Hydrogen Shift Isomerization Study of Doubly Bonded Compounds between Heavy Group 15 Elements HXYH (X,Y = As, Sb, and Bi)

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The lowest singlet and triplet potential energy surfaces of H-shift isomerization for HXYH (X,Y = As, Sb, and Bi) systems have been explored through ab initio calculations. The geometries of the various isomers were determined at the QCISD/LANL2DZdp level of theory and confirmed to be minima by vibrational analysis. Our model calculations indicate that the range of π-bond strength is 12−20 kcal/mol, as indicated by the singlet−triplet gap of the HXYH molecules. The hydrogen-shifted isomers H_2XY in the singlet state are considerably unstable than the singlet-state parent isomers by 24−49 kcal/mol. The triplet isomers are comparable in stability with respect to the parent singlet molecules, HXYH, within 3 kcal/mol for X lighter than Y. The gap increases to 8 kcal/mol for the homonuclear compounds with X = Y. It increases further to 17 kcal/mol for X heavier than Y.

I. Introduction

The development of the chemistry of multiply bonded systems involving elements in higher periods is generally regarded as a renaissance of main group chemistry.[1] In particular, the low-coordination-number chemistry of the group 15 elements has been extensively developed in the past decade thanks to the use of bulky groups.[2] It has been possible to characterize these reactive species due to their kinetics and stabilization afforded by sterically demanding substituents. Among the many stable multiple-bond systems which have been successfully characterized, compounds with π bonds to phosphorus were among the first stable examples to be synthesized [3] and still play an important role in this field.[4,10] In the ensuing period, structural data for at least 20 organo-diphosphenes have been published. In contrast, the number of analogous compounds involving double bonds to the heavier pnictogens has remained quite small. For instance, there are only five structurally characterized molecules with As═As double bonds, diarsenes.[4(e),6,7] There are only three structurally characterized molecules with Sb═Sb double bonds, distibenes, utilizing bulky substituents, such as the 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group (denoted as Tbt hereafter)[8(a)] and 2,6-$Ar_2C_2H_3$ groups (Ar = mesityl or 2,4,6-triisopropylphenyl).[8(b)] Through the elegant studies performed by Tokitoh et al.[9(a)] and Power et al.,[8(b)] kinetically stabilized molecules bearing a Bi═Bi double bond, dibismuthenes, have been synthesized and fully characterized. They are TbtBi═BiTbt[9(a)] and 2,6-$Ar_2C_6H_3$Bi═Bi$Ar_2C_6H_3$ (Ar = mesityl or 2,4,6-triisopropylphenyl).[8(b)] Some interesting comments made by Power et al. have stimulated the present study. They pointed out that the stable dipnictene compounds bear considerable structural similarity to their lighter, congeneric dimines, diphosphenes, and diarenes. They generally have a planar and trans geometry with bond lengths 6−7% shorter than single bonds. The π bonding is quite appreciable in strength in the fifth and sixth periods. The only notable structural difference is the reduction in the bond angle ∠CEE(in CEEC array) from 113.6(2)° with E = N to 100.5(2)° with E = Bi. It is interesting to see if those interesting structural observations can be reproduced by our simplified model compounds with the hydrogen substituent.

There are very few theoretical studies on the compounds containing antimony double bonds reported as yet. The electronic structures of the Sb═Sb symmetrical bond were first explored by Nagase et al.[12] These authors were mainly concerned with the evaluation of the ground-state geometry. Schoeller et al reported MCSCF studies on HSb═SbH and HSb═YH2 (Y = C, Si, Ge, and Sn) systems.[13(a)] These authors investigated the π-bond strengths and singlet−triplet splittings for the structures HSb═SbH and HSb═YH2. Density functional theory (DFT) calculation for the PhBi═BiPh model has also been reported by Cotton, Cowley, and Feng.[13(b)] In a later study by Tokitoh et al,[2(c)] these investigations were supplemented by MP2, B3LYP, and QCISD studies on both parent and phenyl-substituted Sb═Sb doubly bonded systems (i.e., HSb═SbH, PhSb═SbH, and PhSb═SbPh). Nevertheless, none of the studies have dealt with the magnitude of barriers for the isomerizations as well as singlet−triplet energy separations on the Sb═X (X = group 15 elements) unsymmetrical double bonds.

The purpose of the present work is, therefore, to expand upon the previous theoretical approaches by studying the double bonds between group 15 elements. Since we have recently published the nitrogen compounds of N═Y (Y = N, P, As, Sb, and Bi)[5] and the phosphorus compounds have been extensively documented in the literature.[4] Here, we restrict our study on the heavy elements As, Sb, and Bi for the doubly bonded X═Y (HXYH with X, Y = As, Sb, and Bi). Therefore, there are three compounds each for symmetrical and unsymmetrical double bond systems, respectively. Our object is to obtain more insight into the bonding character and to provide theoretical information on the thermodynamic and kinetic stability. To achieve this, it is necessary to determine the transition-state (TS) geometries of the molecules, as well as the ground-state energies, of the

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products of isomerization. Unimolecular reactions pertinent to the stability of X═Y considered here are as follows: (A) *trans*-HX═YH → TS1 → *cis*-HX═YH, (B) *trans*-HX═YH → TS2 → H2X═Y, and (C) *trans*-HY═XH → TS3 → H2Y═X. For comparison, the singlet and triplet XYH2 potential energy surfaces were investigated using the ab initio method QCISD. It is ultimately hoped that this study should be helpful for further developments in group 15 chemistry. In particular, the predicted molecular parameters presented in this paper will act as a guide for any future experimental investigations on some unknown RXYR′ isomers.

II. Methodology

The geometries of all the stationary points were fully optimized using the QCISD method with the frozen core approximation.[14] The stationary points correspond to the stable molecules and transition states on the lowest singlet and triplet potential surfaces for H-shift isomerization for HXYH(X, Y = As, Sb, and Bi) systems. QCISD calculations were carried out using the Gaussian 98 program[15] with relativistic effective core potentials on group 15 elements modeled using the double-ζ (DZ) basis sets[16] augmented by a set of d-type polarization functions.[17] The DZ basis set for the hydrogen element[16(a)] was augmented by a set of p-type polarization functions (p exponents 0.356). The d exponents used for As, Sb, and Bi are 0.286, 0.207, and 0.192, respectively. Accordingly, all the QCISD-(FC) calculations are denoted by QCISD/LANL2DZdp.

All the structures obtained were confirmed to be real minima or transition states via frequency analysis, which was also used to calculate zero-point energies (ZPEs) without scaling. For all the transition states, motion corresponding to the imaginary frequency was checked visually, and most structures were visually optimized to the minima they connected after perturbing the TS geometry.

We have made a test of using the more accurate QCISD(T) method (with QCISD ZPEs without scaling) on the HSbSbH system. There is some deviation up to 2−3 kcal/mol in isomerization energies. For example, trans to cis isomerization energy in singlet HSbSbH decreases by 0.02 kcal/mol. The hydrogen-shift isomerization in the singlet increases by 2.05 kcal/mol and that in the triplet decreases by 0.06 kcal/mol. The triplet−singlet gap increases by 3.12 kcal/mol for the parent HSbSbH molecule and by 3.31 kcal/mol for the hydrogen-shift isomer H_2SbSb. These results indicate some limitations of the accuracy of the present work.

III. Results and Discussion

Three symmetric compounds, HXXH, and the three unsymmetric ones, HXYH, (X, Y = As, Sb, and Bi) are discussed in the following section.

1. HAsAsH. The optimized geometries and relative energies, including the ZPE, for the HAsAsH species on the energetically lowest singlet and triplet potential energy surfaces are summarized in Figure 1.

As mentioned in the Introduction, only five stable compounds with As═As double bonds have been reported recently,[4(e),6,7] i.e., those of 2,6- $Mes_2H_3C_6As$═AsC_6H_3-2,6-Mes_2 (Mes = C_6H_2-2,4,6-Me_3) and 2,6-$Trip_2H_3C_6As$═AsC_6H_3-2,6-Trip2 (Trip = C_6H_2-2,4,6-i-Pr_3)[4(e)] by Power and co-workers and [2,4,6-(t-$Bu)_3C_6H_2$]As═AsCH($SiMe_3)_2$[7(a,b)] and [As-{C($SiMe_3)_3$}]$_2$[7(c)] by Cowley and co-workers. Although only a handful of crystallographic investigations on substituted diarsenes have been carried out during the past two decades, no experimental geometries are so far available in the literature for the parent HAsAsH isomers. Due to this fact, the reliability of the predicted geometries can only be estimated by comparison between different levels of theory. For comparison, the optimized geometries of the HAs═AsH species calculated at the QCISD/LANL2DZdp level of theory are listed in Table 1 along with previous theoretical work.[1(r),18,19] The QCISD results show that the singlet HAs═AsH species have a planar structure in both trans and cis forms. Apparently, the effects of electron correlation are relatively large. Namely, it is seen from Table 1 that electron correlation typically increases the QCISD bond lengths by 0.060−0.034Å and changes the bond angles by 2.3°, in comparison with the HF results.[18] Moreover, our QCISD calculations indicate that *trans*-HAs═AsH is slightly more stable by 2.5 kcal/mol than the cis form, which is in good agreement with the MCSCF value of 2.7 kcal/mol reported by Schoeller et al.[19] It is reasonable to expect that such a small energy difference between *cis*- and *trans*-HAs═AsH would be enlarged when the hydrogen atoms are replaced by the bulkier substituents. Indeed, all the experimentally substituted RAs═AsR′ species reported so far adopt a trans-bent structure. Additionally, their As═As bond lengths determined from X-ray data are in the range of 2.224−2.285Å.[4(e),7] These are in good agreement with our QCISD values (2.287Å), bearing in mind that the experimental structures contain bulkier groups. Besides these, the other relative energies of the singlet HAsAsH structures with respect to *trans*-HAs═AsH can also be found in Figure 1. As mentioned earlier, *trans*-HAs═AsH is slightly more stable by

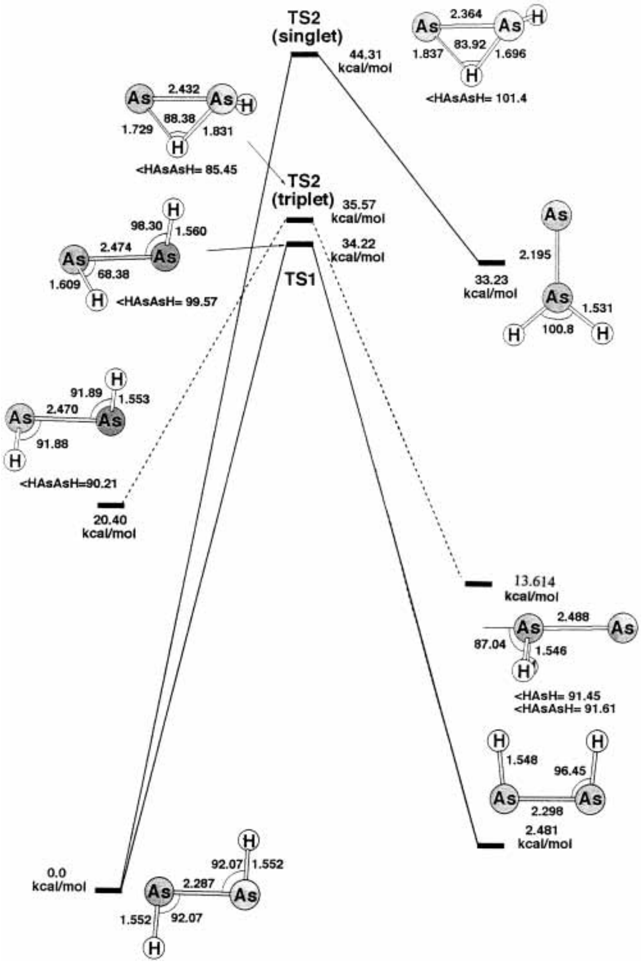


Figure 1. The optimized geometries (in Å and deg) of HAsAsH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HAsAsH species at QCISD/LAN2DZdp level.

TABLE 1: The Molecule Parameters and Relative Energies of Singlet *trans*-HX═XH(X = As, Sb, Bi) Species Based on This Work Compared with the Previous Calculations

	theoretical level					
	HF/DZ(d,p)[11]	MP2/TZ(2d)[1(r)]	B3LYP/ TZ(2d)[1(r)]	QCISD/ TZ(2d)[1(r)]	MCSCF/ECP[13]	QCISD/LANL2DZdp (this work)
			HAs═AsH			
As═As (Å)	2.227	2.279	2.270	2.278	2.326	2.287
As−H (Å)	1.518				1.518	1.552
∠HAsAs (deg)	94.4	92.1	92.6	92.7	94.9	92.1

	theoretical level					
	HF/DZ(d,p)[6]	MP2/TZ(2d)[2(b)]	B3LYP/ TZ(2d)[2(b)]	QCISD/ TZ(2d)[2(b)]	MCSCF/ECP[7]	QCISD/LANL2DZdp (this work)
			HSb═SbH			
Sb═Sb (Å)	2.608	2.674	2.656	2.676	2.73	2.682
As −H (Å)	1.703				1.703	1.738
∠HSbSb (deg)	93.0	90.5	91.2	91.3	92.0	90.7

	theoretical level					
	HF/ECP[5]	MCSCF/ECP[6]	MP2/TZ(2d)[1(i)]	B3LYP/ TZ(2d)[1(i)]	QCISD/ TZ(2d)[1(i)]	QCISD/LANL2DZdp (this work)
			HBi═BiH [l]			
Bi═Bi (Å)	2.719	2.854	2.794	2.767	2.795	2.797
Bi −H (Å)						1.806
∠HBiBi (deg)	91.8	90.1	89.1	90.4	90.2	89.6

2.5 kcal/mol than the cis form, with a barrier height as large as 34 kcal/mol. Moreover, H2AsAs is 33 kcal/mol higher in energy than the trans isomer. The relative energy for the transition structure (*trans*-HAs═AsH → H_2AsAs) is predicted to be 44 kcal/mol. Accordingly, from these computational results, it is predicted that these closed-shell HAsAsH isomers have an order of stability: *trans*-HAs═AsH > *cis*-HAs═AsH ≫ H_2AsAs, together with high (in excess of 34 kcal/mol) isomerization barriers between the isomers.

Let us now consider the first excited state of HAsAsH, a triplet. No experimental study of triplet HAsAsH isomers has appeared to date. As one can see in Figure 1, our QCISD calculations show that the energy of the triplet structure HAsAsH lies significantly above the corresponding singlet *trans*-HAs═AsH, while the energy of triplet H_2AsAs species is closed to that of singlet *trans*-HAs═AsH, as well as of *cis*-HAs═AsH. As a result, H_2AsAs is the more stable of the two triplets. Moreover, unlike the planar geometry adopted by singlet H_2AsAs, it is predicted that triplet H_2AsAs has a nonplanar C_s structure with a ∠HAsH bond angle of 91°. Its pyramidalization angle (or out-of-plane angle, defined as the angle between the As−As bond and the H_2As plane) is 87°. Interestingly, the triplet H_2AsAs is calculated to be 20 kcal/mol (at QCISD) more stable than the singlet H_2AsAs, while the energy of triplet HAsAsH is predicted to lie 20 kcal/mol above singlet HAs═AsH. To our knowledge, no theoretical data are available for the singlet−triplet splitting in diarsenes. Additionally, the activation energy for the 1,2-hydrogen shift (i.e., triplet HAsAsH → TS → triplet H2AsAs) is anticipated to be 15 kcal/mol, while its reverse barrier is predicted to be 34 kcal/mol at the QCISD level. These are large enough for triplet H_2AsAs to have a lifetime sufficient for spectroscopic observation.

In short, our theoretical findings based on the present QCISD method suggest that the stability ordering calculated for the HAsAsH species is singlet *trans*-HAs═AsH > singlet *cis*-HAs═AsH > triplet H_2AsAs > triplet HAsAsH > singlet H_2AsAs.

2. HSbSbH. The HSbSbH species has been attractive to several theoretical groups, as mentioned in the Introduction.[2(b),12,13] The optimized geometries and relative energies of the HSbSbH species on the energetically lowest singlet and triplet potential energy surfaces are shown in Figure 2.

Although so far only three crystal structure determinations on substituted distibenes have been carried out during the past five years,[8] no experimental geometries are so far available in the literature for the parent HSbSbH isomers. The optimized geometries of the HSbSbH species calculated at the QCISD/LANL2DZdp level of theory are listed in Table 1 along with previous theoretical work.[2(b),12,13] It is seen from Table 1 that, on the basis of quantum chemistry theory, the QCISD method computed shorter Sb═Sb and longer Sb−H bond distances than the MCSCF method.[13] Namely, our QCISD results predict that the Sb═Sb and Sb−H bond distances are 2.682 and 2.697 Å and 1.738 and 1.733 Å, while the MCSCF method predicts 2.731 and 2.749 Å and 1.738 and 1.733 Å for *trans*-HSbSbH and *cis*-HSbSbH, respectively. Moreover, it is also found that the QCISD decreases the MCSCF bond angles by 0.6−1.3°. From Figure 2, our computational results indicate that the isomerization barrier for singlet *trans*-HSb═SbH → singlet H_2SbSb is quite large (i.e., 39 kcal/mol), while its reverse barrier is relatively small (i.e., 2.9 kcal/mol). All these suggest that singlet H_2SbSb is kinetically and thermodynamically unstable, and thus should not be detected experimentally.

For the triplet state of HSbSbH, the activation energy for the 1,2-hydrogen shift (i.e., triplet HSbSbH → TS2 → triplet H_2SbSb) is calculated to be 13 kcal/mol, while its reverse barrier is anticipated to be 19 kcal/mol.

Therefore, our theoretical findings based on the present QCISD level of theory indicate that the order of stability calculated for the HSbSbH species is singlet *trans*-HSb═SbH > singlet *cis*-HSb═SbH > triplet H_2SbSb > triplet HSbSbH > singlet H_2SbSb.

3. HBiBiH. Dibismuthene (TbtBi═BiTbt)[9(a)] was the first known compound synthesized containing a bismuth−bismuth double bond, the heaviest double bond containing stable elements. Later on, Power and co-workers also synthesized another type of stable dibismuthene substituted by bulky 2,6-$Ar_2C_6H_3$ groups.[9(b)] Only these two crystallographic investigations on substituted dibismuthenes (shown in Table 1) have been

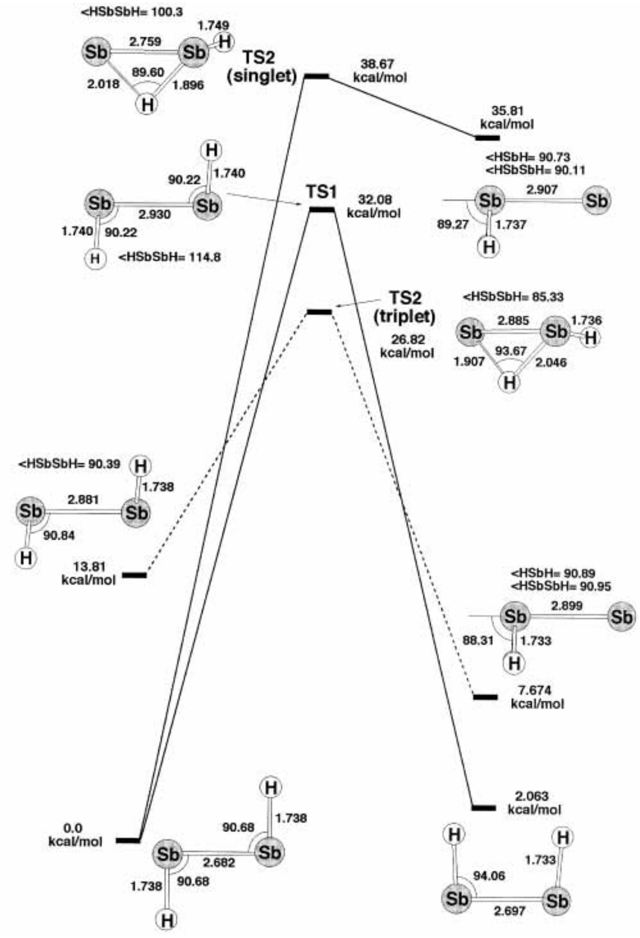


Figure 2. The optimized geometries (in Å and deg) of HSbSbH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HSbSbH species at QCISD/LAN2DZdp level.

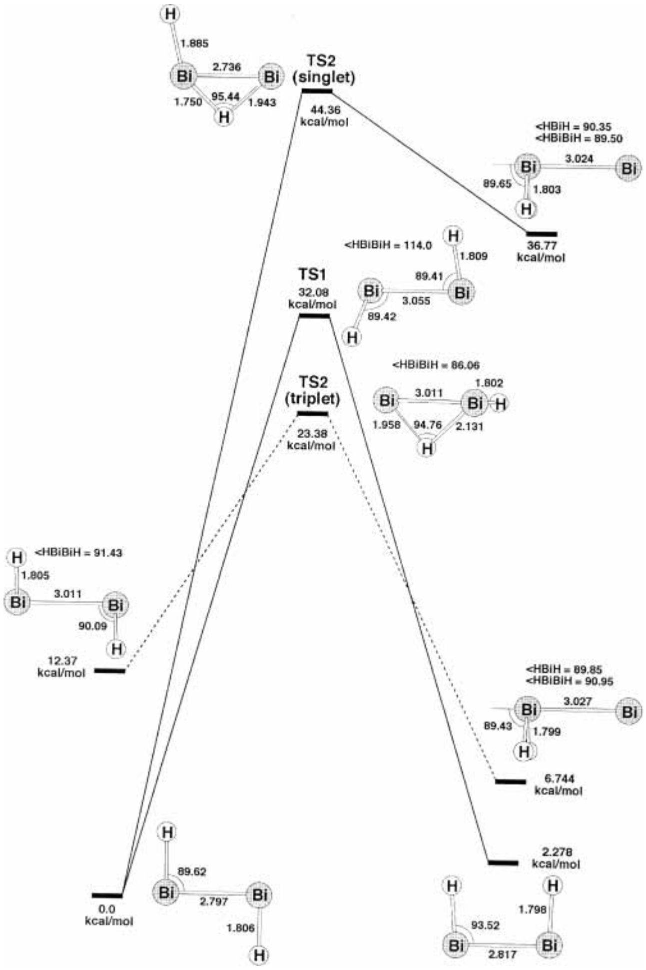


Figure 3. The optimized geometries (in Å and deg) of HBiBiH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HBiBiH species at QCISD/LAN2DZdp level.

carried out during the past five years, and no experimental geometries are so far available in the literature for the parent HBiBiH isomers. Our optimized geometries of the *trans*-HBi═BiH species calculated at the QCISD/LANL2DZdp level of theory are listed in Table 1 along with previous theoretical work and some available experimental data.[9] It is seen from Table 1 that electron correlation typically increases the RHF bond length by 0.078Å and changes the bond angle by 2.2°. Moreover, our QCISD calculations predict that the Bi═Bi bond length and the ∠HBiBi angle are 2.80Å and 89.6°, which are in good agreement with the experimental values (2.82−2.83Å and 100.2−92.5°), as shown in Table 1, bearing in mind that the experimental structures contain bulkier groups. In any event, the good agreement between our computational results and available experimental data is quite encouraging. We therefore believe that the QCISD/LANL2DZdp level employed in this work can provide accurate molecular geometries for those unimolecular isomerization reactions, for which experimental data are not available.

It has to be emphasized here that all the computational results presented in Table 1 predict the ∠HBiBi angle to be about 90°, while the experimentally corresponding angles are 100.5° [9(a)] and 92.5° [9(b)]. These values deviate greatly from the ideal sp^2 hybridized bond angle (120°). The reason for this is understandable in terms of the size difference and energy gap between the valence s and p orbitals being well-known to increase upon going from N to Bi atoms. For the heavy atoms, such as Sb and Bi, the contraction of s orbital due to the relativistic effect can reenforce the s−p difference.[20(i),9,21−23] As a result, the lone pair of bismuth has mostly s-orbital character. According, the σ bond is mostly comprised of p-orbitals. Consequently, the use of almost pure 6p orbitals instead of more hybridized orbitals leads to a bond angle of ∼ 90° at each bismuth.[23] In other words, the reason for RBi═BiR adopting the trans-bent form can be attributed to the phenomenon of orbital nonhybridization (or the so-called “inert s-pair effect”).[22,23]

The results in Figure 3 are very similar to those of the HSb═SbH system, for example, the activation energy for the 1,2-hydrogen shift of triplet HBiBiH → TS2 → triplet H_2BiBi is calculated to be 11 kcal/mol, while its reverse barrier is anticipated to be 17 kcal/mol at the QCISD level. Those of the singlet are 32 and 25 kcal/mol, respectively.

The order of stability calculated for the HBiBiH is the same as that for HSbSbH with the singlet *trans*-HBi═BiH > singlet *cis*-HBi═BiH > triplet H_2BiBi > triplet HBiBiH > singlet H_2-BiBi.

4. HAsSbH. The optimized geometries and relative energies for the HAsSbH species on the energetically lowest singlet and triplet potential energy surfaces from QCISD calculations presented in this work are shown in Figure 4. In many respects, the QCISD results for the HAsSbH isomerization reactions are quite similar to those symmetric compounds discussed earlier.

As can be seen in Figure 4, *trans*-HAs═SbH is predicted to be slightly more stable than *cis*-HAs═SbH by 2.1 kcal/mol at the QCISD level of theory. The inversion barrier for such a

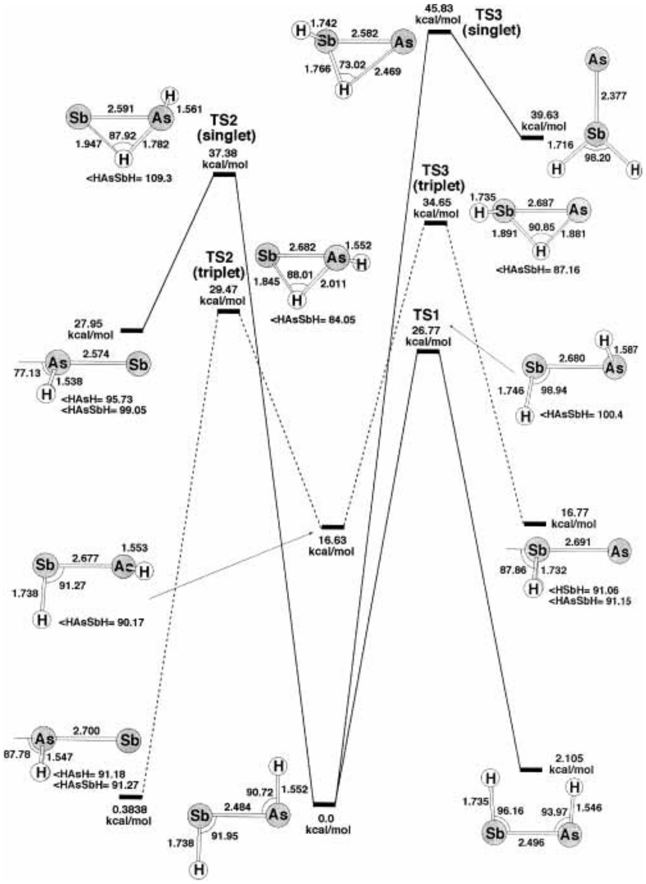


Figure 4. The optimized geometries (in Å and deg) of HAsSbH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HAsSbH species at QCISD/LAN2DZdp level.

trans-cis isomerization is calculated to be 27 kcal/mol, 6−8 kcal/mol lower the trans → cis isomerization of the previous three homonuclear compounds.

On one hand, H_2SbAs (the 1,2-H shifted isomer) possesses the highest energy of all the minima on the HAsSbH surface at the QCISD computational level employed. The energy difference between *trans*-HAs═SbH and H_2SbAs is estimated to be 40 kcal/mol (QCISD). Moreover, the QCISD calculations predict that the activation barrier for this isomerization is sizable (46 kcal/mol). Such a substantial barrier strongly indicates that the H_2SbAs isomer is unlikely to be observed experimentally. On the other hand, it is worth noting that the energy of H_2AsSb is predicted to be about 28 kcal/mol above *trans*-HAs═SbH at the QCISD level. In addition, the energy required for this 1,2-H migration (from *trans*-HAs═SbH to H_2AsSb) is estimated to be about 37 kcal/mol at the QCISD level of theory, while the barrier height for its reverse reaction (from H_2AsSb to trans-HAs═SbH) is predicted to be 9.4 kcal/mol at the same level of theory. This strongly implies that *trans*-HAs═SbH should be stable with respect to unimolecular rearrangement. Consequently, our theoretical investigations suggest that singlet *trans*-HAs═SbH ought to be stable in both a kinetic and thermodynamic sense.

Furthermore, the order of stability of the triplet HAsSbH species is the same as that found for the corresponding singlet HAsSbH system. That is to say, H_2AsSb is the lowest-lying triplet state, with triplet HAsSbH and H_2SbAs lying near 16 kcal/mol higher in energy at the QCISD/LANL2DZdp level. Moreover, triplet H_2AsSb was also found to be the ground state, with singlet H_2AsSb lying 27 kcal/mol higher in energy at the QCISD level. It should be pointed out that the As−Sb bond length (2.691Å) of triplet H_2SbAs is slightly smaller than that in triplet H_2AsSb (2.700 Å).

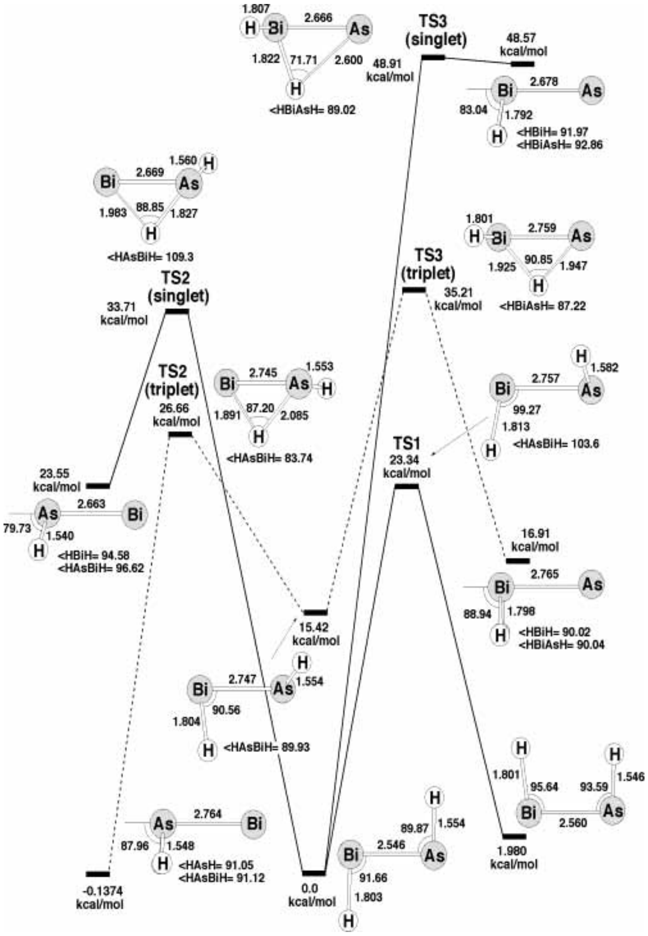


Figure 5. The optimized geometries (in Å and deg) of HAsBiH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HAsBiH species at QCISD/LAN2DZdp level.

To summarize our result, our theoretical investigations based on the present QCISD level of theory indicate that the order of stability of the HAsSbH species is singlet *trans*-HAs═SbH ≈ triplet H_2AsSb > singlet *cis*-HAs═SbH > triplet HAsSbH ≈ triplet H_2SbAs > singlet H_2AsSb > singlet H_2SbAs.

5. HAsBiH. The optimized geometries and relative energies for the HAsBiH species on the energetically lowest singlet and triplet QCISD potential energy surfaces are shown in Figure 5.

It should be noted that the order of stability of the HAsBiH isomers is essentially the same as that calculated for the HAsSbH species. For instance, for the singlet HAsBiH species, *trans*-HAs═BiH is shown to be the lowest-lying isomer, with *cis*-HAs═BiH, H_2AsBi, and H_2BiAs lying about 2.0, 24, and 49 kcal/mol higher in energy, respectively, at the QCISD level. According to our QCISD calculations, *trans*-HAs═BiH and *cis*-HAs═BiH isomers are found to be nearly degenerate in energy, with an energy difference estimated to be only 2.0 kcal/mol. In addition, the *trans*-HAs═BiH → H_2BiAs isomerization occurs via a nonplanar transition state and is predicted to possess a considerable energy barrier of 49 kcal/mol with respect to *trans*-HAs═BiH, with the inverse barrier only 0.34 kcal/mol. We thus conclude that the H_2BiAs species cannot exist. On the other hand, there exists a high activation barrier to separating the H_2AsBi and *trans*-HAs═BiH isomers. Our QCISD calculations predict that the forward barrier for the *trans*-HAs═BiH → H_2-

AsBi isomerization is about 34 kcal/mol, while its reverse barrier is about 10 kcal/mol. As a consequence, all of the above results confirm that *trans*-HAs═BiH should be stable in both a kinetic and a thermodynamic sense.

With the triplet states, we considered five stationary points: HAsBiH, H_2AsBi, H_2BiAs, and the transition states for the isomerization of triplet HAsBiH. It is apparent from Figure 5 that the energy difference between singlet HAs═BiH and triplet HAsBiH is as large as 15 kcal/mol, favoring the former over the latter. In addition, the QCISD calculations indicate that the isomerization barrier for triplet HAsBiH → triplet H_2BiAs is large (i.e., ~ 20 kcal/mol). This suggests that, as in the case of singlet H_2BiAs discussed above, any experimental detection of the triplet H_2BiAs species formed during the reaction is highly unlikely. Additionally, the energy barrier for the unimolecular rearrangement (i.e., triplet HAsBiH → triplet H_2AsBi) is estimated to be about 11 kcal/mol at QCISD. Besides these, our theoretical investigations show that triplet H_2AsBi is the global minimum on the HAsBiH potential energy surfaces. In particular, it is of interest to note that triplet H_2AsBi is found to be nearly degenerate to singlet *trans*-HAs═BiH by 0.14 kcal/mol.

Our theoretical investigations based on the present QCISD level of theory suggest that the stability of the HAsBiH species is in the order triplet H_2AsBi ≈ singlet *trans*-HAs═BiH > singlet *cis*-HAs═BiH > triplet HAsBiH > triplet H_2BiAs > singlet H_2AsBi > singlet H_2BiAs.

6. HSbBiH. So far, only one stable compound with an Sb═Bi double bond has been reported recently, i.e., BbtSb═BiBbt (Bbt = 2,6-[$(Me_3Si)_2CH]_2$-4-[$(Me_3Si)_3C]C_6H_2$) by Tokitoh and co-workers.[11] Nevertheless, definite structural parameters for this substituted Sb═Bi doubly bonded species have not been obtained yet, owing to the inevitable disorder of the antimony and bismuth atoms.[11] Likewise, neither experimental nor theoretical results for the parent HSbBiH isomers are available so far for a definitive comparison. Again, four minima corresponding to *trans*-HSb═BiH, *cis*-HSb═BiH, H_2SbBi, and H_2BiSb were located on the singlet potential energy surface. As usual, the open-shell triplet states of these isomers have also been investigated. The optimized geometries and relative energies for the HSbBiH species on the energetically lowest singlet and triplet potential energy surfaces are shown in Figure 6.

Our calculations show that the *trans*-HSb═BiH → H_2BiSb isomerization occurs via a nonplanar transition state and is predicted to possess a large energy barrier of 38 kcal/mol with respect to *trans*-HSb═BiH. This obviously suggests that such a 1,2-H shift reaction is energetically unfavorable and would be highly endothermic (~ +38 kcal/mol) if it occurs. We thus conclude that the H_2BiSb species cannot exist, with a negligible reversible barrier.

With the triplet states, we considered five stationary points: HSbBiH, H_2SbBi, H_2BiSb, and the transition states for the isomerization of triplet HSbBiH. It is apparent from Figure 6 that the energy difference between singlet HSb═BiH and triplet HSbBiH is as large as 13 kcal/mol, favoring the former over the latter. In addition, our calculations indicate that the isomerization barrier for triplet HSbBiH → triplet H_2BiSb is 14 kcal/mol, while that for unimolecular rearrangement (i.e., triplet HSbBiH → triplet H_2SbBi) is estimated to be about 11 kcal/mol. On the other hand, their reverse barriers are anticipated to be 16 and 21 kcal/mol, respectively. Accordingly, all of these results suggest that the triplet HSbBiH species should not be easily detected experimentally.

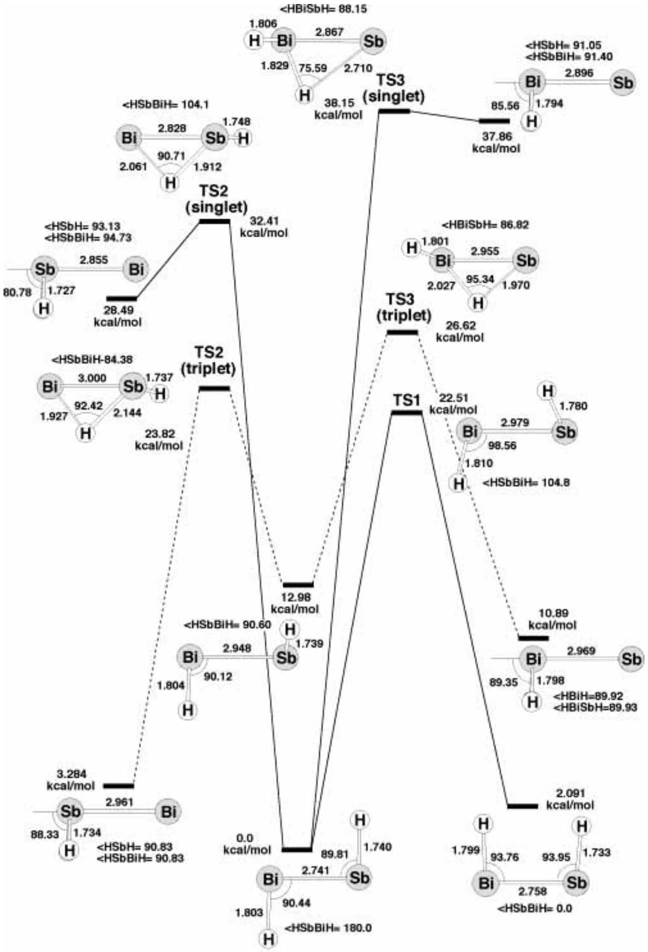


Figure 6. The optimized geometries (in Å and deg) of HSbBiH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HSbBiH species at QCISD/LAN2DZdp level.

TABLE 2: The Triplet−Singlet Energy Gap (*E*(triplet) − *E*(singlet)) in kcal/mol at the QCISD/LAN2DZdp Level for HXYH(X, Y = As, Sb, Bi)

	Y		
X	As	Sb	Bi
As	20.40	16.63	15.42
Sb		13.81	12.98
Bi			12.37

TABLE 3: The (singlet, triplet) Energies in kcal/mol at the QCISD/LAN2DZdp Level for the Isomer H_2XY Relative to the Singlet HXYH

	Y		
X	As	Sb	Bi
As	(33.23, 13.61)	(27.95, 0.38)	(23.55, −0.14)
Sb	(39.63, 16.77)	(35.81, 7.67)	(28.49, 3.28)
Bi	(48.57, 16.91)	(37.86, 10.89)	(36.77, 6.74)

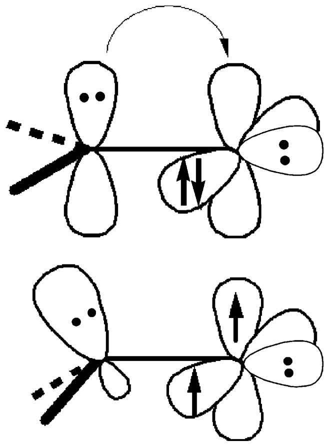
Finally, the HSbBiH species is in the order singlet *trans*-HSb═BiH > singlet *cis*-HSb═BiH > triplet H_2SbBi > triplet H_2BiSb > triplet HSbBiH > singlet H_2SbBi > singlet H_2BiSb.

IV. Summary

Some general comments on the results from Figure 1 to Figure 6 can be given as summarized in Table 2 and Table 3.

(1) The energy gaps of the triplet HXYH relatived to the singlet ones are shown in Table 2. It indicates the strength of

SCHEME 1



the π bond among those heavy group 15 elements. The values ranges from 12 to 20 kcal/mol. They agree reasonably well with the available values for the symmetric compounds by Schoeller et al.[13(a)]

(2) The singlet isomers H_2XX have higher energies of 33−37 kcal/mol than the singlet HXXH (the first entries in parentheses for the diagonal trio in Table 3). For the unsymmetric compounds XYH_2, the values increase to 38−49 kcal/mol with H shifted from the lighter atom, X, to the heavier atom, Y(see lower-left trio). However, the values decrease to 24−28 kcal/mol for the H shifted to the opposite direction (upper-right trio). It reflects not only the σ-bond difference between X−H and Y−H but also has the π-bond contribution that the original covalent π bond is replaced by the donor−acceptor type of π bonding (see Scheme 1). For example, HAsBiH isomerizes to $AsBiH_2$ after the H-shift. It is endothermic since the cleaved As−H bond is stronger than the Bi−H bond. Furthermore, the original π bond is replaced by a π type interaction of Bi lone pair donation to As. In comparison, in the H_2AsBi compound, the σ-bond contribution is more favorable, and the π-bond contribution is less favorable for the lone pair donation from the more electronegative As to Bi. Therefore, H_2AsBi and $AsBiH_2$ are 23.55 and 48.57 kcal/mol, respectively, relative to HAsBiH.

(3) The energy gap, E(triplet) − E(singlet), for H_2XY (the difference between the two energies within parentheses or brakets in Table 3) ranges from −24 kcal/mol for H_2AsBi to −32 kcal/mol for $AsBiH_2$, with all favoring the triplet. It can be easily understood that the triplet H_2XY can be conceived as bonding between the doublet H_2X fragment in **a** pyramidal geometry with the atom Y in the ground quartet state as shown in **b** in Scheme 1, while the singlet molecule is the result of bonding between the H_2X fragment and the excited Y atom in its doublet state shown in a in Scheme 1. Finally, the three triplet compounds H_2AsY (Y = As, Sb, and Bi) have comparable stabilities with the parent singlet compounds HAsYH.

We hope that the present theoretical results can bring more insight into the bonding pattern and provide some useful information on the kinetics and thermodynamic stability on doubly bonded heavy group 15 elements. Successful schemes for the synthesis and isolation of such species are therefore expected to be devised soon.

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