1 are not minima. Therefore, the linear species with inner −SiC− or −PC− bonding are of minute importance compared to cyclic isomer **1** with the Si−C cross-bonding.

Six species belong to the three-membered-ring species of type II in Figure 1. Only P-cCSiSi **3**($^1A_1$) (32.7) is located as a minimum. In fact, it is an excited-state species. Its ground-state structure has one imaginary frequency. After relaxation of symmetry, it will lead to the lowest lying form **1**.

The three-membered-ring species C-cPSi$_2$, C-cSi$_2$P, P-cSi$_2$C, Si-cPSiC, Si-cCPSi, and Si-cSiPC (in type II), the closed species (in type IV), and the branched-chain species (in type V) are not minima at any levels.

To discuss the kinetic stability, one needs to consider various isomerization and dissociation pathways. The lowest dissociation or isomerization barrier usually governs the kinetic stability of an isomer. As shown in Table 3, the relative energies of the dissociation products $SiSi(^3\Pi_g) + CP(^2\Sigma)$, $SiP(^2\Pi) + SiC(^3\Pi)$, $C(^3P) + SiSiP(^2\Pi)$, $Si(^3P) + SiCP(^2\Pi)$, $P(^2D) + SiCSi(^1\Sigma_g)$, and $P(^4S) + cCSi_2(^3B_2)$ are rather high (more than 94.7 kcal/mol at the CCSD(T)//B3LYP level). Therefore, the isomerization process determines the kinetic stability of Si_2CP isomers. On the doublet Si_2CP potential energy surface shown in Figure 3, we can see that five isomers **1**, **5**, **7**, **7′**, and **8** may be of interest with considerable kinetic stabilities with 15.1 (*14.4*) for **1→2**, 9.5 (*13.7*) for **5→8**, 19.8 for **7→7′→4**, 17.7 for **7′→4**, and 12.5 kcal/mol for **8→2** conversions, respectively, at the CCSD(T)//B3LYP and CCSD(T)//QCISD (in italics) levels. Such kinetic stabilities are high enough to allow the existence of the five species under both laboratory and interstellar conditions in low temperatures. Note that the interconversion between **7** and **7′** is as easy as 6.5 kcal/mol for **7→7′** and 4.4 kcal/mol for **7′→7** conversions. At the CCSD(T)//B3LYP level, the lowest isomerization barriers for the remaining species **2**, **4**, and **6** are 3.5 (**2→1**), 3.7 (**4→1**), and 3.7 (**6→1**) kcal/mol, respectively. They may be of little interest as observable species either in laboratory or in space. We should point out that no transition states are associated with the three-membered ring **3** and the four-membered ring **8′**. Yet, any slight geometric perturbation of **3** and **8′** leads to **1** and **8**, respectively. Therefore, both are also kinetically unstable.

3.2. Properties of 1, 5, 7, 7′, and 8 and Chemical Implications. Let us analyze the structural and bonding properties of the five species **1**, **5**, **7**, **7′**, and **8** with particular emphasis on the lowest energy **1** based on the B3LYP level. Isomer cSiSiPC **1** has a crossed SiC bond (1.9360 Å), which is about 0.05 Å longer than the typical Si−C single bond (1.8851 Å).[20] The peripheral SiSi (2.5102 Å) and SiP (2.3073 Å) bond values are slightly longer than the typical Si−Si single bond (2.3547) and Si−P single bond (2.2820 Å in SiH_3PH_2), respectively. The peripheral PC (1.7032 Å) and SiC (1.7517) bonds are between the normal P−C single bond (1.8729 Å in CH_3PH_2) and P═C double bond (1.6702 Å in CH_2PH) as well as the Si−C single bond (1.8851 Å) and Si═C double bond (1.7070 Å). The distribution of the spin densities are 0.663*e*, −0.042*e*, 0.442*e*, and −0.062*e* for P, Si, Si, and C, respectively, along the clockwise ordering as shown in Figure 1. Therefore, isomer **1** can be viewed as associated with the following two resonance structures with form **I** bearing somewhat more weight:



The symbols "•" and "|" denote the unpaired electron and lone-pair electrons, respectively. Structure **I** may contribute

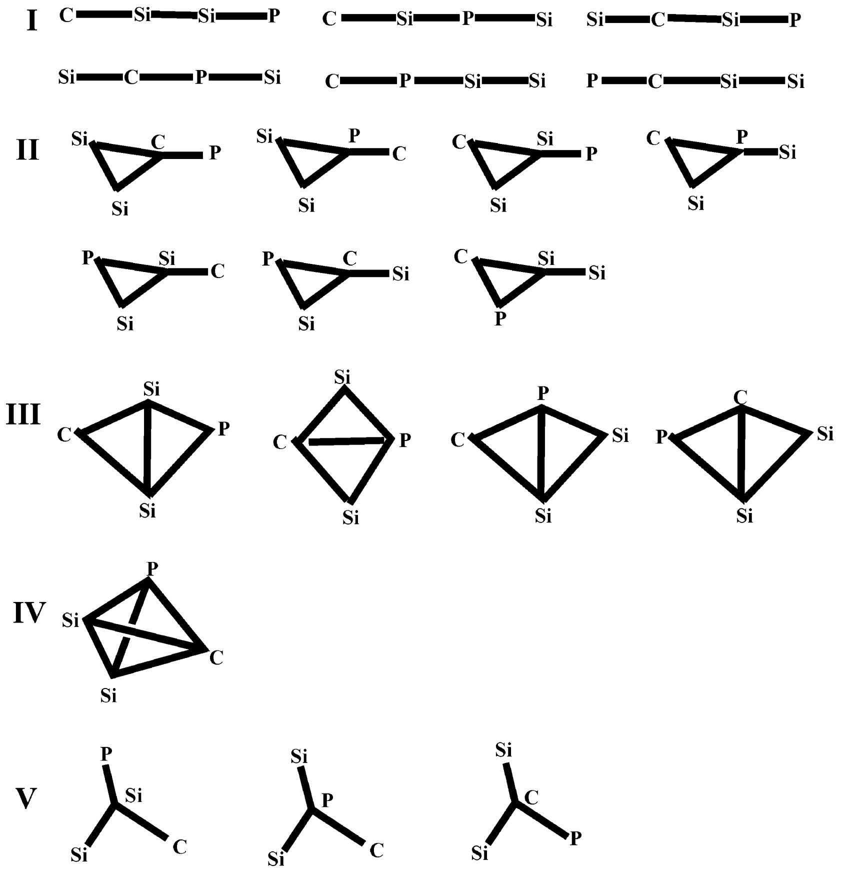


Figure 1. Scheme for the doublet isomeric species search.

somewhat more than **II**. The respective two resonating substructures **a**, **a′** in **I** and **b**, **b′** in **II** may have comparable contributions.

For the three cyclic isomers cSiSiCP **7**, **7′** and cSiPSiC **8**, the respective crossed SiP (2.4408 Å), SiP (2.2260 Å), and SiSi (2.3448 Å) are close to the typical single bonds [$r(\mathrm{Si{-}P}) = 2.2820$ Å and $r(\mathrm{Si{-}Si}) = 2.3547$ Å]. Within **7** and **7′**, the peripheral CP bond distances (1.7394 and 1.7194 Å, respectively) lie closer to the normal C=P (1.6702 Å) than normal C−P (1.8729 Å), suggestive of partial double bonding character. This may result from the delocalization of the P unshared lone pairs to the larger electronegative carbon. The remaining peripheral SiSi, SiP, and SiC bonds of **7** and **7′** are all single bonds. Because the C-atom has no (−0.0029*e*) or small (0.2981*e*) spin density for **7** and **7′**, respectively, both isomers can be considered as cyclic divalent carbene species. Isomer **8** has all single-bonded peripheral bonds with $r(\mathrm{SiC}) = 1.8438$ Å and $r(\mathrm{SiP}) = 2.2362$ Å. The spin densities are mainly on P-atom (0.6755*e*) and minor on C-atom (0.4986*e*). Thus, **8** also features divalent carbene character.

For the linear isomer SiCSiP **5** with $^2\Pi$ electronic state, its calculated outer and inner SiC bond lengths (1.6889 and 1.6903 Å) are between the typical Si=C double bond (1.7069 Å in $\mathrm{SiH_2{=}CH_2}$) and Si≡C triple bond (1.6478 Å), respectively. Its SiP bond length (2.0510 Å) lies well between the Si=P double (2.0804 Å) and Si≡P triple (1.9570 Å) bonds. Thus, isomer **5** may be best described as a resonant structure among |Si=C=Si=P|•, |Si=C•−Si≡P|, and •Si≡C−Si≡P|. The calculated Mülliken spin densities (0.089*e*, 0.211*e*, −0.102*e*, and 0.801*e* for Si, C, Si, and P) indicate that the former two structures bear somewhat more weight than the third. The above structural description is also supported by natural bond orbital (NBO) analysis. The higher energy of **5** relative to **1** is ascribed to the preference of silicon to form σ-bonded species. It is understandable that the Si≡C and Si≡P triply bonded forms have less contribution due to the weak p−p overlap ability of silicon. Yet the π-electron delocalization still contributes to its reasonable kinetic stability. Note that multiple bonding between second-row elements is usually not preferred both thermodynamically and kinetically. In interstellar space with low temperatures, the considerable kinetic stability of isomer SiCSiP **5**($^2\Pi$) may provide a new example with SiC and SiP multiple bonding.

The present calculations show that the cyclic forms dominate for the $\mathrm{Si_2CP}$ radical. Although cyclic silicon-containing molecules such as $\mathrm{SiC_2}$ and $\mathrm{SiC_3}$ have been detected in space, cyclic phosphorus-containing species are still unknown. The isomers **1**, **7**, **7′**, and **8** may serve as such examples containing three types of heavy atoms Si, C, and P. Surely the ground-state isomer **1** deserves the most attention in both the laboratory and interstellar space. The linear isomer **5** is also of great interest due to its dominant cumulenic structure |Si=C=Si=P|. Recently, the sp-hybridized Si species (Si=Si=Si) has been obtained in crystalline form by making use of bulky substitutions.[17] When stabilized by bulky substitutions, the present isomer **5** could also be obtainable. The five species may all be experienced during the vaporization of P-doped SiC clusters. When excess energy is available, the high-energy species **5**, **7**, **7′**, and **8** can isomerize to the lowest lying form **1**.

At the QCISD/6-311G(d) level, the dipole moments of **1**, **5**, and **7′** are 0.7897, 1.6678, and 2.0514 D, respectively. Higher level calculations such as QCISD(T) or CCSD(T) on the dipole moments are difficult due to the unavailability of the gradient and electron density in the Gaussian program. However, we can evaluate the reliability of the QCISD/6-311G(d) results by comparing the QCISD/6-311G(d), CCSD(T)/cc-pVQZ, and

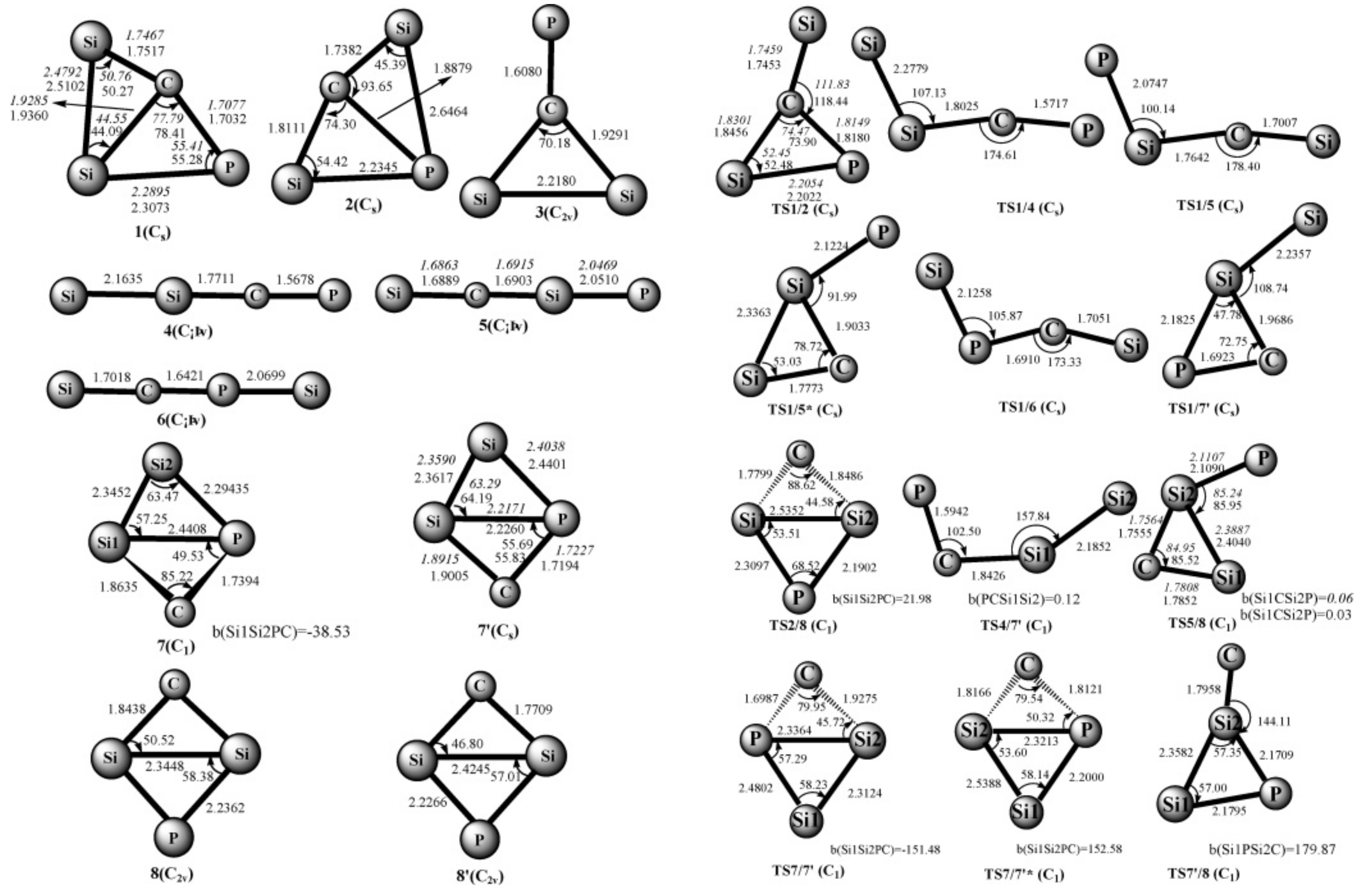


Figure 2. Optimized geometries of doublet Si_2CP isomers and transition states at the B3LYP/6-311G(d) level and geometric parameters (in italics) at the QCISD/6-311G(d) level, respectively. Bond lengths are in angstroms; angles are in degrees.

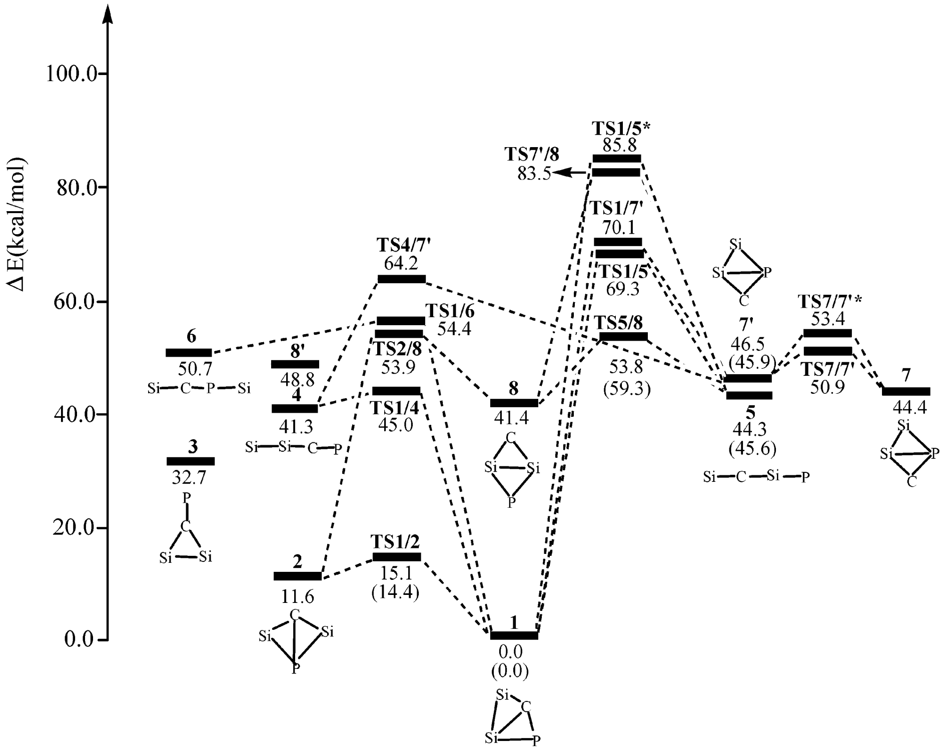


Figure 3. Schematic doublet potential energy surface of Si_2CP at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE level. The relative energies in parentheses are at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level.

experimental values for the known SiCN radical in space. It is shown that our QCISD/6-311G(d) value of 3.02 D lies between the experimental (2.9 D [21]) and CCSD(T)/cc-pVQZ (3.09 D [22]) values. The agreement is good. It seems that microwave detection of **1** is difficult. However, it can be identified by infrared spectrum. **1**, **5**, and **7′** have very acute bands at 692 cm^{-1} (associated with the breathing vibration of the SiC cross-bonding), 1737 cm^{-1} (associated with the stretch vibration of the internal SiC bond), and 575 cm^{-1} (associated with the stretch vibration of the peripheral SiC bond). The corresponding infrared intensities are 57, 2227, and 16 km/mol.

It is worth mentioning that the geometric parameters and spectroscopic properties of the species **1**, **5**, **7′**, **TS1/2**, and **TS5/8** at the B3LYP/6-311G(d) level are in good agreement with those at the QCISD/6-311G(d) level (in Figure 2 and Table 1). The respective relative energies at the CCSD(T)//B3LYP level are rather close to those at the CCSD(T)//QCISD level (in Table 2). Also, the diagnostic factors τ_1 at the single-point CCSD(T)/6-311G(2df) level of isomers **1** and **5** are as small as 0.0289 and 0.0297, respectively. This indicates that the multiconfigurational effect is not significant for the Si_2CP system, and the CCSD(T)//B3LYP method is adequate for calculation of the structures, spectroscopies, and energies.

3.3. Comparison with C_3N, C_3P, SiC_2N, and SiC_2P Analogues. It is of interest to compare the Si_2CP radical with the analogous radicals C_3N,[10] C_3P,[11] SiC_2N,[12] SiC_2P,[13] and Si_2CN[14] that have been either experimentally or theoretically studied. Following the sequence of C_3N, C_3P, SiC_2N, SiC_2P, and Si_2CN, the cyclic forms become increasingly important, which should be attributed to the higher row elements (Si, P) preferring to form σ-bonding more than first-row elements (C, N). For the current Si_2CP radical, the PES is similar to that of Si_2CN; i.e., the ground state is also a four-membered-ring form. However, SiCPSi is not as stable as SiCNSi, which should be attributed to the much less preference of P-atom to form π-bonding than the N-atom.

4. Conclusion

The detailed doublet potential energy surface study on the new Si_2CP molecule was performed at the CCSD(T)/6-311G(2df)//B3LYP/6-311G(d)+ZPVE and CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE (for selected species) levels. Among the total 10 minimum isomers, the lowest lying isomer cSiPSiC **1** (0.0 kcal/mol) contains a four-membered ring with crossed Si−C single bonding. However, the cyclic cSiCSiP **2** with C−P cross-bonding (11.6 kcal/mol), though being the second lowest lying isomer, can very easily isomerize to **1** and is thus kinetically unstable. Alternatively, three cyclic species cSiSiCP **7** (44.4 kcal/mol), **7′** (46.5 kcal/mol) with C−P cross-bonding, and cSiCSiP **8** (41.4 kcal/mol) with Si−Si cross-bonding as well as a linear isomer SiCSiP **5** (44.3 kcal/mol) are found to possess considerable kinetic stability. The three cyclic species **7**, **7′**, and **8** are mainly characterized by the divalent carbene feature, whereas **5** predominantly features the cumulenic |Si═C═Si═P|• containing sp-hybridized silicon bonding. However, the silicon−phosphorus and silicon−carbon triply bonded forms |Si═C•−Si≡P| and •Si≡C−Si≡P| contribute much less and almost none, respectively. The lowest energy isomer **1** should represent an interesting cyclic Si-, C-, and P-containing radical in both the laboratory and interstellar space. The high-energy isomers **5**, **7**, **7′**, and **8** could be produced during the vaporization of P-doped SiC clusters before conversion to **1**. They may be observable even in low-temperature environments. The present study is expected to provide a useful basis for future laboratory and interstellar identification of the Si_2CP radical.

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