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# Predicting potential stable isomers on the singlet surface of the [H,P,C,S] system by the MP2 and QCISD(T) methods

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**Abstract** A detailed singlet potential energy surface of [H,P,C,S] system is investigated by means of the MP2 and QCISD(T) methods. Eight isomers are located on the potential energy surface, and at the final QCISD(T)/6-311++G(3df,2p)//MP2/6-311++G(d,p) level with zero-point energy correction, the chainlike isomer HPCS is found to be kinetically and thermodynamically the most stable species followed by the chainlike HSCP, planar three-membered ring HC(S)P, chainlike HCPS, and stereo three-membered ring HP(C)S, which are predicted to be also kinetically stable isomers and should be experimentally observable provided that accurate experimental conditions are available. The dissociation processes from the kinetically and thermodynamically most stable species HPCS to the low-lying molecular dissociation fragments are not more favorable in energy than the isomerization process from HPCS to HSCP. Therefore, the experimental observation for potential isomer HSCP with  $C \equiv P$  triple bond is possible by means of photoisomerization technology using HPCS as precursor.

**Keywords** [H,P,C,S] system · Potential energy surface · Isomerization

## 1 Introduction

The species HNCO (isocyanic acid) and its sulfur and phosphorous analogues, HNCS (isothiocyanic acid) and HPCO (phosphaketene), have attracted more attention because they are not only simple organic molecules and significant intermediates but also play important roles in atmosphere chemistry and combustion chemistry [1,2]. Many experimental and theoretical studies have been performed for exploring the spectra, structures, stabilities, and dissociation products of the [H,N,C,O] [3–9], [H,N,C,S] [10–22], and [H,P,C,O] [9,23–27] systems. More recently, another analogue system

[H,N,Si,O] has been well studied by Bhanuprakash et al. on its potential energy surface, including many intersystem crossings between the singlet and triplet minima [28]. The excellent work effectively extends the analogous family of [H,N,C,O], especially, the members with the silicon element. But for another member of the [H,N,C,O] family, [H,P,C,S], the phosphorous analog system of [H,N,C,S], which has been proposed to be possible important candidate in interstellar observation [29], is much less known so far about its isomer structures and stabilities.

The [H,P,C,S] system was chosen as our goal of investigation in this work for the following reasons. First, several cyclic isomers of the [H,N,C,O], [H,P,C,O], and [H,N,Si,O] systems were located in the previous studies [4,6,23,28], but no cyclic species were found in the [H,N,C,S] system [10]. Therefore, some differences in the structure and bonding among these analog systems are expected to exist. And then, in view of the higher hypervalent capacities of phosphorous and sulfur than those of nitrogen and oxygen, respectively, one can expect some cyclic isomers to exist in the [H,P,C,S] system. Second, the isomers HPCO and HPCS have been considered as possible interstellar molecules in a previous study [29] in view of the interstellar existence of the HNCO molecule [30–32]. Dimur et al. have studied the species HPCO and HPCS for exploring their theoretical IR spectra and rotational constants [29]. As a result, some available spectroscopic information was suggested to help their future laboratory and spatial identification. Furthermore, the [H,P,C,O] system has also been theoretically investigated on its potential energy surface and dissociation pathways [23,29] for predicting some structural and bonding knowledge of the isomers. Therefore, some information about the geometric structures and stabilities of [H,P,C,S] isomers is necessary and helpful for understanding their existence or not in space or in laboratory. And last, the [H,P,C,S] system may have some isomers with carbon–phosphorous multiple bonding. The chemistry of carbon–phosphorous multiple bonding has been attracting growing interest in comparison to the corresponding carbon–nitrogen multiple bonding [26,33,34]. In particular, the preparation and properties of compounds with

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C  $\equiv$  P triple bond have attracted more attention [34–38] since the first compound containing a triple bond between phosphorous and carbon was found by Gier in 1961 [39]. Many compounds with C  $\equiv$  P triple bond have been experimentally characterized and theoretically investigated [34, 36–53], including the surprisingly stable anions P  $\equiv$  C – O<sup>−</sup> and P  $\equiv$  C – S<sup>−</sup> from lithium bis(trimethylsilyl)-phosphanide and the esters of carbonic or thiocarbonic acid [50,51], respectively. Then, the isomer HSCP, a species containing a C  $\equiv$  P triple bond and the HS- group or as the protonated species of the anion, P  $\equiv$  C – S<sup>−</sup>, may be considered as a stable molecule in laboratory or interstellar space.

Therefore, a detailed knowledge about structures, stabilities, bonding, isomerization properties of various HPCS isomers, and molecular dissociation mechanism is very desirable and helpful for understanding the future experiments and for addressing the chemistry of these interesting species containing carbon–phosphorus triple bond.

Although reasonable valence structures may be drawn for several [H,P,C,S] isomers, relatively little is known about these compounds. Up to now, to our knowledge, only one investigation on the theoretical study of the isomer HPCS is available [29], in which Dimur and Puzat gave the theoretical rotational constants and IR band, and none of the HPCS isomers was isolated experimentally. But the existence of the surprisingly stable P  $\equiv$  C – S<sup>−</sup> anion has been suggested experimentally [50,51], which makes us believe that its protonated product and relevant isomers may be stable. Therefore, in this paper, we report a detailed computational study on the singlet potential energy surface of [H,P,C,S] system with attempts to investigate the possible isomer forms, bonding, and fragmentation patterns and to predict the potential isomers that are kinetically stable.

## 2 Computational details

All computations were carried out with the Gaussian98 program package [54] running on the SGI/Origin300 server. The optimized geometries of molecular fragments, isomers, and the interconversion transition states of the [H,P,C,S] system were obtained at the MP2/6-311++G(d,p) level of theory [55, 56]. The nature of stationary points is confirmed by calculating their vibrational frequencies at the MP2/6-311++G(d,p) level, i.e., isomers with all real frequencies and transition states with only one imaginary frequency. In order to obtain more reliable energies, the MP2/6-311++G(d,p)-optimized geometries are further employed to calculate single-point energies using the quadratic configuration interaction calculation method QCISD(T) [57,58] with the 6-311++G(3df,2p) basis set. Unless otherwise noted, all energies used in the following discussions are calculated at the single-point QCISD(T)/6-311++G(3df,2p)//MP2/6-311++G(d,p) level with zero-point vibrational energy correction. In order to confirm whether the transition states connect the correct isomers, intrinsic reaction coordinate (IRC) calculations [59,60] are carried out at the MP2/6-311++G(d,p) level of theory.

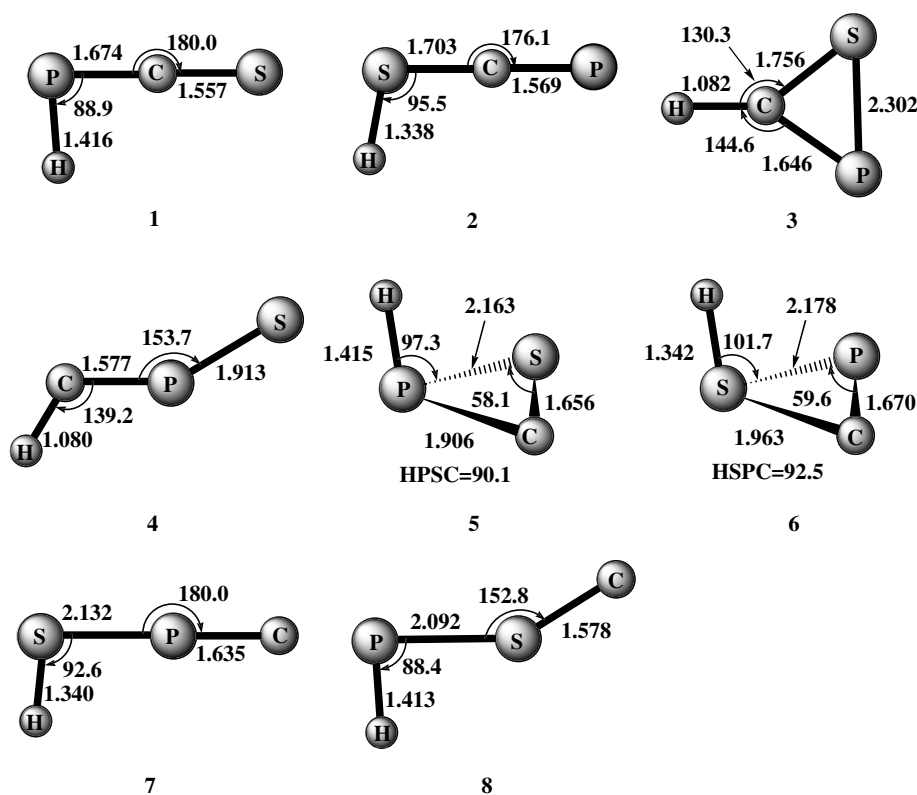
## 3 Results and discussion

### 3.1 Isomers

For such a small tetra-atomic molecular system, [H,P,C,S], it is feasible to search for possible isomeric forms on its potential energy surface. We have performed geometrical surveys on nearly all possible isomers including linear, chainlike, cyclic, and stereo structures followed by vibrational analysis to confirm whether the obtained structure is a local minimum or not. The calculated results indicate that eight isomers were located successfully on the potential energy surface of [H,P,C,S] singlet system. The optimized geometric parameters of isomers are shown in Fig. 1, while their total energies, zero-point energies, and relative energies are listed in Table 1. From Table 1, we can obtain the energetic ordering of the eight [H,P,C,S] energy minima. Generally, the species with lower total energy has higher thermodynamical stability. At the single-point QCISD(T)/6-311++G(3df,2p) level with zero-point energies inclusion, the thermodynamical stability order is then **1**(0.00) > **2**(0.43) > **3**(9.59) > **4**(27.50) > **5**(37.41) > **6**(44.25) > **7**(66.57) > **8**(76.32). The values in parentheses are relative energies in kcal/mol with respect to **1**. It is clear that the isomer **1** is thermodynamically the most stable species.

In isomer **1**, the heavy atom chain PCS is 180.0°, and the  $\angle$ HPC is 88.9°. The result suggests that the PCS is a linear chain at the MP2/6-311++G(d,p) level, which is similar to the NCS chain with  $\angle$ NCS = 179.9 in the HNCS molecule. But at the same level, the HNCO isomer is found to have a trans bent equilibrium structure with the NCO angle of 171.5°, being in accordance with the previous experimental determination [61]. The calculated phosphorous–carbon bond length (1.674 Å) in **1** is slightly longer than the P=C double bond length [1.650 Å at the MP2/6-311++G(d,p) level in HP = CH<sub>2</sub>], but shorter than the carbon–phosphorous single bond distance 1.856 Å in the species PH<sub>2</sub> – CH<sub>3</sub>. Therefore, the bond can be considered as a double bond with some single bond contribution. Note that the phosphorous–carbon bond length (1.674 Å) in **1** is slightly shorter than that (1.685 Å) in the species HPCO [23], which results from the stronger electronegativity of the oxygen atom than that of the sulfur atom. The carbon–sulfur bond (1.557 Å) in isomer **1** can be regarded as an intermediate between carbon–sulfur double and triple bonds by comprising with bond lengths 1.614 Å in H<sub>2</sub>C = S and 1.540 Å in CS molecules, respectively, at the MP2/6-311++G(d,p) level. Therefore, the HPCS species can be viewed as two resonance structures, the H – P = C = S form with a CP double bond characteristic and H – P – C  $\equiv$  S form with a CP single bonding nature. Of course, the former has more weight in the two forms considering the relevant bond lengths. The structural nature of the isomer HPCS has some distinctness from its oxygen analog HPCO, in which only the H – P = C = O form was suggested [23,29].

The second low-lying isomer **2** is a chainlike HSCP connectivity with 1.703 Å sulfur–carbon and 1.569 Å carbon–phosphorus bond distances. The SCP heavy atom chain is



**Fig. 1** Calculated structures of molecular fragments and isomers of the [H,P,C,S] system at the MP2/6-311++G(d,p) level of theory. Bond lengths are in angstroms, and bond angles in degrees

**Table 1** Total energies (TE, in au), single-point energies (SE, in au), zero-point vibrational energies (ZPVE, in hartree/particle), and relative energies (RE, in kcal/mol) of isomers, molecular dissociation fragments, and transition states of the [H,P,C,S] system

Species	TE <sup>a</sup> /Hartree	SE <sup>b</sup> /Hartree	ZPVE <sup>a</sup> /Hartree	RE <sup>c</sup> /kcal/mol
<b>1</b>	-777.06282	-777.21928	0.01365	0.00
<b>2</b>	-777.06714	-777.21936	0.01441	0.43
<b>3</b>	-777.04463	-777.20698	0.01663	9.59
<b>4</b>	-777.00633	-777.17676	0.01495	27.50
<b>5</b>	-776.98820	-777.15984	0.01381	37.41
<b>6</b>	-776.98068	-777.14930	0.01419	44.25
<b>7</b>	-776.94180	-777.11499	0.01233	64.62
<b>8</b>	-776.91421	-777.09566	0.01164	76.32
<b>TS1/2*</b>	-776.93540	-777.10640	0.01008	68.60
<b>TS1/2</b>	-777.00211	-777.16501	0.01246	33.31
<b>TS1/3</b>	-776.98576	-777.15074	0.01438	43.48
<b>TS2/6</b>	-776.96527	-777.13394	0.01315	53.25
<b>TS3/4</b>	-776.95752	-777.14008	0.01405	49.96
<b>TS3/4*</b>	-776.86899	-777.04656	0.01425	108.77
<b>TS3/7</b>	-776.93318	-777.11336	0.01192	65.39
<b>TS2/7</b>	-776.93349	-777.11465	0.01211	64.69
<b>TS5/8</b>	-776.90883	-777.08952	0.01078	79.63
<b>TS5/8*</b>	-776.90586	-777.08234	0.01116	84.38
<b>TS1/5</b>	-776.94981	-777.12070	0.01224	60.98
<b>TS1/5*</b>	-776.94439	-777.11684	0.01265	63.66
<b>TS3/5</b>	-776.95108	-777.12091	0.01086	59.98
<b>TS3/6</b>	-776.95292	-777.12064	0.01117	60.35
<b>P<sub>1</sub>PH(<sup>1</sup>Π) + CS(<sup>1</sup>Σ)</b>	-776.89762	-777.06843	0.00869	91.55
<b>P<sub>2</sub>PH(<sup>3</sup>Σ) + CS(<sup>1</sup>Σ)</b>	-776.95893	-777.11301	0.00862	63.54
<b>P<sub>3</sub>CH(<sup>2</sup>Π) + PS(<sup>2</sup>Π)</b>	-776.84118	-777.01887	0.00918	122.95
<b>P<sub>4</sub>SH(<sup>2</sup>Π) + CP(<sup>2</sup>Σ)</b>	-776.86963	-777.02720	0.00920	117.74

<sup>a</sup> At the MP2/6-311++G(d,p) level

<sup>b</sup> At the QCISD(T)/6-311++G(3df,2p)//MP2/6-311++G(d,p) level

<sup>c</sup> At the QCISD(T)/6-311++G(3df,2p)//MP2/6-311++G(d,p) level with zero-point vibrational energy correction

almost collinear with the angle SCP of  $176.1^\circ$ , being somewhat less than the OCN value of  $180.0$  in species HOCN at the same theory level. The angle HSC has a value of  $95.5^\circ$  in structure **2**, resulting from the effect of lone-paired electrons of sulfur atom on the  $\sigma_{S-H}$  bond electrons. The CP bond length ( $1.569 \text{ \AA}$ ) in HSCP is in good agreement with the value of  $1.567 \text{ \AA}$  in the HOCN species [23], and slightly longer than the experimental value of  $1.544 \text{ \AA}$  in the species  $\text{CH}_3\text{CP}$  by Kroto et al. [62]. Since the normal C=P double and C  $\equiv$  P triple bond distances at the MP2/6-311++G(d,p) level are  $1.650 \text{ \AA}$  (in  $\text{HP} = \text{CH}_2$ ) and  $1.559 \text{ \AA}$  (in  $\text{H-C} \equiv \text{P}$ ), respectively, species **2** can be regarded as a  $\text{H-S-C} \equiv \text{P}$  form. Therefore, from the structural point of view, HOCN and HSCP are two typical molecules with C  $\equiv$  P triple bond, which can be formed from the substitution of H in HCP by HO and HS, respectively.

The low-lying species **3**, which is predicted to be less stable than isomer **1** by  $9.59 \text{ kcal/mol}$ , has a HC(P)S form containing a CSP three-membered ring with a C=P double bond ( $1.646 \text{ \AA}$ ) and a somewhat weak P-S single bond ( $2.302 \text{ \AA}$ ) considering a normal C=P double bond length of  $1.650 \text{ \AA}$  in  $\text{HP} = \text{CH}_2$ , a C  $\equiv$  P triple bond length of  $1.559 \text{ \AA}$  in HCP, and a P-S single bond length of  $2.135 \text{ \AA}$  in  $\text{PH}_2 - \text{SH}$ . The CS bond ( $1.756 \text{ \AA}$ ) in isomer **3** should be viewed as a slightly strong single bond considering the normal C-S single and C=S double bond lengths of  $1.813$  and  $1.614 \text{ \AA}$  in  $\text{H}_2\text{C} - \text{SH}$  and  $\text{H}_2\text{C} = \text{S}$ , respectively, at the MP2/6-311++G(d,p) level of theory. Furthermore, the values of  $\angle\text{HCP}$  ( $144.6^\circ$ ) and  $\angle\text{HCS}$  ( $130.3^\circ$ ) in **3** are very close to the corresponding values of  $\angle\text{HCP}$  ( $149.9^\circ$ ) and  $\angle\text{HCO}$  ( $125.7^\circ$ ) in the species HC(P)O. But considering the PO bond distance  $2.009 \text{ \AA}$  in species HC(P)O [23], we cannot suggest a PCO three-membered ring to be formed in isomer HC(P)O. Therefore, the molecule HC(P)S is a species with a three-membered ring, but for the isomer HC(P)O, it is a normal branching chain species [23].

Isomer **4** possesses a *trans*-HCPS structure with the angle CPS of  $153.7^\circ$ , similar to the species HCPO [23], in which the angle CPO is  $153.5^\circ$ . It lies  $27.50 \text{ kcal/mol}$  above isomer **1**. The phosphorus-sulfur bond ( $1.913 \text{ \AA}$ ) can be considered as a double bond with some triple bond contribution in view of the P=S double bond distance  $1.947 \text{ \AA}$  in the  $\text{H-P}=\text{S}$  molecule at the MP2/6-311++G(d,p) level. But the carbon-phosphorus bond length ( $1.577 \text{ \AA}$ ) is shorter than the C=P double bond distance  $1.650 \text{ \AA}$  in species  $\text{CH}_2 = \text{PH}$  and very close to the C  $\equiv$  P triple bond distance  $1.559 \text{ \AA}$  (in  $\text{H-C} \equiv \text{P}$ ). Therefore, we think that it has some triple bond characteristics. Accordingly, the isomer *trans*-HCPS can be written as a  $\text{H-C} \equiv \text{P} \equiv \text{S}$  form with two  $\Pi_{3c}^{4e}$  bonds. But in the HCPO isomer, the phosphorus-oxygen bond is a normal double bond. The differences in PO and PS bonding result from the stronger hypervalence characteristics of the sulfur atom rather than the oxygen [23, 29].

The low-lying isomer **5** is higher in energy than isomer **1** by  $37.41 \text{ kcal/mol}$ , and is a stereo HP(S)C form with a PSC three-membered ring and an exocyclic HP bonding. The calculated results show that the CS bond ( $1.656 \text{ \AA}$ ) is a standard

double bond, while the PS and CP ( $2.163 \text{ \AA}$  and  $1.906 \text{ \AA}$ , respectively) bonds are found to have obvious weak single bonding characteristics.

The remaining isomers **6**, **7**, and **8** lie higher in energy, and in view of the higher energies and lower kinetic stability (as discussed in Sect. 3.2), their structural details are not presented here. We expect them to be of minor importance.

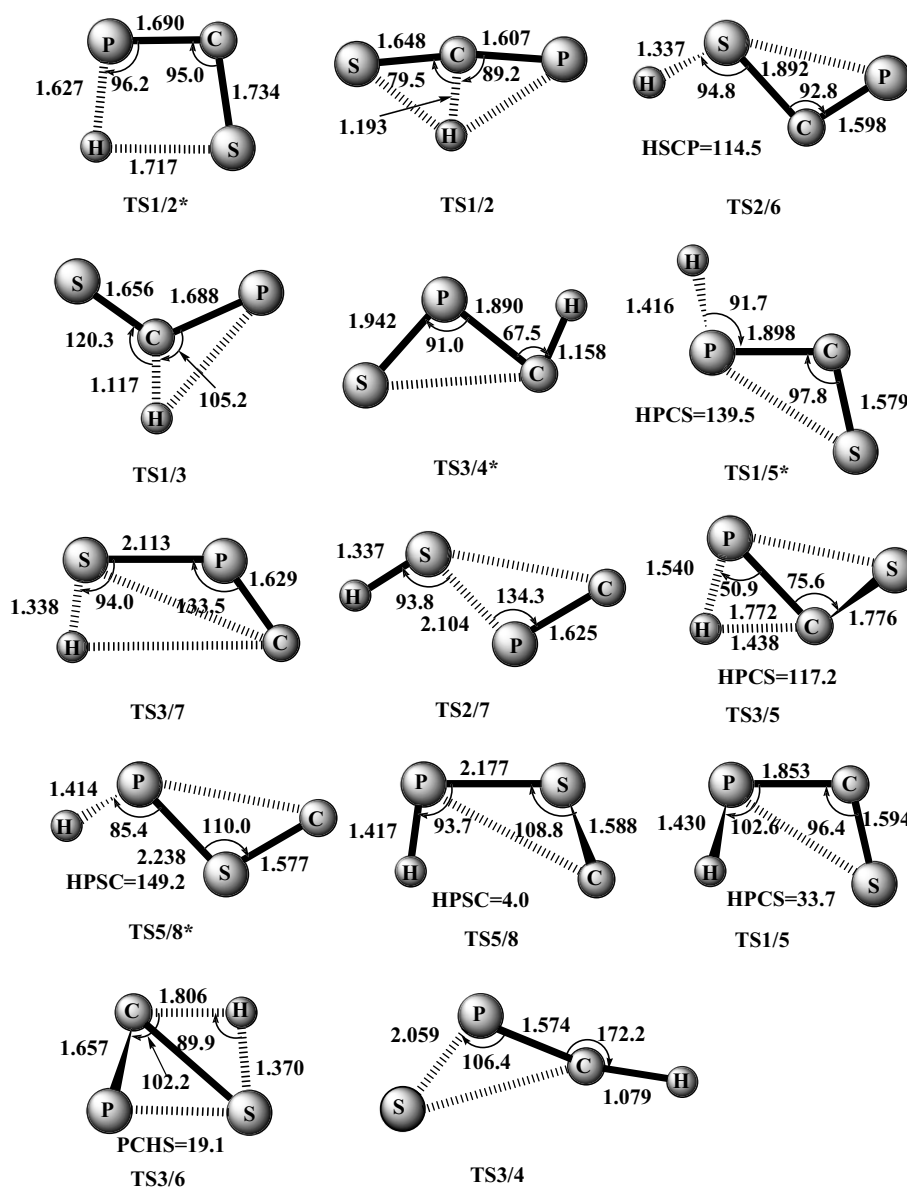
It should be pointed out that three cyclic isomer, species **3**, **5**, and **6**, containing PCS three-membered rings with exocyclic CH, PH, and SH bonding, respectively, were located on the potential energy surface. Furthermore, no chainlike HCSP structural isomer was found in the optimizations, but in the [H,P,C,O] system, a kinetically unstable chainlike minimum HCOP has been suggested theoretically [23].

### 3.2 Kinetic stability and isomerization pathways

Let us turn our attention to the kinetic stabilities of the various optimized [H,P,C,S] system isomers. Fourteen inter-conversion transition states were located on the potential energy surface, and their total, zero-point, and relative energies are given in Table 1, while the detailed geometries are summarized in Fig. 2. Note that **TSm/n** denotes the transition state connecting the species **m** and **n**. Their connections are checked by IRC calculations at the MP2/6-311++G(d,p) level. By means of these obtained isomers and transition states, a schematic potential energy surface is plotted in Fig. 3, in which, for simplicity, the structural details of the transition state are omitted. Furthermore, the possible several molecular dissociation fragments are also shown on the surface.

Here, we will briefly discuss the kinetic stability of the located isomers in terms of isomerizations and direct dissociation channels. The lowest-lying isomer **1** is kinetically the most stable species with the smallest reaction barrier of  $33.31 \text{ kcal/mol}$ , corresponding to the conversion of **1**  $\rightarrow$  **2** via a direct H-shift transition state **TS1/2**. The isomers **2**, **3**, **4**, and **5** have comparable smallest isomerization barriers ( $32.88 \text{ kcal/mol}$  for **2**  $\rightarrow$  **1**,  $33.89 \text{ kcal/mol}$  for **3**  $\rightarrow$  **1**,  $22.46 \text{ kcal/mol}$  for **4**  $\rightarrow$  **3**, and  $22.57 \text{ kcal/mol}$  for **5**  $\rightarrow$  **3**). Accordingly, the five isomers should be kinetically stable species in controlled experimental conditions. The remaining isomers **6**, **7**, and **8** may be considered as kinetically unstable toward isomerizations since the corresponding reaction barriers are just  $9.00$  (**6**  $\rightarrow$  **1**),  $0.07$  (**7**  $\rightarrow$  **2**), and  $3.31$  (**8**  $\rightarrow$  **5**)  $\text{ kcal/mol}$ , respectively.

All predicted isomerization channels on the potential energy surface of the [H,P,C,S] system can happen via normal single-bond rupture or formation processes, such as H-shift transition states (**TS1/2\***, **TS1/3**, **TS3/5**, and **TS3/6**), ring-open or ring-close transition states (**TS2/6**, **TS3/4\***, **TS5/8\***, **TS5/8**, **TS1/5**, and **TS3/4**), and group-exchange transition state (**TS2/7** for  $-\text{CP} \leftrightarrow -\text{PC}$ ). The coinstantaneous ruptures of two bonds, C-H and C-S, are included in the isomerization channel **3**  $\rightarrow$  **7** via **TS3/7** with a higher reaction energy. It is worth mentioning that the isomerization **2**  $\rightarrow$  **1** via H-shift



**Fig. 2** Calculated transition state structures of the [H,P,C,S] system at the MP2/6-311++G(d,p) level of theory. Bond lengths are in angstroms, and bond angles in degrees

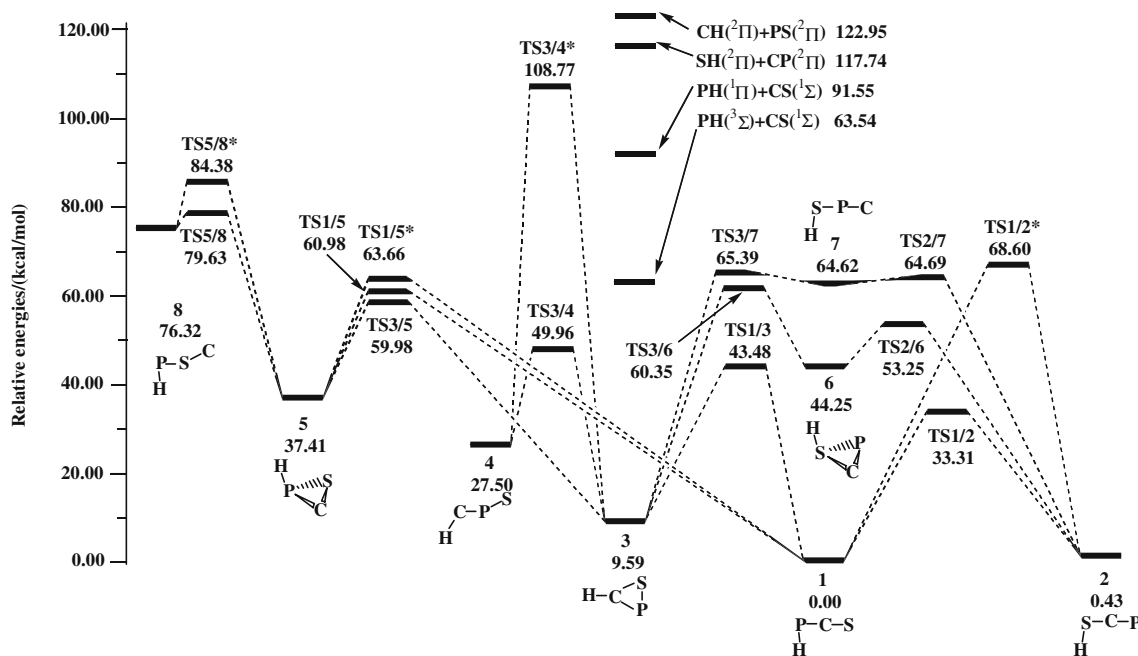
transition state **TS1/2** includes the formation of a C-H bond followed by its rupture.

Note that several H-shift pathways from sulfur to phosphorus with lower barriers via possible four-membered ring transition states are expected to exist in the isomerization process **2**  $\rightarrow$  **1**. But the located two cyclic transition states, **TS1/2** and **TS1/2\***, are slightly higher in energy than those expected. We also attempted to optimize a planar S-shift transition state that connects isomers **4** and **3** with lower isomerization barrier, but all attempts failed. Furthermore, a three-membered ring H-shift transition state (**3**  $\rightarrow$  **2**) from carbon to sulfur was believed to exist, but the optimized stationary point has two imaginary vibrational frequencies, and the relaxation of symmetry leads to the transition state **TS3/6**.

3.3 Isomer dissociation channels, comparison with analogous systems, and implication for possible experiments

As discussed above, the isomers **1**, **2**, **3**, **4**, and **5** are suggested to be kinetically stable, and should be experimentally observable. For favoring the further experimental observation, their harmonic vibrational frequencies, dipolar moments, and rotational constants are listed in Table 2.

As shown in Fig. 3, the four lowest-lying molecular fragment patterns,  $\text{P}_1\text{HP}({}^3\Sigma) + \text{CS}({}^1\Sigma)$ ,  $\text{P}_2\text{HP}({}^1\Pi) + \text{CS}({}^1\Sigma)$ ,  $\text{P}_3\text{SH}({}^2\Pi) + \text{CP}({}^2\Pi)$ , and  $\text{P}_4\text{CH}({}^2\Pi) + \text{PS}({}^2\Pi)$  at 63.54, 91.55, 117.74, and 122.95 kcal/mol above isomer **1**, respectively, are listed on the potential energy surface. Other



**Fig. 3** Schematic reaction potential energy profile of the [H,P,C,S] system at the QCISD(T)/6-311++G(3df,2p)//MP2/6-311++G(d,p) level of theory with zero-point vibrational energy correction

**Table 2** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ), infrared intensities ( $\text{km/mol}$ ) (in parentheses), dipole moment (Debye), and rotational constants (GHz) of the isomers of the [H,P,C,S] system at the MP2/6-311++G(d,p) level of theory

Species	Frequencies $\text{cm}^{-1}$ (infrared intensity/KM/mole)	Rotational (GHz) constant	Dipole moment (Debye)
1	294.7(3.0), 342.9(14.1), 607.7(0.1), 812.9(37.8), 1504.6(333.6), 2460.8(23.5)	253.2149, 3.0331, 2.9972	0.63
2	269.2(9.5), 291.0(18.0), 554.9(2.8), 956.1(26.2), 1504.2(52.8), 2772.3(4.7)	292.5116, 2.9460, 2.9167	1.21
3	360.8(5.3), 729.3(68.8), 732.5(62.6), 1026.6(2.5), 1162.3(13.3), 3278.0(6.5)	25.0903, 6.0286, 4.8607	2.34
4	244.8(7.1), 501.6(90.7), 520.5(32.3), 641.1(35.1), 1276.2(45.3), 3341.9(59.6)	232.8397, 3.9763, 3.9096	2.46
5	475.8(9.1), 528.4(16.8), 677.1(11.6), 909.9(14.8), 999.4(52.8), 2459.5(89.7)	23.1343, 6.5297 5.2957	1.96

dissociation products with higher energies are omitted in view of minor importance. We paid a lot of work to search for the direct dissociation transition states of relevant isomers on the potential energy surface, but unfortunately, no such saddle points were located. The calculated results indicate that the listed four direct dissociation products are somewhat higher in energy than several important transition states connecting isomers **1**, **2**, **3**, **4**, and **5**. For example, the possible fragment patterns  $\mathbf{P}_1$  and  $\mathbf{P}_2$  are 63.54 and 91.55 kcal/mol higher than the isomer **1**, respectively, indicating that the dissociation processes are more unfavorable in energy than the isomerizations  $1 \rightarrow 2$  and  $1 \rightarrow 3$  with isomerization barriers of 33.31 and 43.48 kcal/mol, respectively. Therefore, the experimental observation of the isomer **2** is possible by means of photoisomerization from **1** to **2**. The experimental technology has been successfully applied to the observation of isomers HSCN and HSNc from precursor HNCS [19]. But the experimental method is unsuitable for the preparation of

the species HOCP (at 20.3 kcal/mol, relative to the isomer HPCO [23]) from the precursor HPCO. Because the energies of the direct dissociation fragments  $\text{HP}(^1\Pi) + \text{CO}(^1\Sigma)$  (at 60.4 kcal/mol) and spin-conserved  $\text{HP}(^3\Sigma) + \text{CO}(^1\Sigma)$  (at 32.4 kcal/mol) are lower than the isomerization barriers 66.9 and 106.8 kcal/mol from HPCO to HOCP via two four-membered ring transition states, the direct dissociation of HPCO molecule is more favorable than isomerizations toward other isomers. And thus, the molecule HPCO cannot be considered as the appropriate precursor of reactions yielding species HOCP. For the HNCO system, no direct isomerization transition states connecting species HNCO and HOCN were found on the singlet surface in previous investigations [2, 4].

As described in Sect. 3.2, species **1**, **2**, **3**, **4**, and **5** are predicted to be kinetically stable isomers by means of theoretical methods. In the previous studies, the existence of the molecules HNCO, HCNO, HONC, and HOCN has been suggested in the [H,N,C,O] system [4]. For the [H,N,C,S] system, the

chainlike HNCS radical has been identified by many investigators [13–15], and species HCNS, HSNC, and HSCN have also been predicted to be kinetically stable in Bak's theoretical work [10]. Very recently, the HSCN and HSNC isomers were experimentally observed by Wierzejewska and Mielke [19]. But for the [H,P,C,O] system, only the chainlike HPCO isomer is experimentally available [24,29], and the other two chainlike species HOCP and HCPO were theoretically predicted to be kinetically stable isomers and should be experimentally observed [23]. It should be noted that no cyclic isomers were considered in [H,P,C,O] system.

For [H,P,C,S] system, the identification of the kinetically and thermodynamically stable isomer HPCS is believed to be reasonable by comparison with the existence of the species HNCO, HPCO, and HNCS. Furthermore, based on the observed surprising stability of  $^-$ SCP anion [51] and the predicted higher stabilities of HSCN, HOCP, and HOCN, we believe that the second low-lying species 2, H – S – C  $\equiv$  P, the protonation product of well experimentally characterized  $^-$ SCP anion, should be detected in experiments, provided that appropriate precursors are available. It should be pointed out that no cyclic isomers were found to be kinetically stable or to exist for the [H,N,C,O], [H,N,C,S], and [H,P,C,O] systems. But in the [H,P,C,S] system, two cyclic isomers 3 and 5 were predicted to be kinetically stable species. The stabilities of the two isomers are believed to come from the normal bonding of sulfur and phosphorus atoms with stronger hypervalent capacity. For the oxygen atom, PCO or NCO three-membered rings cannot be formed normally and stably in corresponding species, resulting from the lower hypervalent capacity and lesser covalence radius of the oxygen atom. For the isomers 4 and 5, the experimental observation in future possibly requires quite accurate experimental conditions because of the low reaction barriers of 22.46 and 22.57 kcal/mol, respectively.

#### 4 Conclusion

A detailed singlet potential energy surface of the [H,P,C,S] system was investigated at the MP2/6-311++G(d,p) and QCISD(T)/6-311++G(3df,2p) (single-point) levels. The global minimum was found to be the chainlike HPCS 1, followed by the chainlike isomer HSCP (2), PCS-three-membered isomers HC(P)S 3 and HCPS 4, and stereo isomer HP(S)C 5 at 0.43, 9.59, 27.50, and 37.41 kcal/mol, respectively, with respect to 1. The structural and bonding properties of the relevant species were analyzed. The calculated results indicate that isomers 1, 2, 3, 4, and 5 are stable species, and they should be experimentally observable due to their high kinetic stabilities. Furthermore, the results also show that isomer 1 can dissociate into  $P_1$  and  $P_2$  with 63.54 and 91.55 kcal/mol dissociation energies, respectively. But the dissociation processes are not more favorable in energy than the isomerization processes HPCS  $\rightarrow$  HSCP and HPCS  $\rightarrow$  HC(S)P. Therefore, the experimental observation of isomer

HSCP is possible by means of a photoisomerization method from HPCS to HSCP.

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