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Theoretical Study of HNXH (X = N, P, As, Sb, and Bi) Isomers in the Singlet and Triplet States

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The lowest singlet and triplet potential energy surfaces for all group 15 HNXH (X = N, P, 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 and confirmed to be minima by vibrational analysis. In the case of nitrogen and phosphorus, the global minimum is found to be a singlet *trans*-HN=XH structure. Moreover, both singlet and triplet H_2NX (X = N and P) species are also found to be local minima surrounded by large activation barriers, so that they should be observable. For arsenic, theoretical investigations demonstrate that the stability of HNAsH isomers decreases in the order triplet H_2NAs > singlet *trans*-HN=AsH ≈ singlet *cis*-HN=AsH > singlet H_2NAs > triplet HNAsH > triplet H_2AsN > singlet H_2AsN. For antimony and bismuth, the theoretical findings suggest that the stability of HNXH (X = Sb and Bi) systems decreases in the order triplet H_2NX > singlet H_2NX > singlet trans-HN=XH ≈ singlet *cis*-HN=XH > triplet HNXH > triplet H_2XN > singlet H_2XN. Our model calculations indicate that the relativistic effect on heavier group 15 elements should play an important role in determining the geometries as well as the stability of HNXH molecules. The results obtained are in good agreement with the available experimental data and allow a number of predictions to be made.

I. Introduction

The chemistry of doubly bonded group 15 elements has been the subject of intense experimental and theoretical interest over the last few decades.[1] During this period, several multiple bonded species and heterocycles have been synthesized and characterized spectroscopically and structurally. In particular, the double-bonded nitrogen structure, —N=N—, has been well-known for many years in the form of diazene (also called diimine or diimide), HN=NH, and substituted diazenes (also called azo compounds), RN=NR.[2] In fact, diazene is an important compound that is widely used in organic chemistry as a synthetic reagent for the stereospecific reduction of olefins[3] as well as in inorganic chemistry as a ligand for transition metal complexes.[4] It is also the parent molecule for a large number of azo compounds. Not surprisingly, diazene has been the subject of numerous investigations, both experimental [5,6] and theoretical.[7,8]

The second row analogue is the mixed compound phosphazene (also called iminophosphane or phosphinimine), HN=PH.[9] A substituted molecule containing the —N=P— group was first reported in 1973.[10] Since then, many schemes have been devised, and N=P double bonds are now considered as commonplace by experimentalists.[11] Like their nitrogen analogues, phosphazenes have already received much attention from a number of theoretical chemists.[12]

Nevertheless, the interest in arsenic, antimony, and bismuth is quite recent. Indeed, relatively little is known about the corresponding arsenic analogue, arsanazene (also called iminoarsane), HN=AsH.[13] At present, only trans arsanazenes with bulky substituents have been isolated and the main information available so far concerns their synthesis and X-ray structure.[14] On the other hand, up to now, neither N=Sb nor N=Bi double bonds have been experimentally identified. Moreover, to the best of our knowledge, no theoretical study concerning either antimonazene, HN=SbH, or bismuazene, HN=BiH, has been reported to date.

In this paper, we present a theoretical study of HNXH potential energy surfaces, with X varying from nitrogen to bismuth. Our goal is to obtain more insight into the bonding character of their various isomers and to provide structural and energetic data. In addition, the purpose of the work reported in this paper is to provide theoretical information on the thermodynamic and kinetic stability of the various HNXH isomers. 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 products of isomerization. Unimolecular reactions pertinent to the stability of HN=XH considered here are as follows: (A) *trans*-HN=XH → TS1 → *cis*-HN=XH, (B) *trans*-HN=XH → TS2 → H_2N=X, and (C) *trans*-HN=XH → TS3 → H_2X=N. For comparison, the singlet and triplet NXH_2 potential energy surfaces were investigated using the ab initio method (QCISD). It is believed that this study should be helpful for further developments in group 15 chemistry. In particular, the predicted molecular parameters and harmonic vibrational frequencies could aid experimental study of some unknown HNXH (X = N, P, As, Sb, and Bi) isomers.

II. Methodology

The geometries of all of the stationary points were fully optimized at the QCISD(FC) level of theory.[15] QCISD calculations were carried out using the Gaussian 98 program[16] with

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TABLE 1: Computed and Observed Molecular Parameters for Isomers of Singlet HNNH[a]

	trans−HN═NH		*cis*−HN═NH		N═NHH	
	QCISD/LANL2DZdp	expt.	QCISD/LANL2DZdp	expt.	QCISD/LANL2DZdp	expt.
r(N−N)	1.268 Å	1.252 Å[b]	1.266 Å		1.243 Å	
r(N−H)	1.043 Å	1.028 Å[b]	1.048 Å		1.047 Å	
∠HNN	105.5°	106.8°[b]	111.3°		123.4°	
A (cm^{-1})	9.742584	10.001203[c]	9.585951		10.955892	
B (cm^{-1})	1.2728940	1.3043373[c]	1.268024		1.247790	
C (cm^{-1})	1.1258049	1.1499757[c]	1.119886		1.120207	
ν_1 (cm^{-1})	3282	3128[c]	3237	2966[d]	3147	2862[e]
ν_2 (cm^{-1})	1615	1582[c]	1604	1558[d]	1705	1645[e]
ν_3 (cm^{-1})	1588	1529[c]	1374	1390[d]	1574	1574[e]
ν_4 (cm^{-1})	1304	1286[c]	1232	1259[d]	943	1003[e]
ν_5 (cm^{-1})	3272	3120[c]	3134	2984[d]	3135	2805[e]
ν_6 (cm^{-1})	1335	1322[c]	1547	1439[d]	1290	1288[e]

[a] All were calculated at the QCISD(FC)/LANL2DZdp level of theory, see the text. [b] See ref 5b. [c] See ref 5d. [d] Estimated values, based on approximate force field deriver from *trans*-HNNH. See ref 5d. [e] See ref 6b and c.

relativistic effective core potentials on group 15 elements modeled using the double-ζ (DZ) basis sets[17] augmented by a set of d-type polarization functions.[18] The DZ basis set for the hydrogen element[17a] was augmented by a set of p-type polarization functions (p exponents 0.356). The d exponents used for N, P, As, Sb, and Bi are 0.736, 0.364, 0.286, 0.207, and 0.192, respectively. Accordingly, all of the QCISD(FC) calculations are denoted by QCISD/LANL2DZdp.

All of 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 of 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.

III. Results and Discussion

1. HNNH. It is now firmly established that there exist three stable closed-shell structures on the HNNH potential energy surface.[5−8] They are *trans*-HN═NH, *cis*-HN═NH, and planar H_2NN (isodiazene). Both ab initio and density functional calculations[7,8] on the relative stability of these closed-shell HNNH isomers have consistently shown an order of stability, *trans*-HN═NH > *cis*-HN═NH > H_2NN, together with very high (in excess of 50 kcal/mol) isomerization barriers between the isomers (vide infra). It should be pointed out that the order of thermodynamic stabilities calculated for these isomers is in line with experimental observation.[5] Nevertheless, relatively little is known about the open-shell triplet state of these isomers,[7g] which will be discussed in more detail below.

The geometrical parameters predicted for the three closed-shell HNNH isomers as well as the vibrational frequencies and rotational constants, calculated based on the QCISD/LANL2DZdp level of theory, are collected in Table 1, where they are compared with some available experimental values.[5b] The optimized geometries and relative energies, including the ZPE for the HNNH species on the energetically lowest singlet and triplet potential energy surfaces, are summarized in Figure 1. The vibrational frequencies predicted for both singlet and triplet HNNH isomers, as well as the calculated rotational constants, dipole moments, and net atomic charges are collected in Table A in the Supporting Information.

Unfortunately, to our knowledge, experimental geometries are only available for *trans*-HN═NH.[5b] In fact, the QCISD results show that the HN═NH species have a planar structure in both trans and cis forms. The ∠NNH angle is significantly larger in the cis form than in the trans form, whereas the N═N bond lengths in both forms are nearly the same (∼1.267 Å). These trends can be explained well in terms of steric repulsion between the hydrogens. Moreover, the QCISD calculations indicate closer agreement with experiment at the LANL2DZdp level. The bond lengths are within 0.015 Å, and the ∠HNN bond angle is within 1.3° of experiment. One would therefore expect that the same relative accuracy should also apply to the geometries predicted for *cis*-HN═NH and isodiazene.

Computed and observed vibrational frequencies can also be found in Table 1. The vibrational spectroscopy of *trans*-HN═NH was discussed in detail in the work of Martin and Taylor, [5l,8o] whereas too little experimental information is available for *cis*-HN═NH and isodiazene to make a meaningful comparison possible. An inspection of the vibrational frequencies of *trans*-HN═NH presented in Table 1 reveals that the average deviation between our theoretical and experimental values for *trans*-HN═NH is about 5.0%, well within the estimated error range.[19] On the other hand, the predicted QCISD frequencies for *cis*-HN═NH are within 9.1%, when compared with estimated experimental results.[5d] Nevertheless, QCISD results for isodiazene were found to reproduce the experimental frequencies with smaller errors. In particular, it is interesting to see that the QCISD value for the ν_3 vibrational frequency (1574 cm^{-1}) of H_2NN is in perfect agreement with the experimental data (1574 cm^{-1}).[6b]

The QCISD/LANL2DZdp rotational constants for the three closed-shell HNNH isomers are also compared with the experimental results in Table 1. Again, experimental data is only available for *trans*-HNNH.[5d] The QCISD/LANL2DZdp results were once again found to be in good agreement with available experimental values. For example, an excellent agreement is found between the rotational constants (B and C) calculated at the QCISD level and experimental data. Nevertheless, there is one significant discrepancy. The rotational constant A is predicted to be lower by about 0.26 cm^{-1} than its corresponding experimental value. In fact, the predicted rotational constant A for *trans*-HN═NH is smaller than the experimental value by only 2.6%.

The transition states and barrier heights for isomerization between the trans and cis forms of singlet HN═NH via inversion have been studied extensively by several groups,[7] along with the barriers and transition states for the isomerization of HN═NH to H_2NN.[8] In particular, trans and cis isomerization of HN═NH has been previously studied using the Gaussian-2 (G2) method.[8f] The relative energies of the HNNH structures with respect to *trans*-HN═NH are given in Table 2. As concluded previously (ref 8f), *cis*-HN═NH is slightly more stable by 5.0

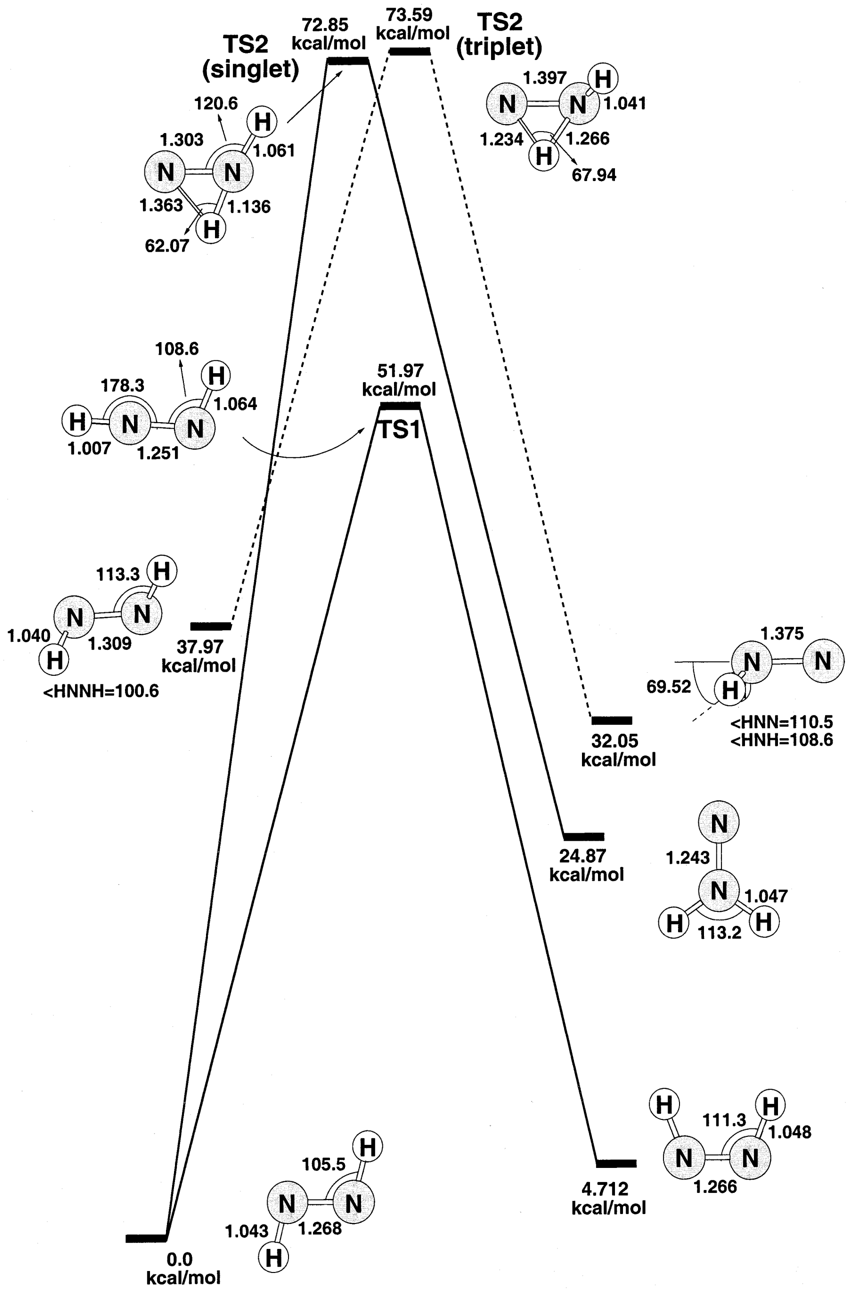


Figure 1. Optimized geometries (in Å and deg) of the HNNH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HNNH species at the QCISD/LANL2DZdp level.

TABLE 2: Calculated Relative Energies in kcal/mol for Isomers and Transition Structures of HNNHat the QCISD Level of Theory Compared with the Previous Results

species	QCISD[a]	G2[b]
$H_2N{=}N$	25	24
TS ($H_2N{=}N \rightarrow$ *trans*-HNNH)	73	70
trans-HNNH	0.0	0.0
TS (*trans*-HNNH → *cis*-HNNH)	52	50
cis-HNNH	4.7	5.0

[a] Based on the QCISD/LANL2DZdp geometry, see the text. [b] See ref 8(f).

kcal/mol than the trans form. Moreover, H_2NN is 24 kcal/mol higher in energy than the trans isomer. The relative energy for transition structure ($H_2NN \rightarrow$ trans-HN=NH) is predicted to be 70 kcal/mol. From Table 1, it is apparent that our QCISD/LANL2DZdp results are in excellent agreement with the G2 energies. In the best case, the energies differ by less than 0.3 kcal/mol.

Let us now consider the first excited state of HNNH, a triplet, which has been the subject of a limited number of theoretical treatments.[7b,l,12i] No experimental study of triplet HNNH isomers has appeared to date. As one can see in Figure 1, our QCISD calculations show that the energies of the triplet structures H_2NN and HNNH both lie significantly above the corresponding singlets. H_2NN is the more stable of the two triplets. Moreover, unlike the planar geometry adopted by singlet H_2NN, it is predicted that triplet H_2NN has a nonplanar C_s structure with a ∠HNH bond angle of 109°. Its pyramidalization angle (or out-of-plane angle, defined as the angle between the N−N bond and the H_2N plane) is 69.5°. On one hand, the singlet−triplet separation for H_2NN, of 7.2 kcal/mol (QCISD), is in good agreement with the earlier highly accurate studies, 7.9 (CASSCF) and 7.3 (GVB) kcal/mol.[12i] However, the energy of triplet HNNH is predicted to lie 38 kcal/mol above singlet HN=NH. To our knowledge, no theoretical data are available for the singlet−triplet splitting in diazene. Additionally, the activation

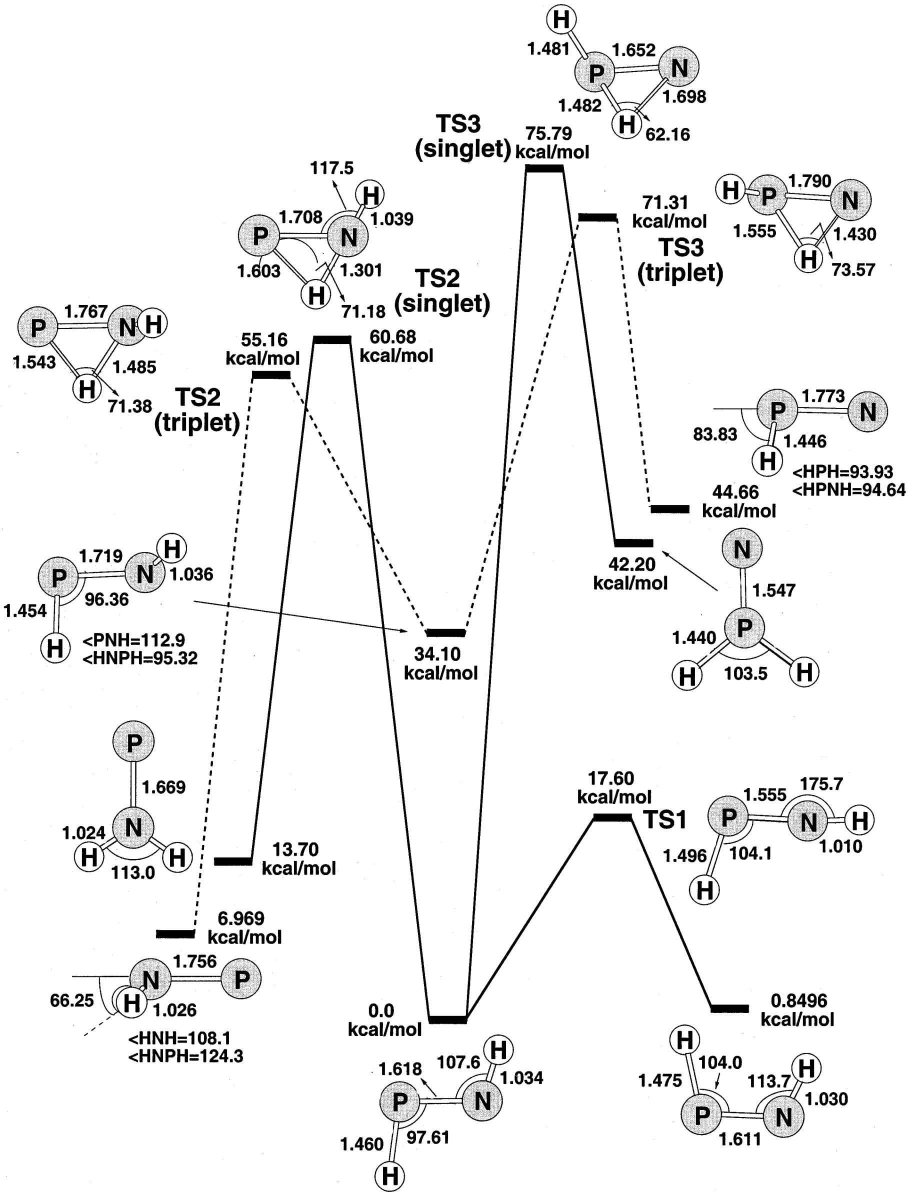


Figure 2. Optimized geometries (in Å and deg) of the HNPH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HNPH species at the QCISD/LANL2DZdp level.

energy for the 1,2-hydrogen shift (i.e., triplet HNNH → TS → triplet H_2NN) is anticipated to be 36 kcal/mol, whereas its reverse barrier is predicted to be 42 kcal/mol at the QCISD level. These are large enough for both triplet HNNH and H_2NN to have a lifetime sufficient for spectroscopic observation.

In brief, our theoretical findings based on the present QCISD level of theory suggest that the stability ordering calculated for the HNNH species is singlet *trans*-HN=NH > singlet *cis*-HN=NH > singlet H_2NN > triplet H_2NN > triplet HNNH.

Finally, taking together all of the above investigations of molecular properties and relative energies using the QCISD method, we therefore conclude that the QCISD method with the LANL2DZdp basis set should be accurate and reliable for the computational study of the isomerization reactions of these and similar molecular systems (vide infra).

2. HNPH. The study of the parent phosphazene, HNPH, parallels the study of diazene, HNNH. In fact, the HNPH species has attracted considerable theoretical interest[12] since the first dialkylphosphazene, *trans*-(t-Bu)P=N(t-Bu), was detected by Niecke el al. in 1981.[10b] Four stable closed-shell structures have been reported on the HNPH potential energy surface using ab initio methods.[12] They are *trans*-HN=PH, *cis*-HN=PH, planar H_2NP, and planar H_2PN. In addition, the open-shell triplet states of these isomers have also been investigated.[12b,g] The optimized geometries and relative energies of the HNPH species on the energetically lowest singlet and triplet potential energy surfaces from QCISD calculations presented in this work are shown in Figure 2. The vibrational frequencies, as well as the rotational constants, dipole moments, and net atomic charges calculated for both singlet and triplet HNPH isomers are collected in Table A in the Supporting Information.

Although a large number of crystallographic investigations on substituted phosphazenes have been carried out during the last two decades (ref 9b), no experimental geometries are so far available in the literature for the parent HNPH isomers. As shown in Figure 2, our computational results indicate that the singlet *trans*-HN=PH isomer is lower in energy than the singlet *cis*-HN=PH isomer by 0.85 kcal/mol at the QCISD level of theory. The inversion barrier for such a cis−trans isomerization is predicted to be 18 kcal/mol. Additionally, our QCISD calculations on the relative stability of the four closed-shell HNPH isomers show an order *trans*-HN=PH > *cis*-HN=PH

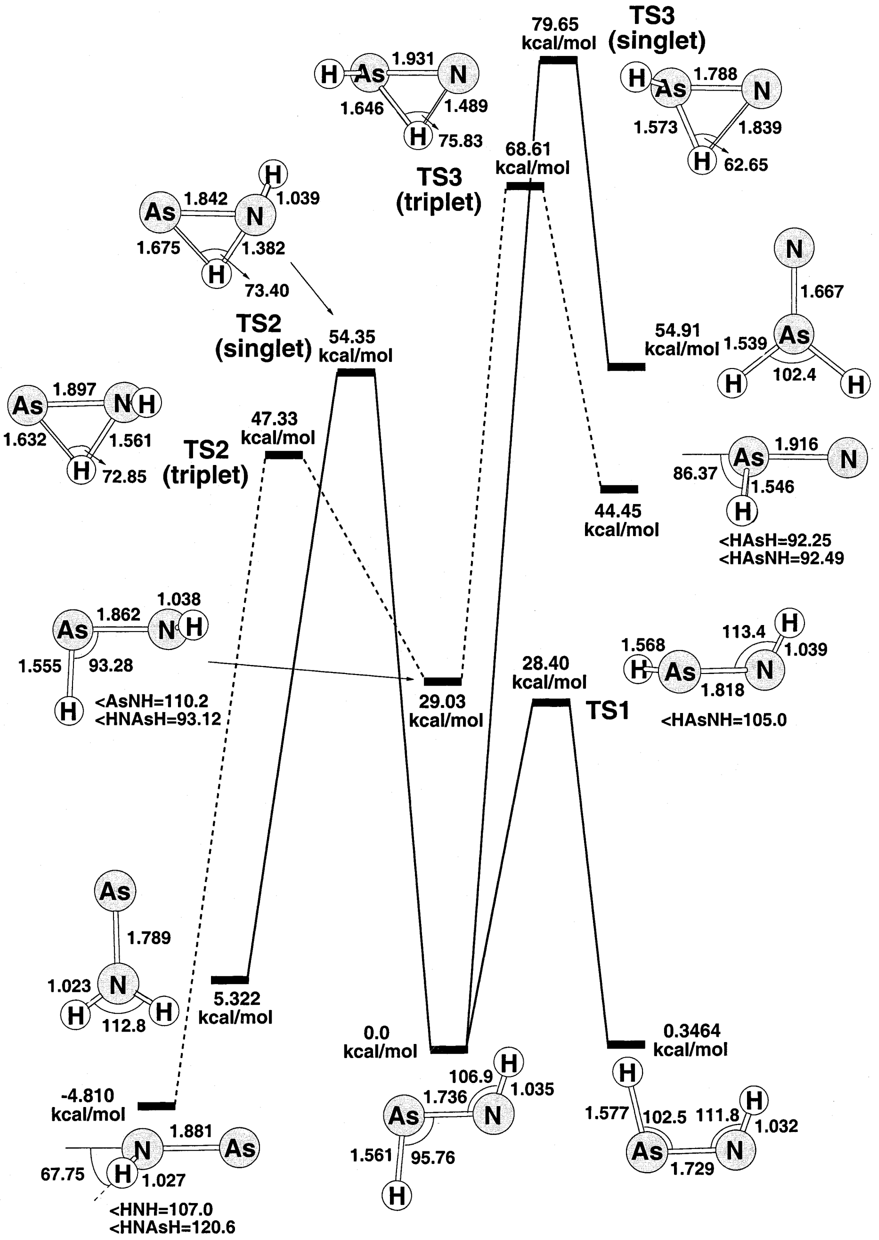


Figure 3. Optimized geometries (in Å and deg) of the HNAsH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HNAsH species at the QCISD/LANL2DZdp level.

> H_2NP > H_2PN. In particular, in the singlet states, the QCISD barriers for the unimolecular isomerization reactions decrease in the order *trans*-HN=PH → H_2PN (76 kcal/mol) > *trans*-HN=PH → H_2NP (61 kcal/mol) > *trans*-HN=PH → *cis*-HN=PH (18 kcal/mol). As a result, this strongly implies that 1,2-H shifts are unlikely to proceed at room temperature.

The singlet and triplet isomerization hypersurfaces from HNPH to the corresponding H_2PN and H_2NP isomers are nearly parallel, with the triplet remaining higher in energy throughout the path. As expected, all of the triplet structures are nonplanar. In short, our theoretical findings based on the present QCISD level of theory indicate that the order of stability calculated for the HNPH species is singlet *trans*-HN=PH > singlet *cis*-HN=PH > triplet H_2NP > singlet H_2NP > triplet HNPH > singlet H_2PN > triplet H_2PN. This ordering is consistent with those previously calculated by Trinquier[12b] and Nagase et al.[12g]

3. HNAsH. To date, a very small number of substituted arsanazenes (RN=AsR) have been isolated and characterized unequivocally.[14] All of their structures have been found to be trans, although only a few details concerning their geometrical parameters are as yet available. In addition, very few theoretical results have been reported on the N=As doubly bonded species.[13j,k]

In parallel with the above studies of diazenes and phosphazenes, we have also undertaken a systematic theoretical investigation of the parent arsanazene molecule, HNAsH, and its isomers in their closed-shell singlet states, in low-lying open-shell triplet states, and also in the transition states separating these isomers. The optimized geometries and relative energies including the ZPE for the HNAsH species on the energetically lowest singlet and triplet potential energy surfaces are given in Figure 3. The vibrational frequencies predicted for both singlet and triplet HNAsH isomers as well as the calculated rotational constants, dipole moments, and net atomic charges are collected in Table A in the Supporting Information.

As usual, four minima on the singlet potential energy surface were found which correspond to *trans*-HN=AsH, *cis*-HN=AsH, H_2NAs, and H_2AsN. All of these molecules are planar. Although little is known experimentally about arsanazenes, we may compare some of our results with those obtained for substituted

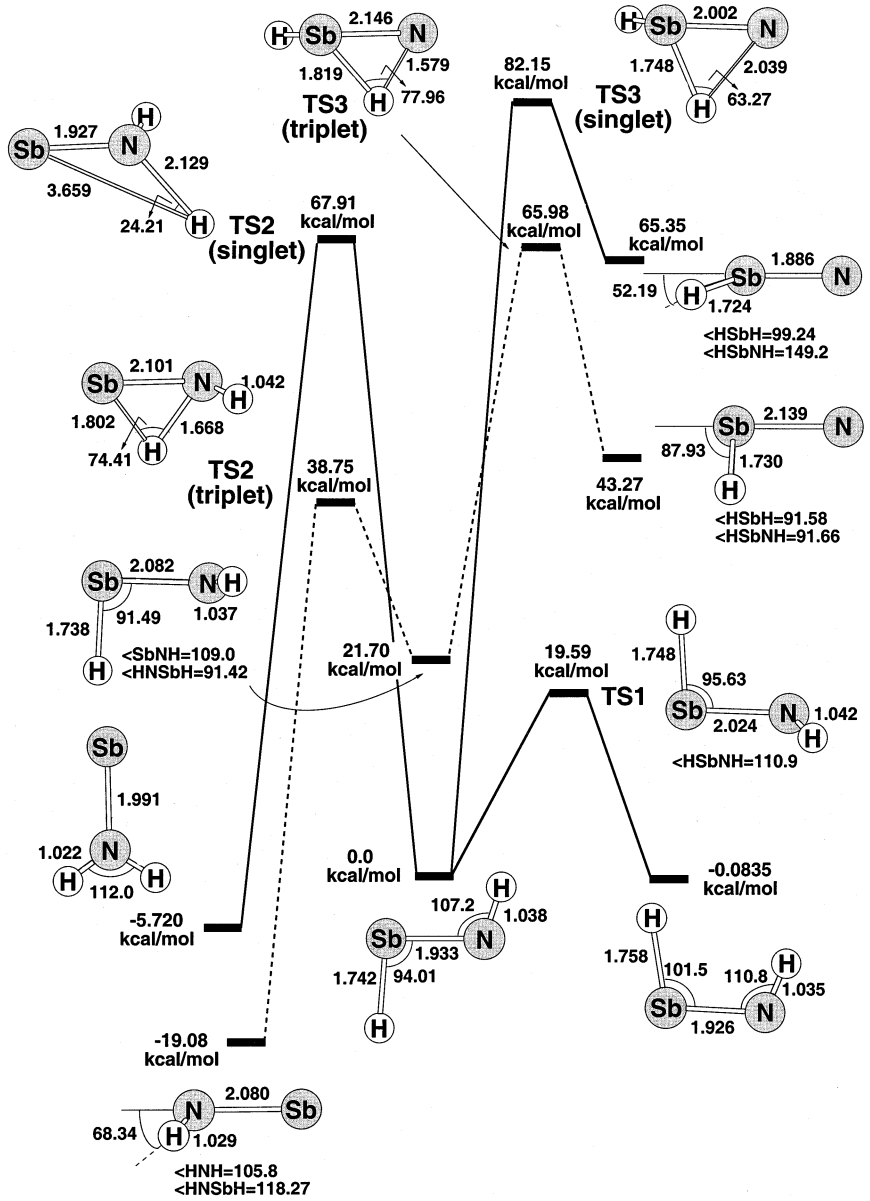


Figure 4. Optimized geometries (in Å and deg) of the HNSbH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HNSbH species at the QCISD/LANL2DZdp level.

arsanazenes. The calculated N═As bond length in *trans*-HN═AsH (1.736 Å at QCISD) compares favorably with trans N═As bond lengths determined from X-ray data in aminoarsanazene (1.714 Å) synthesized by Lappert et al.,[14a] the arsanazene (1.707 Å) prepared by Roesky et al.,[14f] and the arsanazene (1.708 Å) reported by Ross et al.[14g] In these three compounds, the valence angles on arsenic (98.8°, 96.3°, and 104°, respectively) and nitrogen (123°, 126°, and 112°, respectively) are less sharp than in our calculated trans isomer (95.8° on arsenic and 107° on nitrogen, at the QCISD level). This is probably due to steric interaction that may cause substituted arsanazenes to have larger bond angles than the parent arsanazene itself.

For the triplet states, we considered five stationary points: HNAsH, H_2NAs, H_2AsN, and the transition states for the isomerization of triplet HNAsH. In short, our theoretical investigations based on the present QCISD level of theory indicate that the order of stability for the HNAsH species is triplet H_2NAs > singlet *trans*-HN═AsH ≈ singlet *cis*-HN═AsH > singlet H_2NAs > triplet HNAsH > triplet H_2AsN > singlet H_2AsN.

4. HNSbH. As mentioned in the Introduction, neither experimental nor theoretical results for the antimonazene species are yet available for a definitive comparison. For consistency with the above studies, four stable closed-shell structures on the HNSbH potential energy surface have been considered in the present work, i.e., *trans*-HN═SbH, *cis*-HN═SbH, H_2NSb, and H_2SbN. Likewise, the open-shell triplet states of these isomers have also been investigated. The optimized geometries and relative energies for the HNSbH species on the energetically lowest singlet and triplet potential energy surfaces from QCISD calculations presented in this work are shown in Figure 4. The calculated vibrational frequencies for singlet and triplet HNSbH isomers as well as the calculated rotational constants, dipole moments, and net atomic charges are collected in Table A in the Supporting Information. In many respects, the QCISD results for the HNSbH isomerization reactions are quite similar to those discussed earlier for the HNXH (X = N, P, and As) systems. It is our conviction that for the HNSbH species under study, for which the rotational constants and vibrational IR spectra are still unknown, the presented QCISD results (Table A) should be of the same accuracy as we have already discussed earlier.

As may be seen in Figure 4, the trend in the order of stability of the HNSbH species is analogous to that in the HNAsH

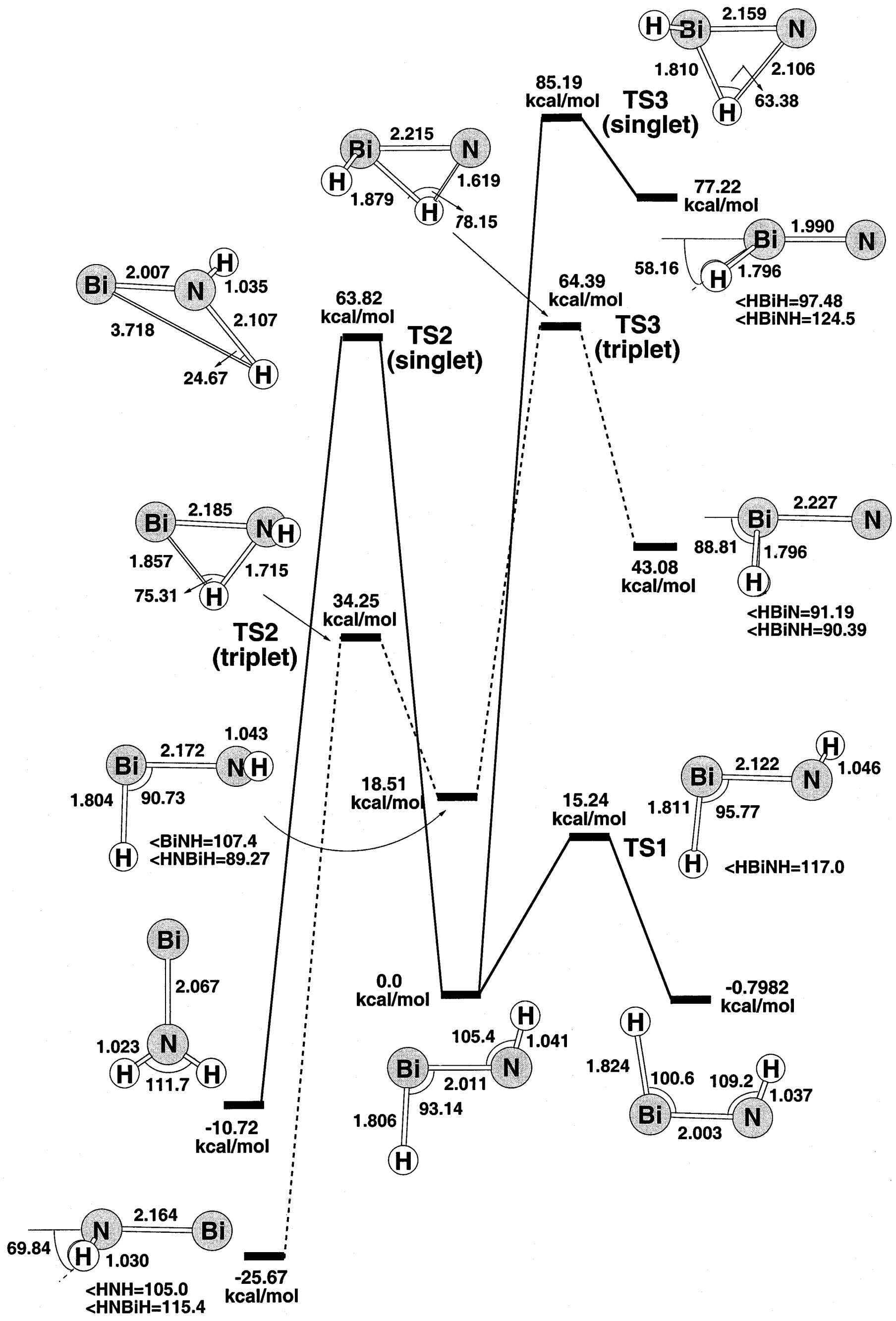


Figure 5. Optimized geometries (in Å and deg) of the HNBiH isomers and relative energies (in kcal/mol) of the pathways for isomerization of the singlet (plain line) and triplet (dashed line) HNBiH species at the QCISD/LANL2DZdp level.

system. In short, our theoretical investigations based on the present QCISD level of theory indicate that the order of stability of the HNSbH species is triplet H_2NSb > singlet H_2NSb > singlet trans-HN═SbH ≈ singlet *cis*-HN═SbH > triplet HNSbH > triplet H_2SbN > singlet H_2SbN.

5. HNBiH. To date, neither experimental nor theoretical results for the bismuazene species are available for a definitive comparison. Again, four minima corresponding to *trans*-HN═BiH, *cis*-HN═BiH, H_2NBi, and H_2BiN 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 HNBiH species on the energetically lowest singlet and triplet QCISD potential energy surfaces are shown in Figure 5. The calculated vibrational frequencies for singlet and triplet HNBiH isomers as well as the calculated rotational constants, dipole moments, and net atomic charges are collected in Table A in the Supporting Information.

It should be noted that the order of stability of the HNBiH isomers is essentially the same as that calculated for the HNSbH species. With the triplet states, we considered five stationary points: HNBiH, H_2NBi, H_2BiN, and the transition states for the isomerization of triplet HNBiH. In short, our theoretical investigations based on the present QCISD level of theory suggest that the stability of the HNBiH species is in the order triplet H_2NBi > singlet H_2NBi > singlet *cis*-HN═BiH ≈ singlet *trans*-HN═BiH > triplet HNBiH > triplet H_2BiN > singlet H_2BiN.

6. Overview of HNXH (X = N, P, As, Sb, and Bi) Systems. Because the relative QCISD energies of the various states are already shown in Figures 1−5, Figures 6 and 7 present the trend in relative stabilities for the closed-shell and open-shell triplet

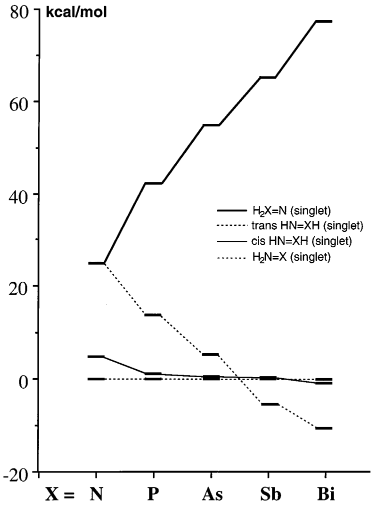


Figure 6. Evolution of QCISD relative energies (in kcal/mol) of the closed-shell singlet states (minima on the potential enegy surface) with regard to the *trans*-HN═XH isomer, taken as energy reference.

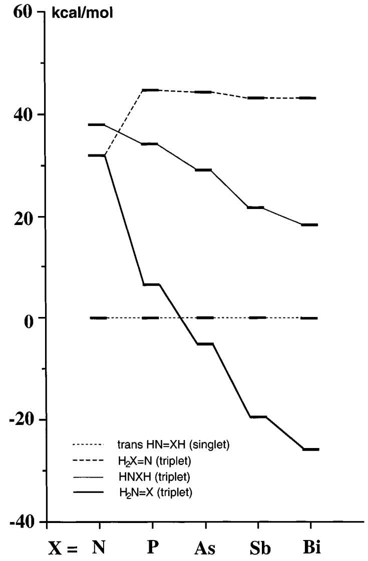


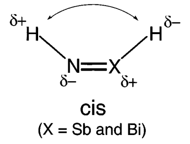
Figure 7. Evolution of QCISD relative energies (in kcal/mol) of the open-shell triplet states (minima on the potential enegy surface). Zero energy corresponds to the closed-shell singlet *trans*-HN═XH isomer.

minima on the HNXH (X = N, P, As, Sb, and Bi) potential energy surfaces. For each figure, the energy reference is the *trans*-HN═XH isomer. The major conclusions that can be drawn from Figures 6 and 7 are as follows:

(1) Both *trans*- and *cis*-HN═XH molecules are the minima on the singlet potential energy surfaces. Moreover, the sizable barriers calculated show that these compounds should be kinetically stable with respect to isomerization. As such, one may then foresee that the *trans*- and *cis*-HN═XH species would serve as candidates for experimental observation.

(2) When X is nitrogen or phosphorus or arsenic, the *trans*-HN═XH isomer is more stable than its corresponding cis isomer. It is found, however, that the *cis*-HN═XH isomer is slightly more stable than the *trans*-HN═XH species, as X goes from antimony to bismuth.

Conventionally, the trans isomer is more stable than the corresponding cis isomer due to reduced steric repulsion. In the case of HN═SbH and HN═BiH, however, this situation may change. It is well established that the charge distribution is determined by the electronegativities. For most cases, the charge distribution leads to X(δ^+)−H(δ^-), except in the case of N where it leads to N(δ^-)−H(δ^+). In particular, the atomic charges of these two hydrogens would be enhanced as X is a much heavier element (such as antimony and bismuth; see Table A in the Supporting Information). In this regard, the electrostatic attraction between the N−H and X−H moieties tends to favor the cis isomer over the trans isomer, as demonstrated in **1**.



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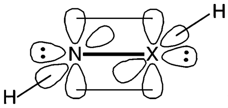
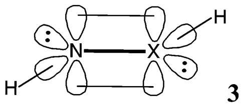
(3) In the singlet *trans*-HN═XH species, the ∠NXH angle decreases and the N═X bond length increases as X changes from N to Bi.

For instance, as seen in Figures 1-5, the bond angle ∠NXH in the singlet *trans*-HN═XH species decreases in the order N (105°) > P (98°) > As (96°) > Sb (94°) > Bi (93°). In addition, the N═X bond length increases in the order N (1.268 Å) < P (1.618 Å) < As (1.736 Å) < Sb (1.933 Å) < Bi (2.011 Å).

In singlet *trans*-HN═XH, it thus appears that, as the X atom becomes heavier, a bond angle (∠NXH) approaching 90° is preferred. The reason for this may be due to the relativistic effect.[20] As X changes from nitrogen to bismuth, the valence s orbital is more strongly contracted than the corresponding p orbitals.[21] Namely, the size difference between the valence s and p orbitals increases from N to Bi (the significant 6s orbital contraction originates mostly from the relativistic effect). Consequently, the valence s and p orbitals differ in spacial extension and overlap less to form strong hybrid orbitals.[20,21] It is therefore expected that in phosphazenes, arsanazenes, antimonazenes, and bismuazenes an increased tendency toward sp hybridization occurs on going from phosphane to bismuth; that is, bond formation of type **2** is preferred over type **3**. In other words, the so-called "inert s-pair effect" (or "nonhybridization effect")[20,21] occurs on moving from phosphane to bismuth, where sp hybridization is preferred to sp^2. As a result, the bond angle ∠NXH (X = P, As, Sb, and Bi) in singlet *trans*-HN═XH species is much smaller than the bond angle ∠NNH in singlet *trans*-HN═NH and approaches 90° as the X atom becomes heavier.



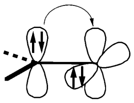
2



3

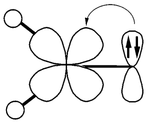
(4) Singlet HN═XH, H$_2$N═X, and H$_2$X═N isomers possess a planar geometry, except for the cases of singlet H$_2$SbN and H$_2$BiN with pyramidal conformations. On the other hand, all HNXH species with open-shell triplet states adopt a nonplanar geometry. Namely, the triplet HNXH molecules are twisted, whereas the triplet H$_2$NX and H$_2$XN compounds are pyramidal.

The reason for these phenomena can be easily understood with reference to their electronic structures. In the singlets, two kinds of interactions exist that determine the geometries of the singlet H$_2$XN and H$_2$NX species.[12b] One is the delocalization of the p−π lone pair of the central atom into the empty p valence orbital of the terminal atom (i.e., p−π(X) → p−π(N)), as shown in **4**.



4

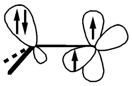
The other is a “back-bonding” effect, in which delocalization of the p−π lone pair of the terminal atom into the unoccupied d orbital (of the appropriate symmetry) occurs on the central atom (i.e., d(X) ← p−π(N)), as shown in **5**.



5

If the above two affects are dominant, then both singlet H_2XN and H_2NX molecules definitely prefer a planar structure, because these effects lead to a maximum overlap between nitrogen and X atoms. In contrast, if the delocalizations are weak, then the central atom will tend to adopt a nonplanar geometry at the expense of π bonds. In a phenomenological sense, this can be considered to be a higher-row manifestation of the “inert s-pair effect”.[20,21] For example, when X is Sb or Bi, the tendency to pyramidalize prevails over these weak delocalizations, allowing the H_2SbN and H_2BiN isomers to be nonplanar. All of these predictions have been confirmed by our calculations as given in Figures 1−5.

On the other hand, as can be seen in **6**, becuase of the repulsion between the electron pair on the central atom and the single electron on the terminal atom, triplet H_2NX and H_2XN species should favor the formation of pyramidal structures over planar structures.



6

(5) The N−X bond length in the singlet H_2XN molecule is shorter than that in the corresponding singlet H_2NX isomer. As can be seen in Figures 1−5, for example, it is found that the N−X bond lengths in singlet H_2XN and H_2NX are as follows: P (1.547 Å < 1.669 Å), As (1.667 Å < 1.789 Å), Sb (1.886 Å < 1.991 Å), and Bi (1.990 Å < 2.067 Å). By contrast, it is found that the N−X bond length in the triplet H_2XN isomer is longer than that in the corresponding triplet H_2NX isomer. For instance, the N−X bond length in triplet H_2XN and H_2NX are as follows: P (1.773 Å > 1.756 Å), As (1.916 Å > 1.881 Å), Sb (2.139 Å > 2.080 Å), and Bi (2.227 Å > 2.164 Å).

The reason for the difference in geometrical parameters can be traced to the delocalization effects shown in **4** and **5**. In the case of singlet state H_2XN, these two delocalization effects are important, and thus, its electronic structure can be depicted as

$$H_2\ddot{X} \rightleftarrows N \qquad (1)$$

Indeed, because the central atom X has lone pairs that can participate in p−π conjugation as demonstrated in **4**, we might consider the H_2XN species to be of the resonance form as shown in **7**.

$$H_2\ddot{X}{-}N \longleftrightarrow H_2X^{+}{=}N^{-}$$

7

On the contrary, in the case of singlet H_2NX, the delocalization of the nitrogen p-π lone pair toward the terminal atom X (i.e., p-π (N) → p-π(X)) runs counter to the electronegativities of the two atoms. Namely, it is well-known that the electronegativity of N is larger than that of the other group 15 elements, i.e., 3.07, 2.25, 2.22, 1.98, and 2.10 for N, P, As, Sb, and Bi, respectively.[22] This tends to make it difficult for nitrogen to donate a lone pair of electrons to X (i.e., when P, As, Sb, or Bi), and the delocalization from X to N will be small. On the other hand, because the 3d orbitals of N are too high in energy to be involved in delocalization, the 3d(N) ← p−π(X) back-bonding effect (i.e., **4**) is expected to be nearly nonexistent. It is thus reasonable to describe the electronic structure of H_2NX as

$$H_2\ddot{N}\xrightarrow{\quad}X \qquad (2)$$

Again, in resonance language, the above electronic structure, eq 2, can be regarded as $H_2N^{+}{=}X^{-}$. This resonance form, however, has little contribution to the N−X bonding.

Thus, a comparison between the electronic structures of H_2XN (eq 1) and H_2NX (eq 2) reveals that delocalization effects are responsible for the shorter N−X bond length in the singlet H_2XN compared to the singlet H_2NX.

In the case of the triplet H_2NX and H_2XN molecules, the difference in N−X bond length can be attributed to electrostatic interactions. For the triplet H_2NX species, the nitrogen atom bears negative charge, whereas the X atom is positively charged. For instance, the atomic charges on the central nitrogen and the terminal atom X derived from a Mulliken population analysis[23] are as follows: X = P (−0.47 e, 0.14 e), X = As (−0.51 e, 0.17 e), X = Sb (−0.63 e, 0.26 e), and X = Bi (−0.66 e, 0.30 e), respectively. On the other hand, for the triplet H_2XN species, the magnitude of the partial charge on the nitrogen atom is smaller than that on the heavier X atom as follows: X = P (−0.22 e, 0.39 e), X = As (−0.21 e, 0.36 e), X = Sb (−0.29 e, 0.65 e), and X = Bi (−0.31 e, 0.75 e). An increased magnitude charge causes the valence orbitals at N to expand, whereas the positive charge contracts the valence orbitals of X.[24] As a result, the higher polarity in triplet H_2NX leads to an increase in the π overlap and the strength of the chemical bond between N and X. Accordingly, the N−X bond length is shorter in triplet H_2NX than that in triplet H_2XN. Moreover, our model calculations also show that the triplet H_2NX is more stable than the corresponding triplet H_2XN for the same reason.

(6) For X = N, P, and As, the stability of the singlet isomers decreases in the order *trans*-HN=XH > *cis*-HN=XH > H_2NX > H_2XN. In contrast, for X = Sb and Bi, the stability is in the order H_2NX > *cis*-HN=XH ≈ *trans*-HN=XH > H_2XN. This finding suggests that Sb and Bi are more reluctant to form doubly bonded compounds than N, P, and As.

Again, the answer lies in the dramatic contraction of the Sb 5s and Bi 6s orbitals due to relativistic effects,[21,22] which reduces their tendency to form hybrid orbitals. This, results in Sb and Bi preferring to maintain the $(5s)^2(5p)^3$ and $(6s)^2(6p)^3$ valence electron configurations, respectively. The use of these three orthogonal 5p (or 6p) orbitals without significant hybridization leads to the presence of two lone pairs at Sb (or Bi). It is therefore apparent that the structures with the most lone pairs are more stable. In short, the reason for the reluctance in forming NSb (or NBi) multiple bonds is the significant contraction of the Sb and Bi valance s orbitals.

(7) The H_2NX isomer is always more stable than the corresponding H_2XN isomer for X = P, As, Sb, and Bi, irrespective of the singlet or triplet states they adopt. In fact, the theoretical investigations strongly suggest that both singlet and triplet H_2XN (for X = P, As, Sb, and Bi) molecules are thermodynamically and kinetically unstable, and thus should not be observable.

The reason for this trend can readily be understood in terms of the $N-H$ vs $X-H$ bond energies. In the H_2NX isomers, there are two $N-H$ bonds, whereas there are two $X-H$ bonds in the H_2XN isomers. Experimental values of the $X-H$ bond energy are in the order: $N-H$ (93 kcal/mol) > $P-H$ (78 kcal/mol) > $As-H$ (71 kcal/mol) > $Sb-H$ (61 kcal/mol).[25,26] Therefore the H_2NX isomer should always be more stable than the H_2XN isomer.

The other feature of interest concerns the pyramidalization angle at the central atom X of the triplet H_2XN species. In particular, this angle (the out-of-plane angle, defined as the angle between the $N-X$ bond and the H_2X plane) increases in the order N (70°) < P (84°) < As (86°) < Sb (88°) < Bi (89°). Again, the pyramidalization angles in triplet H_2SbN and H_2BiN are close to 90° and provide evidence for the core-like nature of the 5s and 6s electrons, that is, the so-called "inert s-pair effect",[20,21] discussed earlier.

(8) For X = N and P, the stability of the triplet isomers decreases in the order HNXH > H_2NX > H_2XN. In contrast, for X =As, Sb, and Bi, the stability is in the order H_2NX > HNXH > H_2XN. Moreover, ab initio calculations indicate that the ground state of the HNNH and HNPH species is the closed-shell singlet *trans*-$HN{=}XH$, whereas for the HNXH species, it is the open-shell triplet H_2NX, as X goes from arsenic to bismuth.

Figure 7 clearly illustrates that, when going down group 15, the triplet pyramidal H_2NX structure appears to be more and more favored, whereas the singlet *trans*-$HN{=}XH$ structure becomes less favored. In other words, triplet H_2NX (X = As, Sb, and Bi) is the globally most stable structure and lies 4.8, 13, and 15 kcal/mol, respectively, below the most stable singlet HNXH (X = As, Sb, and Bi) species. However, for triplet state H_2NN and H_2NP, the twisted structure was found to be the local minimum isomer lying 32 and 7.0 kcal/mol in energy above singlet *trans*-$HN{=}NH$ and *trans*-$HN{=}PH$, respectively.

Furthermore, as expected, the triplet state is characterized by a large twist angle or a high degree of pyramidalization on the central atom, and a $N-X$ distance which is considerably longer than that in the singlet state. All of these changes are not surprising because the triplet states result from the excitation from a bonding π or nonbonding n to an antibonding π^* orbital. Our calculations have confirmed these predictions as already given in Figures 1−5. It is interesting to note that the energy difference favoring triplet H_2NX over singlet H_2NX is calculated to be much smaller than that favoring triplet H_2XN over singlet H_2XN, when X goes from As to Bi.

IV. Conclusion

Experimental and theoretical studies of unsaturated heavier pnicogen compounds have produced a wealth of new and unexpected phenomena, and more is sure to come. In fact, many of the results of this work suggest that a replacement of nitrogen by other heavier pnicogen atoms in HNXH molecules may be rewarding. In particular, unsaturated compounds of the form HNXH differ dramatically as X goes down the periodic table from nitrogen to bismuth. For instance, the most stable conformation of the singlet state is $HN{=}XH$ (both trans-bent and cis-bent) from both kinetic and thermodynamic viewpoints, when X is nitrogen or phosphorus. However, when X is arsenic, antimony, or bismuth, the global minimum on the triplet surface is predicted to be pyramidal H_2NX, with the singlet *trans*-$HN{=}XH$ species higher in energy by about 5.0−26 kcal/mol. Nevertheless, the new insight given by the present study shows that there should be no reason for the $N{=}X$ double bonds to be out of reach of experimentalists. Indeed, both trans-bent and cis-bent structures for singlet $HN{=}XH$ (X = As, Sb, and Bi) are also found to be minima on the singlet potential energy surfaces and possess relatively large activation barriers with respect to unimolecular isomerization, so that they should be suitable candidates for spectroscopic observation.

We hope that the present theoretical results will convince experimental chemists that a molecule containing a $N{=}Sb$ or $N{=}Bi$ bond is not an unrealistic proposition. Successful schemes for the synthesis and isolation of such doubly bonded species are therefore expected to be devised soon.

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Supporting Information Available: The vibrational frequencies predicted for both singlet and triplet HNNH isomers, as well as the calculated rotational constants, dipole moments, and net atomic charges (Table A). This material is available free of charge via the Internet at http://pubs.acs.org.

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