

Two Novel Isomers of HPS₃ System

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Abstract: Two new isomers of HPS₃ system, HP(S)S₂ and HSSPS, are predicted by means of B3LYP method with 6-311++G(3df,3pd) basis set. The two isomers can isomerize into thermodynamically the most stable species HSPS₂, which have been experimentally identified, with relatively higher reaction barriers. In view of their higher thermodynamical and kinetic stability and the experimental observation for HP(O)O₂ and HOOPO in previous study, we can reasonably believe that the two species can be spectroscopically characterized in future experiments.

Keywords: HPS₃ system, stability, isomer, isomerization.

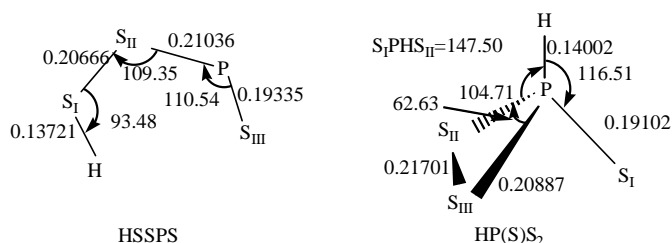
A few experimental studies about simple thiohydrides of phosphorus and pure phosphorus-sulfur clusters have been carried out, and several species have been identified, such as P_xS_y¹, H₂PSH², H₃PS₄³, HSPH₂, HPS₂, and HSPS₂⁴, while some relative systems have been theoretically studied^{5,6}. In an experimental study performed by Mielke and Andrews⁴, argon/phosphine samples were reacted with discharged S₈/Ar mixtures and the products were trapped in solid argon for infrared spectroscopic analysis, and three phosphorus thiohydrides, HSPH₂, HPSS, and HSPS₂, were characterized. The new species, HSPS₂, an isomer of HPS₃ system, was predicted to be a planar molecule with HSP(S)S connectivity. Up to now, no other isomers of HPS₃ system were theoretically and experimentally suggested. But in an earlier experimental study for the oxygen analog of HPS₃, HPO₃ system, Withnall and Andrews suggested the existence of three isomers, HOPO₂, HP(O)O₂, and HOOPO⁷. Then, can species HP(S)S₂ and HSSPS exist stably in experimental system? A detailed knowledge about the structure, stability, bonding and isomerization properties of HP(S)S₂ and HSSPS is very desirable and helpful for comparing with the available experiment of HPO₃ system and for addressing the chemistry of these interesting phosphorus-sulfur-containing species. Therefore, in this letter, we report a detailed computational study using density function theory on isomers HP(S)S₂ and HSSPS with an attempt to predict their structures and stability and the nature of bonding.

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All computations are carried out with Gaussian98 program package running on the SGI/Origin300 server. All stationary points and zero-point energies are obtained at the B3LYP/6-311++G(3df,3pd) level of theory. The calculated geometries of isomers HP(S)S₂ and HSSPS are shown in **Figure 1**. Intrinsic reaction coordinate (IRC) calculations are carried out at the same level. All energies used in the letter are at the B3LYP/6-311++G(3df,3pd) level with zero-point energies included.

In isomer HP(S)S₂, which lie 83.42 kJ/mol higher than thermodynamically the most stable planar isomer HSPS₂(C_s) and has a C_s symmetry with ¹A' electronic state and PSS three-membered ring, the length of two equivalent P-S bonds is 0.20887 nm. Based on the comparison with P-S single bond length (0.21417 nm in H₂PSH at the B3LYP/6-311++G(3df,3pd) level), we can consider the two bonds as single bond. The remaining P-S bond (0.19102 nm) can be regarded as a double bond for the normal P=S double bond length is 0.19326 nm in species HPS at the B3LYP/6-311++G(3df,3pd) level. The S-S bond (0.21701 nm) in isomer HP(S)S₂ can be suggested as a slightly weak single bond in view of normal single bond distance 0.20735 nm in molecule HSSH at the B3LYP/6-311++G(3df,3pd) level. The calculated results indicated that isomer HP(S)S₂ can isomerize into a stereo species HSPS₂(C_s) *via* a hydrogen shift channel from P atom to S atom followed by next isomerization to thermodynamically the most stable planar isomer HSPS₂(C_s) which have been identified by previous experiment⁴. Because the isomerization barrier is 167.30 kJ/mol, and the dissociation limits are also very high, we can considered isomer HP(S)S₂ as kinetically stable species.

Figure 1 Predicted two isomers of HPS₃ system at B3LYP/6-311++G(3df,3pd) level of theory.



Bond lengths are in nanometers, and bond angles in degrees

Planar species HSSPS has a bent chain structure with C_s symmetry and is higher in energy than thermodynamically the most stable planar isomer HSPS₂(C_s) by 44.61 kJ/mol. The terminal P-S bond distance 0.19335 nm suggests it a normal double bond structure, while the middle P-S and S-S bonds should be considered as single bond for the 0.21036 nm and 0.20666 nm bond lengths, respectively. Theoretical results in present study show that isomer HSSPS can also isomerize into the most stable planar isomer HSPS₂(C_s) *via* a reaction pathway including several isomerizations. Because the reaction barrier (203.24 kJ/mol) is somewhat higher, the transition reaction along the channel hardly happens in thermochemistry system. Furthermore, the dissociation energies of several fragment channels are somewhat higher than the isomerization barriers. Therefore, species HSSPS is a kinetically stable isomer.

As discussed above, species HP(S)S₂ and HSSPS have higher thermodynamical and kinetic stability, and are identified to have the similar structure of oxygen analogs HP(O)O₂ and HOOP⁷, we hope that the isomers HP(S)S₂ and HSSPS can be spectroscopically characterized in future experiments.

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