Structures and Stability of HNS$_2$ Isomers

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Potential energy surface of HNS$_2$ is investigated by means of second-order Moller-Plesset perturbation theory (MP2) and QCISD(T) (single-point) methods. At final QCISD (T)/6-311++ G(3df,2p)//MP2/6-311++ G(d,p) level with zero-point vibrational energies included, cis-HNSS is found to be global minimum on the potential energy surface, followed by low-lying trans-HNSS, HN(S)S(C_{2v}), cis-HSNS, cis-HSSN, trans-HSNS, trans-HSSN, and HN(S)S(C_s) by 13.46, 66.92, 78.25, 80.38, 81.22, 81.38 and 86.40 kJ/mol, respectively. A new high-lying HS(N)S isomer with C_s symmetry is located on the potential energy surface. The kinetic stabilities of all isomers are predicted. Comparisons are made for HNS$_2$ with its analogues, HNO$_2$, HPS$_2$ and HPO$_2$. The causes that lead to the differences between HNS$_2$ and its analogues are hypervalent capacity of phosphorus and distinct electronegativities of hydrogen, nitrogen and phosphorus.

Keywords   potential energy surface, HNS$_2$ molecule, isomerization, stability

Introduction

The nitrogen-sulfur containing compounds have attracted much attention in the fields of polymeric materials and atmosphere chemistry.[1-4] And some available experimental and theoretical information was reported about these compounds with H-element or other functional groups.[5,6] In this paper, the hydrogen-nitrogen-sulfur containing compound, HNS$_2$, was selected as our goal because of following reasons. Firstly, species HONO and HOPO play very important roles in the areas of atmospher-

ic chemistry, chemical kinetics, combustion and material synthesis, and many experimental and theoretical studies have been performed on their spectra, geometries, electronic structures and relative stabilities.[6-9] In 1993, Mielke and his coworkers firstly identified HPS$_2$ species,[10] the analogue of HONO and HOPO, by discharging the mixtures of PH$_3$ and S$_8$/Ar, and affirmed the structure to be cis-HPSS.[10] But in our current theoretical study, it was found that besides a small quantity of cis-HPSS, the products in the experiment are mostly a stereo HP(SS) structure with PSS three-membered ring.[11] Up to now, to our knowledge, there is only a literature reported on the structure of isomers of HNS$_2$, which is isovalent with HNO$_2$, HPO$_2$ and HPS$_2$, by Nakamura and his coworkers.[6] Their calculated results indicated that the most stable isomer in HNS$_2$ is cis-HNSS. They also conjectured other several isomers as stable species based on their energies with reference to cis-HNSS, but didn't discuss the kinetic stabilities, and thus, the stabilities of these isomers did not be confirmed. Another reason is that the global minimums on the potential energy surfaces of HNO$_2$, HPO$_2$, HPS$_2$ and HAsO$_2$[12] are trans-HONO, cis-HOPO, trans-HSPS and cis-HOAsO, respectively, and then, which form is the global minimum on the HNS$_2$ potential energy surface? Some differences are expected to exist because different electronegativities between oxygen and sulfur or nitrogen and phosphor, despite they are isovalent. Therefore, the study on the potential energy surface of HNS$_2$ molecule is helpful not only for predicting

the possible isomers and their relative stabilities but also for understanding the nature of the bonding in HBO_2[13], HNO_2, HPO_2, HPS_2 and $HAsO_2$.

Computational methods

The equilibrium geometries and transition states are optimized using analytical gradient methods with second-order Moller-Plesset perturbation theory (MP2) using the split valence 6-311G basis set. In this paper, the structural parameters and zero-point vibrational energies are obtained at MP2/6-311++G(d,p) level of theory. The single-point energies of all stationary points are calculated at QCISD(T)/6-311++ G(3df,2p)//MP2/6-311++ G(d,p) level of theory. QCISD(T) method is one of configuration interaction calculations and includes single and double substitutions with a triple contribution to the energy added. The energies at QCISD(T)/6-311++ G(3df,2p)//MP2/6-311++ G(d,p) level with zero-point vibrational energies inclusion are used on the potential energy surface and in all discussions of the paper. In order to confirm whether the obtained transition states connect the right reactants and products, the intrinsic reaction coordinate (IRC) calculations are carried out at the MP2/6-311++ G(d,p) level of theory. All calculations have been carried out using the GAUSSIAN98 package[14] running on the LEGEND/PIII800EB computer.

Results and discussion

Structures of isomers

The optimized geometry parameters of nine HNS_2 isomers at MP2/6-311++ G(d,p) level of theory are shown in Fig. 1. Isomers 1 and 2 are *cis*- and *trans*-HNSS chainlike species, respectively. The S—S bonds (about 0.19 nm) in 1 and 2 are normal double bond, as discussed by Nakamura.[6] But at MP2/6-311 ++ G(d, p) level, the N—S bonds are about 0.16 nm and longer than that at HF/6-31G(d,p) level by about 0.01 nm, which indicates that they are not normal double bonds predicated by Nakamura,[6] but intermediates between single and double bond. Isomer 3 is planar HN(S)S, which has C_{2v} symmetry and $^1A_1$ electronic state. The N—S bond distance in 3 is 0.16435 nm, and may be regarded as the

intermediate between single and double bond. Species 4 and 6 are *cis*- and *trans*-HSNS chainlike structures, respectively. The terminal N—S bonds (about 0.16 nm) are intermediates between single and double bond. But the H-site S—N bonds (0.16664 nm and 0.17013 nm in 4 and 6, respectively) can be considered as single bonds. And likewise, the S—S bonds in 5 and 7, which are *cis*- and *trans*-HSSN chainlike structural isomers, can be regard as single bonds, despite the bond distances of S—S are somewhat longer than corresponding normal S—S single bond distance. But in 5 and 7, the S—N bond distances are 0.14503 nm and 0.14484 nm, respectively, and somewhat shorter than S—N double bond distance, thus, they have some triple bonding characters. Isomer 8 has a stereo HN(S)S form with NSS three-membered ring and C_s symmetry. Only a cyclic isomer is located on the HNS_2 singlet potential energy surface. In isomer 8, the N—S and S—S bond lengths are 0.17842 nm and 0.20862 nm, and can be considered as single bonds, though the N—S bond length is slightly longer than normal N—S single bond distance. No experimental and theoretical information is available for calculated isomer 9 in this study, which is found firstly to be local energy minimum with all real vibrational frequencies on the potential energy surface of HNS_2. It has a HS(S)N form, and the N—S bond length (0.14672 nm) is somewhat shorter than normal double bond length. Therefore, the bond has some triplet bond characters. But the S—S bond length is 0.18879 nm, and can be considered as an intermediate between single bond and double bond.

From our calculated results, the energetic ordering of the HNS_2 local energy minimums at the single-point QCISD(T)/6-311 ++ G(3df,2p) level of theory can be obtained. Generally, the species with lower total energy has higher thermodynamical stability. At QCISD(T)/6-311++ G(3df,2p) level with zero-point vibrational energies inclusion, then the thermodynamical stability order is 1 (0.00) > 2 (13.46) > 3 (66.92) > 4 (78.25) > 5 (80.38) > 6 (81.22) > 7 (81.38) > 8 (86.40) > 9 (218.45). The values in parentheses are relative energies in kJ/mol with reference to 1. It is clear that 1 is the thermodynamical most stable species. Species 2, 3, 4, 5, 6, 7 and 8 can be considered as low-lying because for lower relative energies. Isomer 9 is very high-lying, and in view of rather high energy, it is expected to be of minor importance in experiments.
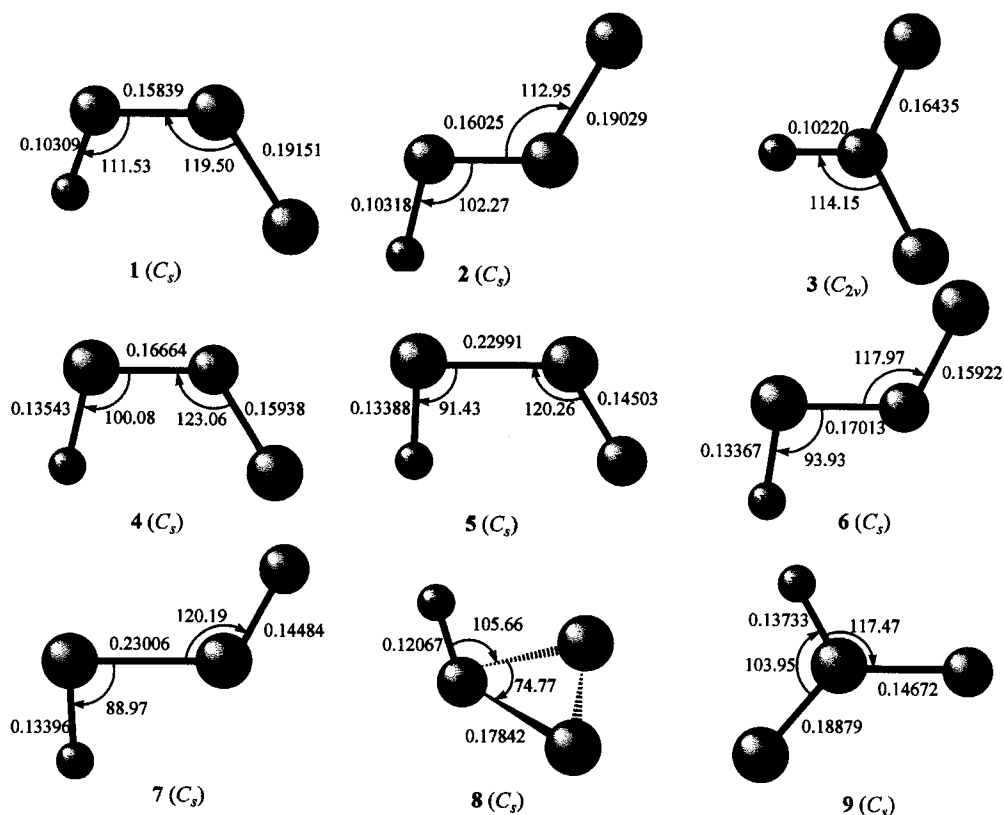
Fig. 1 Calculated equilibrium geometries for HNS$_2$ system at MP2/6-311++ G(d,p) level of theory (bond lengths are in nanometers, and bond angles in degrees).

Stabilities and isomerizations of isomers

Let us turn to the kinetic stabilities of various HNS$_2$ isomers. Ten interconversion transition states of HNS$_2$ molecule are obtained at MP2/6-311++ G(d,p) level of theory, and their structures are shown in Fig. 2. Their connections are checked by IRC calculations at MP2/6-311++ G(d, p) level. **TSm/n** denotes the transition state connecting the species **m** and **n**. By means of the isomers and transition states, a schematic potential energy surface is plotted in Fig. 3. For simplicity, the details of the obtained ten transition states are omitted. Practically, we can briefly discuss the kinetic stability of the obtained isomers in terms of the smallest barrier of isomerization. From Fig. 3, it can be seen that isomer **2** can isomerize into **1** via transition state **TS1/2** by a 74.45 kJ/mol barrier height. But note that isomer **2** is slightly higher in energy than **1** by 13.46 kJ/mol and **1** and **2** are in a deeper well, and thus, the low-lying isomers **1** and **2** can be considered as kinetically stable species, and may be experimentally observed in normal conditions. The iso-

mers **3**, **5**, **7** and **8** may also be considered to be kinetically stable species based on corresponding lowest conversion barriers, *i. e.*, 190.78 kJ/mol (**3**→**6**), 110.19 kJ/mol (**5**→**1**), 110.40 kJ/mol (**7**→**5**) and 179.57 kJ/mol (**8**→**2**). Because isomers **4** and **6** also reside in a deeper potential well (176.48 kJ/mol for **6**→**3**), they are kinetically stable species. It is noted that the barriers height of **6**→**4** and **4**→**6** are only 53.38 kJ/mol and 56.35 kJ/mol, and then both should coexist. For isomer **9**, we can not say more because it is difficult to estimate correctly its kinetic stability for 106.34 kJ/mol reaction barrier height from **9** to **7**. But in view of the lowest thermodynamical stability in all isomers, isomer **9** is expected to be of minor importance. We also attempted to locate S-shift transition state from **3** to **2** and H-shift transition state from **8** to **6**, which were expected to have lower barrier. But all attempts failed. Furthermore, we also expected a transition state, which can connect **5** with **6** via a simple NSS three-membered ring, to exist, but most optimizations lead to the transition state **TS1/5**.
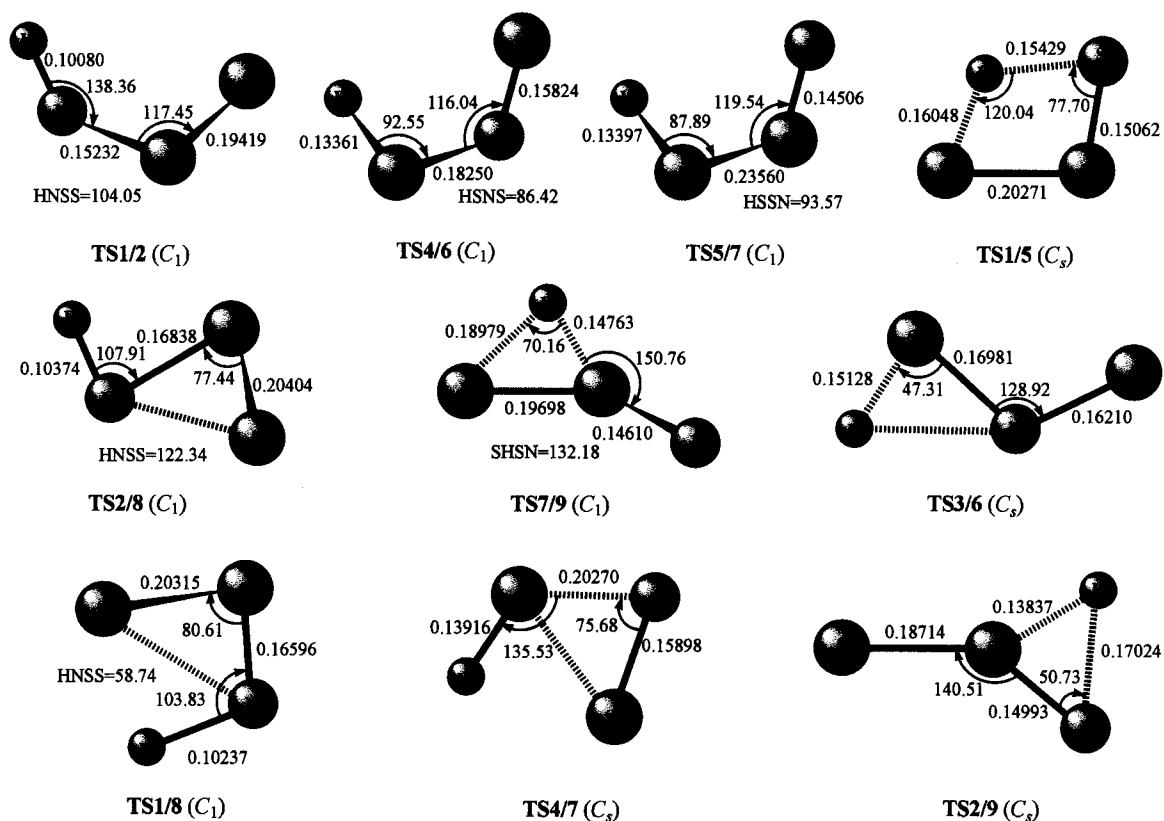
Fig. 2 Optimized transition state geometries for HNS$_2$ molecule at MP2/6-311++ G(d, p) level of theory (bond lengths are in nanometers, and bond angles in degrees).
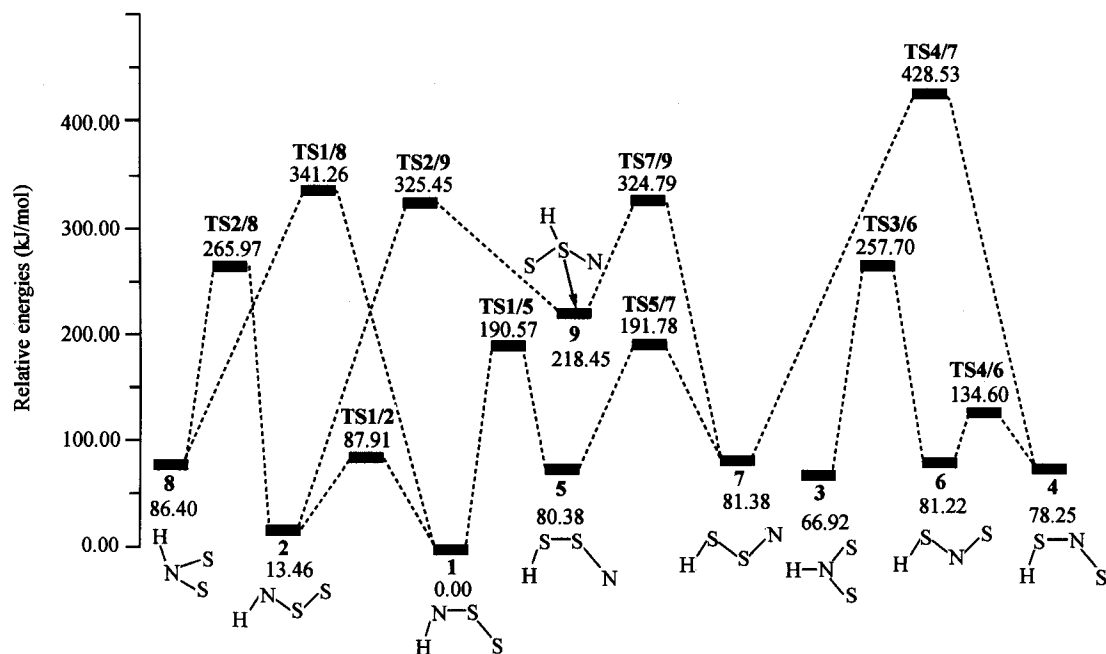

Fig. 3 Schematic energetic profile of HNS$_2$ system at QCISD(T)/6-311++ G(3df,2p)// MP2/6-311++ G(d,p) level of theory with zero-point vibrational energies included.

Comparison with other analogues

Based on the potential energy surface of HNS$_2$ system, it can easily be knowed that the global minimum is *cis*-HNSS, which is in agreement with the predication by Nakamura.[6] Whereas, the global minimums of potential energy surfaces of HNO$_2$, HPO$_2$ and HPS$_2$ are *trans*-HONO, *cis*-HOPO and *trans*-HSPS, respectively. It is worthy to note that, in HPS$_2$ isomers, *cis*-HPSS is predicted to be a kinetically stable species in laboratory conditions, and has been experimentally observed. But the *cis*-HPOO easily isomerizes toward another stereo isomer HP(O)O which has C_s symmetry.

It is surprising that eight isomers in HNS$_2$ system are kinetically stable species. The result can be estimated by means of these isomers' relative energies and be approved accurately by calculated potential energy surface. Isomers **2—8** are higher in energy by 90.00 kJ/mol than isomer **1**, thus, they can be considered as low-lying species, and exist with a reasonable energy range. But in HPO$_2$, HPS$_2$, and HNO$_2$, only *cis*- and *trans*-HOPO, HSPS and HONO, HP(O)O (C_{2v}), HP(S)S (C_{2v}), HP(S)S (C_s) and HN(O)O (C_{2v}) are lower-lying isomers, despite there are several high-lying species which are kinetically stable.

The primary causes that lead to the obvious differences between HNO$_2$ and HNS$_2$ are electronegativities of oxygen and sulfur and hypervalent capacity of sulfur atom, as discussed by Nakamura and his coworkers.[6] But for HNS$_2$ and HPS$_2$, the dominating cause begetting differences should be electronegativities of hydrogen, nitrogen and phosphorus. It is widely known that sulfur atom easily transfer between two atoms, which have similar electronegativities. Thus, in HPS$_2$, the S-shift processes between another sulfur atom and phosphorus atom often lead to some lower-barrier isomerizations, which make these species unstable. Practically, for the low electronegativities of sulfur and phosphorus, hydrogen atom also shifts easily from an atom to another atom with lower conversion barriers. Whereas in HNS$_2$, there is a stronger bonding between hydrogen and nitrogen, which makes H-shift or interconversion reaction happen difficultly. Therefore, there are many kinetically stable iso-

mers in HNS$_2$.

Conclusion

(1) On the potential energy surface of HNS$_2$ system, *cis*-HNSS isomer is found to be the global minimum, and eight isomers are found to be kinetically stable species, which should be experimentally observed. A new isomer HS(N)S with C_s symmetry is located on the potential energy surface.

(2) Comparisons are made among HNO$_2$, HNS$_2$, HPO$_2$ and HPS$_2$ about the global minimums and kinetically stable isomers. The obvious differences between HNS$_2$ and HPS$_2$ in isomers' stabilities are resulted from hypervalent capacity of phosphorus and distinct electronegativities of hydrogen, nitrogen and phosphorus.

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