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Proton Transfer Reactions of Hydrazine-boranes.

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Abstract

Hydrazine-borane and hydrazine-diborane contain respectively 15.4 and 16.9 wt% of hydrogen and are potential materials for hydrogen storage. In this work we present the gas-phase complexation energies, acidities and basicities of hydrazine-borane and hydrazine-bisborane calculated at MP2/6-311+G(d,p) level. We also report the release of dihydrogen from both protonated complexes ($G_{hydrazine\text{-}borane}$ = –20.9 kcal/mol and $G_{hydrazine\text{-}bisborane}$ = –27.2 kcal/mol) which is much more exergonic than from analogues amine-boranes. The addition of the first BH_3 to the hydrazine releases 17.1 kcal/mol and the second addition releases 15.8 kcal/mol. The attachment of BH_3 also increases the N-H acidity of hydrazine by 46.3 kcal/mol. It was found that the B-H deprotonation leads to intramolecular rearrangement. The basicity values for hydrazine-borane and –bisborane are 180 and 172.8 kcal/mol respectively. For both complexes the protonation centres are located at the boron moiety. The protonated structure of hydrazine-bisborane is cyclic and can be described as H_2 captured between a negatively charged B-H hydrogen and positive boron (B-H••H2••B). Atoms in Molecules analysis is used to investigate bond paths in concerning structures.

Keywords: ab initio calculations, gas-phase, hydrazine, borane, complex, acidity, basicity, dihydrogen

Introduction

Hydrazine is a well-known compound with many applications; for example it is used as rocket fuel and a precursor in polymer foam industry. It is toxic and dangerously unstable. The history of hydrazine complex with borane ($N_2H_4 \cdot\cdot BH_3$) dates back more than 50 years since its synthesis and thermal decomposition were first described by Ricker and Goubeau.[1] The addition of borane changes the properties of free hydrazine considerably and new possible applications for the resulting complex are being investigated. One of the important features is the decrease in the activation energy of the H_2 release reaction[2] and therefore it has been suggested as a potential hydrogen storage material.[3, 4] The hydrogen content in $N_2H_4BH_3$ is very high (15.37 wt %) and comparable to ammonia-borane (19.6 wt %).

Unlike ammonia-borane, the hydrazine-borane has uneven amount hydrogens atoms – four protic ($H^{\delta+}$) and three hydridic ($H^{\delta-}$) and it is hard to separate all the hydrogen by simple thermal treatment. One option is to add metal hydrides like LiH and it has been shown that such an approach improves the dihydrogen release from the obtained salt significantly.[3] Temperatures about 150 °C are common in the H_2 extraction process and in the case of hydrazine-borane the reaction can be controlled up to 200 °C. The bisborane complex is less stable towards the heating. High energy content of hydrazine becomes evident when applying the same treatment to hydrazine-bisborane, as the explosive decomposition is reported to start at temperatures about 160 °C.[3]

The dihydrogen release from neutral hydrazine-borane has also been studied computationally. Vinh-Son *et al.*[2] have found that the $N_2H_4 \rightarrow N_2H_2 + H_2$ reaction is endothermic by 22.1 kcal/mol (for the trans conformer at the CCSD(T)/CBS limit at 0 K) and the addition of BH_3 fundamentally changes the thermochemistry. ΔH value of -4.7 kcal/mol was predicted for the $BH_3NH_2NH_2 \rightarrow BH_2NHNH_2 + H_2$ reaction.

Amine-boranes are analogues to hydrazine-boranes as they also contain the N-B bond and they have gained significantly more attention. The hydrogen release reaction as well as intrinsic properties related to hydrogen storage, like gas-phase basicity and acidity have been studied. [5, 6, 7] It has been found that complexation

greatly alters the properties of amines, for example the acidity is enhanced by 30-50 kcal/mol.[7, 8] The protonation centre of such complexes is located on the boron moiety and the resulting structure can be described as $R_1R_2R_3N\text{-}BH_2^+ \bullet\bullet H_2$.[5, 6] The dihydrogen is connected to the remaining complex with S-shaped 3-centre-2-electron bonds and its removal is clearly an exergonic process.[5] The Gibbs free energy change for the dihydrogen dissociation reaction for amine-boranes varies from -11 to -5 kcal/mol. This kind of protonated structure is common for protonated borane complexes – for example the protonated phosphine boranes are very similar and also exhibit the hydrogen releasing properties.[9]

In this work we present the results related to proton transfer reactions of hydrazine-borane ($N_2H_4BH_3$) and hydrazine-bisborane ($BH_3N_2H_4BH_3$). At the first glance the structures seem to be very similar to amine-boranes, but some properties related to proton transfer reactions are not, for example the energetics of the dihydrogen release reactions are drastically different. In the past, the electronic structure of neutral hydrazine-borane and hydrazine-bisborane have been investigated,[10, 11] in this work we also report the structure and interactions present in protonated and deprotonated species.

Computational details

The calculations were carried out using the GAUSSIAN 09[12] program package under standard conditions (298.15 K and 1 atm). In our work we used MP2[13-17] method with 6-311+G(d,p)[18-21] basis set. MP2/6-311+G(d,p) is an adequate and relatively cheap method for calculating systems discussed in this study. For example in Ref 7 and Ref 8 acidity of ten similar systems – amine-boranes have been calculated with G4 and MP2/6-311+G(d,p) methods and the mean absolute error between the results is under 1 kcal/mol. A full conformational search was done for each species and vibrational analyses for zero-point energies, and thermal corrections were performed. All stationary points were found to be true minima (NImag=0). For protonated and deprotonated species all possible protonation and deprotonation centres were investigated and only the most stable structures were used. For a free proton, the free energy value of 0.01 au. (ca. 627.5 kcal/mol) was used; derived from statistical thermodynamics. In the case of complexation

energies and dihydrogen removal reaction, basis set superposition error (BSSE) was calculated using the counterpoise method of Boys and Bernardi.[22] The BSSE estimations for MP2/6-311+G(d,p) calculations were quite constant, approximately 4-5 kcal/mol for complexation reactions and about 2 kcal/mol for dihydrogen removal. We use Gibbs free energy changes for all studied reactions in this work. Calculated enthalpies can be found in the supplementary information.

To investigate the electronic structure of the complexes in more detail, we performed Bader's Atoms in Molecules (AIM) analysis.[23, 24] It allows us to track electron density between atoms and therefore draw conclusions about the character and the strength of the bonds present in a molecule. Two important characteristics of the AIM analysis are the electron density (ρ) and the laplacian of the electron density ($\nabla^2\rho$) in the bond critical point (BCP, where the electron density is minimal along the bond path). Electron density at the BCP indicates the amount of electrons involved in the bond formation and higher density refers to a stronger bond. The laplacian of the electron density in the BCP characterizes the curvature of the electron density distribution and is an indicator of bond covalency. Negative values generally refer to more covalent interactions.

Results and discussion

It is known that hydrazine-borane and hydrazine-bisborane are both stable solids at normal temperatures. Our computations confirm that both complexes are also stable in the gas-phase and our calculated Gibbs free energy changes for the following complexation reactions are as follows:

$$N_2H_4 + BH_3 \rightarrow NH_2NH_2\text{-}BH_3 \qquad \Delta G = -17.1 \text{ kcal/mol}$$

$$NH_2NH_2\text{-}BH_3 + BH_3 \rightarrow H_3B\text{-}NH_2NH_2\text{-}BH_3 \qquad \Delta G = -15.8 \text{ kcal/mol}$$

The energy released in the first and second complexation step is very close, which allows us to conclude that the first addition of BH_3 has very little effect to the electron donating ability of the second nitrogen. Both values are also comparable to complexation values of amine-boranes. For example ΔG for unsubstituted amine-borane is -14.1 kcal/mol and values for substituted complexes vary from -15 to -22

kcal/mol, if we leave aside phenyl substituted amine-borane with an exceptionally low stability.[8]

Deprotonation and gas-phase acidity

Gas-phase acidity (GA) is defined as the Gibbs free energy change for the reversible deprotonation reaction. For hydrazine-borane and hydrazine-bisborane the theoretical deprotonation reactions would be as follows:

$$N_2H_7B \leftrightarrows N_2H_6B^- + H^+$$

$$N_2H_{10}B_2 \leftrightarrows N_2H_{10}B_2^- + H^+$$

There are three possible different deprotonation centres in N_2H_7B and two in $N_2H_{10}B_2$. The enthalpies and Gibbs free energies as well as relative energies and corresponding acidity values for all the deprotonation centres for both complexes are presented in Table 1. Our computations show, that the removal of proton from BH_3 initiates intramolecular rearrangements leading to the destruction of the complex. The dissociated structures (result of B-H deprotonation) are clearly energetically more favourable than the N-H reversibly deprotonated species. The dissociated structures are presented in Figures 1 and 2. The gap between the dissociated structure and the most favoured reversibly deprotonated structure (which corresponds to the N-H acidity centre on nitrogen interacting with BH_3) is 37.2 kcal/mol for hydrazine-borane and 36.4 kcal/mol for hydrazine-bisborane.

Since the B-H deprotonation leads to irreversible rearrangements resulting in energetically favourable structures we cannot calculate the true acidity for that deprotonation centre. Comparing the reactions resulting in “broken” deprotonated hydrazine-borane (Figure 1) and hydrazine-bisborane (Figure 2) we see that the deprotonation for the latter is about 25 kcal/mol more favourable. One of the reasons is the additional BH_3 in hydrazine-bisborane which helps to stabilize the negative charge left by the removal of proton. The NBO charges of neutral and deprotonated complexes are presented in Table 2 and although the absolute values of atomic charges are dependent on the method the trends are not and are therefore useful in discussing structural and reactivity.[25, 26] The NBO values show that the B-H

deprotonated hydrazine-borane dissociates into ammonia and negatively charged BH_2NH^- while B-H deprotonated hydrazine-bisborane dissociates into double bonded BH_2NH_2 and $BH_3NH_2^-$. Since both deprotonated species separate into two, the changes in atomic charges are considerable. The interaction distances between the ammonia and BH_2NH^- in deprotonated hydrazine-borane as well as between BH_2NH_2 and $BH_3NH_2^-$ in deprotonated hydrazine-bisborane are clearly longer than normal N-H bonds (the N-H interaction distance in hydrazine-borane is 1.95 Å and 1.83 Å in hydrazine-bisborane). The electron density at the BCP is also considerably lower (0.03 hydrazine-borane and 0.04 in hydrazine-bisborane) compared to the covalent N-H bonds in ammonia (ca. 0.30)

We have calculated the gas-phase acidity of free hydrazine to be 393.9 kcal/mol and the addition of a BH_3 increases the acidity of the N-H group considerably. Attaching BH_3 to the nitrogen involved in the acidity centre enhances the acidity by 46.3 kcal/mol and attaching BH_3 to the farther nitrogen increases the proton donating ability by 24.7 kcal/mol. With BH_3 molecules added to both nitrogen we get the hydrazine-bisborane complex where the acidity of the N-H centre is enhanced by 72.3 kcal/mol. Based on these values it is evident that the N-H group in hydrazine-bisborane is 26 kcal/mol more acidic than in the hydrazine-borane.

The N-H acidity of hydrazine-borane is close to amine-boranes. For example the acidity calculated with MP2/6-311+G(d.p) method for methyl amine-borane is 349.5 kcal/mol and 347.3 kcal/mol for dimethyl amine-borane. The acidity of the N-H group in hydrazine-bisborane (321.6 kcal/mol) is clearly higher than the most acidic studied amine-borane – phenyl amine-borane (327.3 kca/mol).

Since the B-H deprotonations are followed by intramolecular rearrangements the calculated acidity values do not give us information from which centre will the proton be actually removed. To estimate the probabilities of N-H and B-H deprotonations we have calculated the so-called vertical deprotonation energies (proton removal energies without geometry relaxation) for both N-H and B-H hydrogens. It was found that the vertical deprotonation in the case of hydrazine-borane favours the N-H acidity by 70 kcal/mol over the B-H deprotonation and the result is similar for hydrazine-bisborane, as the removal of N-H hydrogens is favoured by 77 kcal/mol over the B-H hydrogens. We also used an approach where a dimer

consisting of two complexes was constructed positioned in a way that the competing deprotonation centres were facing each other. Both acidity centres were deprotonated and one proton was placed in the line between nitrogen and boron. Several distances around the centre of the direct line between the N and B atoms were chosen and for each case the geometry was allowed to relax. In all cases the relaxation resulted in the formation of the B-H bond. As a result we can conclude that the N-H should be more favourable deprotonation centre.

Gas-phase basicity

Gas-phase Basicity (GB) is defined as the negative Gibbs free energy change for the reversible protonation reaction. For hydrazine-borane and hydrazine-bisborane the protonation reactions are as follows:

$NH_2NH_2BH_3 + H^+ \leftrightarrows NH_2NH_2BH_2^+ \bullet\bullet H_2$ GB=183.0 kcal/mol

$H_3BNH_2NH_2BH_3 + H^+ \leftrightarrows H_3BNH_2NH_2BH_2^+ \bullet\bullet H_2$ GB=172.8 kcal/mol

For both complexes the favoured protonation site is clearly on the boron moiety and the resulting structures can be described as dihydrogen connected to the rest of the positively charged complex. The protonated structures together with bond paths obtained by Bader's AIM theory are presented in Figures 3 and 4. We can see from the Figure 3 that in protonated hydrazine-borane the dihydrogen is connected to boron by a 3-centre-2-electron bond. Such curved bond paths are also present in amine-boranes,[5] while in analogous phosphine-boranes the bond-paths are different.[9] AIM analyses also shows that the interactions in $H_2 \bullet\bullet B$ moiety in amine-boranes and hydrazine-borane are very similar. The ρ value in the BCP of the curved B-H_{H2} interaction is 0.084 in hydrazine-borane and 0.0853 in unsubstituted amine-borane. This is also the case for the Laplacian of the electron density at the BCP's as the $\nabla^2\rho$ value in hydrazine-borane is 0.1310 and 0.1210 in amine-borane.[9]

It can be concluded that the different electronic structure of hydrazine compared to amines has very little effect to the basicity of the borane complex (compared to free BH_3, GB = 133 kcal/mol, the addition of Lewis base of course enhances the basicity greatly). The basicity value for hydrazine-borane is 183.0

kcal/mol and for ammonia-borane it is 185.4 kcal/mol[5] (both values were obtained using MP2/6-311+G(d.p) method). Bulkier carbon based N-substitutions in amine-boranes usually increase the basicity and small electron withdrawing groups have the opposite effect.[5] The chloro substitution in the amine for example reduces the proton affinity of the complex by ca. 13 kcal (G2MP2) and fluoro substitution reduces it by ca. 21 kcal/mol (G2MP2).[27, 28] If we presume that entropy terms for the reactions involving substituted and unsubstituted complexes are close, we can estimate the basicity difference to be comparable to proton affinity differences. The hydrazine also possesses the electron withdrawing abilities and thus reduces the proton accepting ability of the complex compared to ammonia-borane.

Although the basicity of hydrazine-borane differed very little from amine-boranes, it is important that the second nitrogen provides an additional complexation centre and the attachment of the second BH_3 supports the formation of a considerably different protonated structure. The additional link in the backbone of the species allows a formation of a cyclic structure. In the new structure the H_2 is captured between positively charged boron and negatively charged hydrogen (charges are presented in Table 2). “Regular” protonated structure with two S-shaped interactions like in protonated hydrazine-borane also exists for hydrazine-bisborane, but it is about 3.6 kcal/mol less stable than the cyclic structure. If we compare the most favourable basicity centres of both species we can conclude that the bis complex is by 10 kcal/mol less basic compared to hydrazine-borane. Those values suggest that the additional complexation with BH_3 decreases the basicity of hydrazine-borane about 13.6 kcal/mol.

If we compare the bond paths in the protonated hydrazine-bisborane to the ones in hydrazine-borane we see that one of the curved H_2••B interactions is replaced by the new B-H••H_2 interaction involving the second borane moiety. According to AIM analyses the two H_2••B interactions in hydrazine-borane are characterized by the distance of 1.44 Å and electron density of 0.084 at the BCP. The new interaction in hydrazine-bisborane is weaker – it is longer (1.74 Å) and the electron density at the BCP is smaller (0.023).

The structure of protonated hydrazine-bisborane is similar to the molecular tweezer like structures of some amine- and phosphine-boranes, where the H_2 can be

captured between a boron and a π-system, for example like in benzyl amine-borane.[5] In protonated hydrazine-bisborane negatively charged hydrogen replaces the π-system. If we compare the interaction in hydrazine-bisborane to the interaction in benzyl amine-borane, we see that the negatively charged B-H hydrogen replaces the π-system. As a result the interaction is stronger and shorter than in the amine complex, electron densities at BCP were 0.023 and 0.015 respectively and distances were 1.74 Å and 2.40 Å respectively. It should be noted that such interactions were not found in protonated trifluoroethyl amine-borane and chloroethyl amine-borane, where chain length would allow similar interactions.[5] It suggests that the second boron plays important role in this tweezer like interaction.

H_2 release from protonated structures

Protonated borane complexes contain a weakly bound dihydrogen and to assess the stabilities of the hydrazine-borane species we have calculated the Gibbs free energies for the following H_2 dissociation reactions:

$NH_2NH_2BH_2^+ \bullet\bullet H_2 \rightarrow NH_2NH_2BH_2^+ + H_2$ -20.9 kcal/mol

$H_3BNH_2NH_2BH_2^+ \bullet\bullet H_2 \rightarrow H_3BNH_2NH_2BH_2^+ + H_2$ -27.2 kcal/mol

Both reactions are much more exergonic than the analogues reactions for amine-boranes and phosphine-boranes.[5, 9] The reason can be found in the resulting structures which are presented on Figures 5 and 6.

The dihydrogen release from protonated hydrazine-borane leads to the formation of a positively charged three membered cycle. After the removal of H_2 an empty orbital is left on boron and there is a free electron pair on the second nitrogen – an intramolecular Lewis complexation reaction takes place, a cycle is formed and 20.9 kcal/mol of energy is released. A different kind of cycle forms when H_2 is removed from protonated hydrazine-bisborane. In protonated complex the H_2 was captured between the negatively charged hydrogen and positive boron (B-H••**H_2**••B), after the dihydrogen release a direct interaction that can be described as a 3-centre-

2-electron B-H-B bond is formed (the B-H distances in this interaction are 1.324 Å and electron densities at the BCP-s are 0.103).

Conclusions

In this work we presented the gas-phase complexation energies, acidities, basicities, and Gibbs free energy changes for the dihydrogen release reactions from protonated complexes for hydrazine-borane and hydrazine-bisborane. All values were calculated at MP2/6-311+G(d.p) level. The formation of both complexes was energetically favourable – addition of the first BH_3 releases 17.1 kcal/mol and the second addition releases 15.8 kcal/mol. There are two competing deprotonation centres (N-H and B-H) in both complexes. The N-H deprotonations are reversible but B-H deprotonations are not, leading to intramolecular rearrangements. Although the rearranged results of the B-H deprotonations are energetically more favourable, we concluded that the N-H deprotonations are more probable to occur. Compared to hydrazine the attachment of BH_3 increases the N-H acidity by 46.3 kcal/mol. For both complexes the protonation centre is located at the boron moiety. The basicity values found for hydrazine-borane and –bisborane are 180 and 172.8 kcal/mol respectively. The protonated structure of hydrazine-bisborane is cyclic and can be described as H_2 captured between a negatively charged B-H hydrogen and positive boron (B-H••H2••B). The release of dihydrogen from protonated complexes ($G_{hydrazine\text{-}borane}$ = –20.9 kcal/mol and $G_{hydrazine\text{-}bisborane}$ = –27.2 kcal/mol) is more exergonic than from amine-boranes. The resulting positively charged structures are cyclic, which is the reason behind the unexpectedly favourable H_2 release.

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Table 1. Comparison of different acidity centres in hydrazine-borane and hydrazine-bisborane. The acidity centres on hydrazine-borane are numbered as follows (in superscript): $N^2H_2N^1H_2$-BH_3.

Deprotonation centre		H (Hartree)	G (Hartree)	ΔG (kcal/mol)	GA (kcal/mol)
Hydrazine-borane	B	-137,540835	-137,577417	0,0	310,4
	N1	-137,487437	-137,518151	37,2	347,6
	N2	-137,452501	-137,483756	58,8	369,2
Hydrazine-bisborane	B	-164,094824	-164,135515	0,0	285,2
	N1	-164,042469	-164,077531	36,4	321,6

H – enthalpy of the deprotonated structure; G – free energy of the protonated structure; ΔG gap compared to the most stable structure; GA – gas-phase acidity calculated using the given deprotonation centre.

Table 2. The NBO charges on neutral, deprotonated (both B-H deprotonation resulting in “broken” structure and “regular” N-H deprotonation), and protonated complexes calculated with MP2/6-311+G(d,p).

	Hydrazine		Hydrazine-Borane				Hydrazine-Bisborane			
	Neutral	Deprot.	Neutral	B-H deprot.	N-H deprot.	Protonated	Neutral	B-H deprot.	N-H deprot.	Protonated
B	-	-	-0.033	0.391[a]	-0.008	0.171	-0.042	0.509[a]	-0.023	0.111
H	-	-	-0.089	-0.194[a]	-0.140	0.016	-0.101	-0.150[a]	-0.122	0.005
H	-	-	-0.096	-0.205[a]	-0.148	0.191	-0.078	-0.160[a]	-0.129	0.179[c]
H	-	-	-0.110	-	-0.188	0.000	-0.101	-	-0.112	0.020
H	-	-	-	-	-	0.198	-	-	-	0.260[c]
N	-0.655	-0.754	-0.525	-1.264[a]	-0.718	-0.576	-0.499	-1.084[a]	-0.531	-0.551
H	0.336	0.274	0.390	0.441[b]	0.274	0.426	0.410	0.471[a]	0.371	0.449
H	0.319	0.274	0.376	0.296[a]	-	0.407	0.410	0.373[a]	0.371	0.436
N	-0.655	-1.034	-0.617	-1.094[b]	-0.669	-0.584	-0.499	-1.115[b]	-0.679	-0.505
H	0.336	0.240	0.368	0.315[b]	0.301	0.375	0.410	0.317[b]	0.324	0.427
H	0.319	-	0.338	0.313[b]	0.296	0.378	0.410	0.317[b]	-	0.426
B	-	-	-	-	-	-	-0.042	-0.015[b]	-0.032	-0.020
H	-	-	-	-	-	-	-0.101	-0.150[b]	-0.145	-0.095
H	-	-	-	-	-	-	-0.078	-0.164[b]	-0.122	-0.036
H	-	-	-	-	-	-	-0.101	-0.150[b]	-0.172	-0.105

[a] and [b] mark the atoms belonging into separate substructures presented in Figures 1 and 2. [c] marks the H_2 captured into the tweezer.

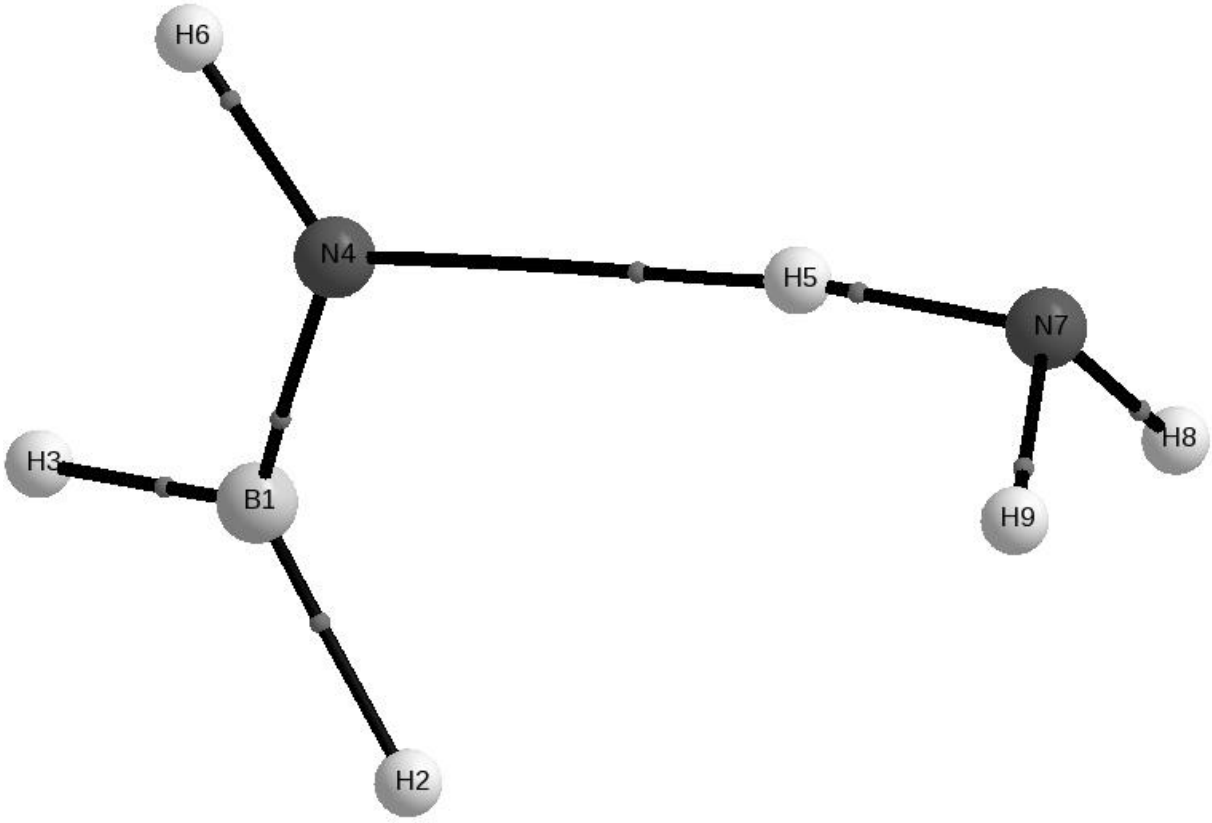

Figure 1. Optimized structure resulting from B-H deprotonation of hydrazine-borane

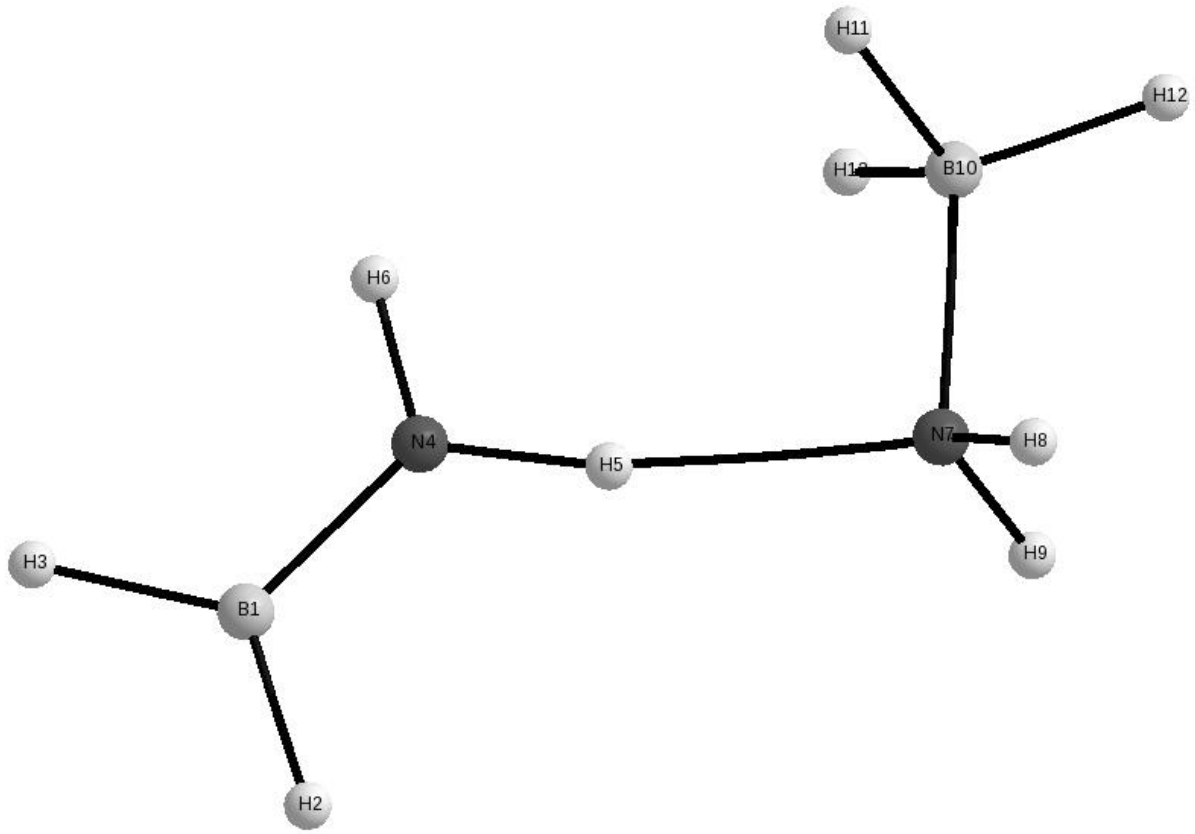

Figure 2. Optimized structure resulting from B-H deprotonation of hydrazine-bisborane

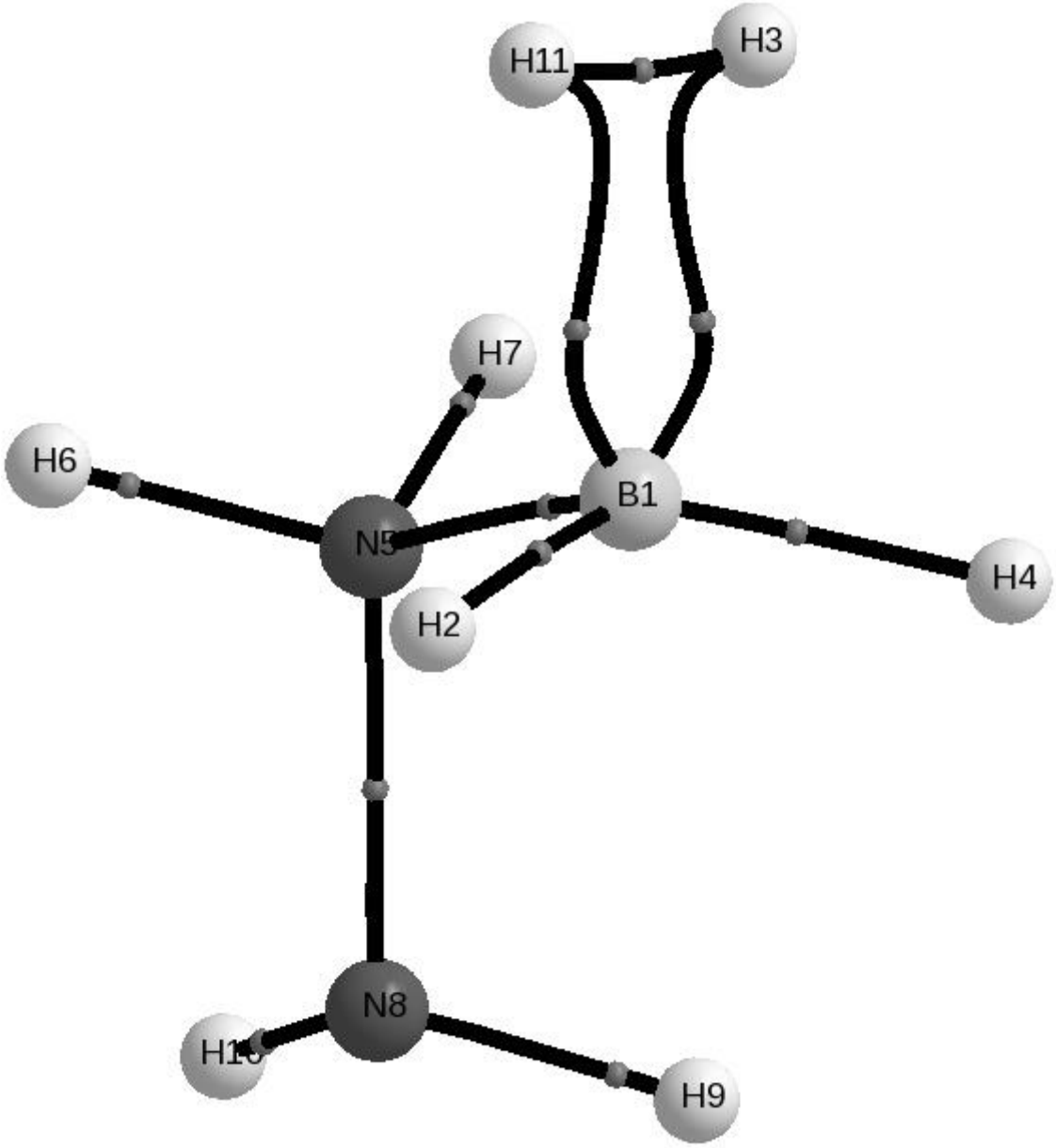

Figure 3. Protonated hydrazine-borane

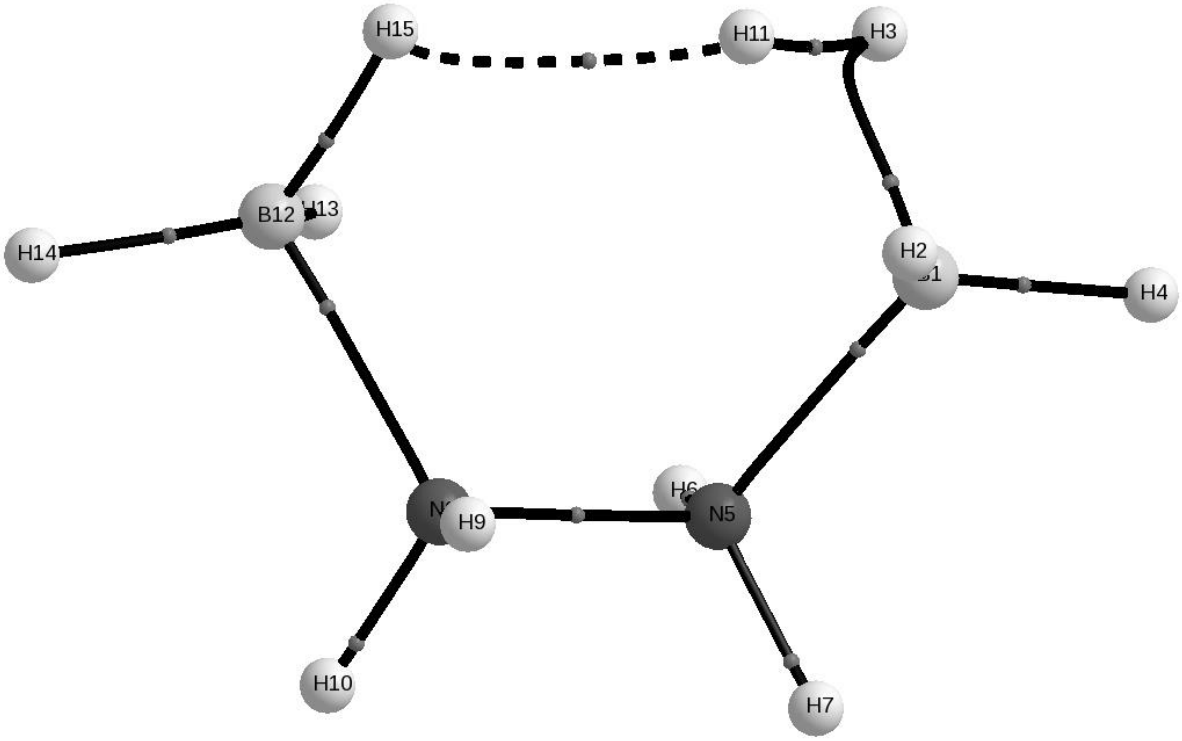

Figure 4. Protonated hydrazine-bisborane

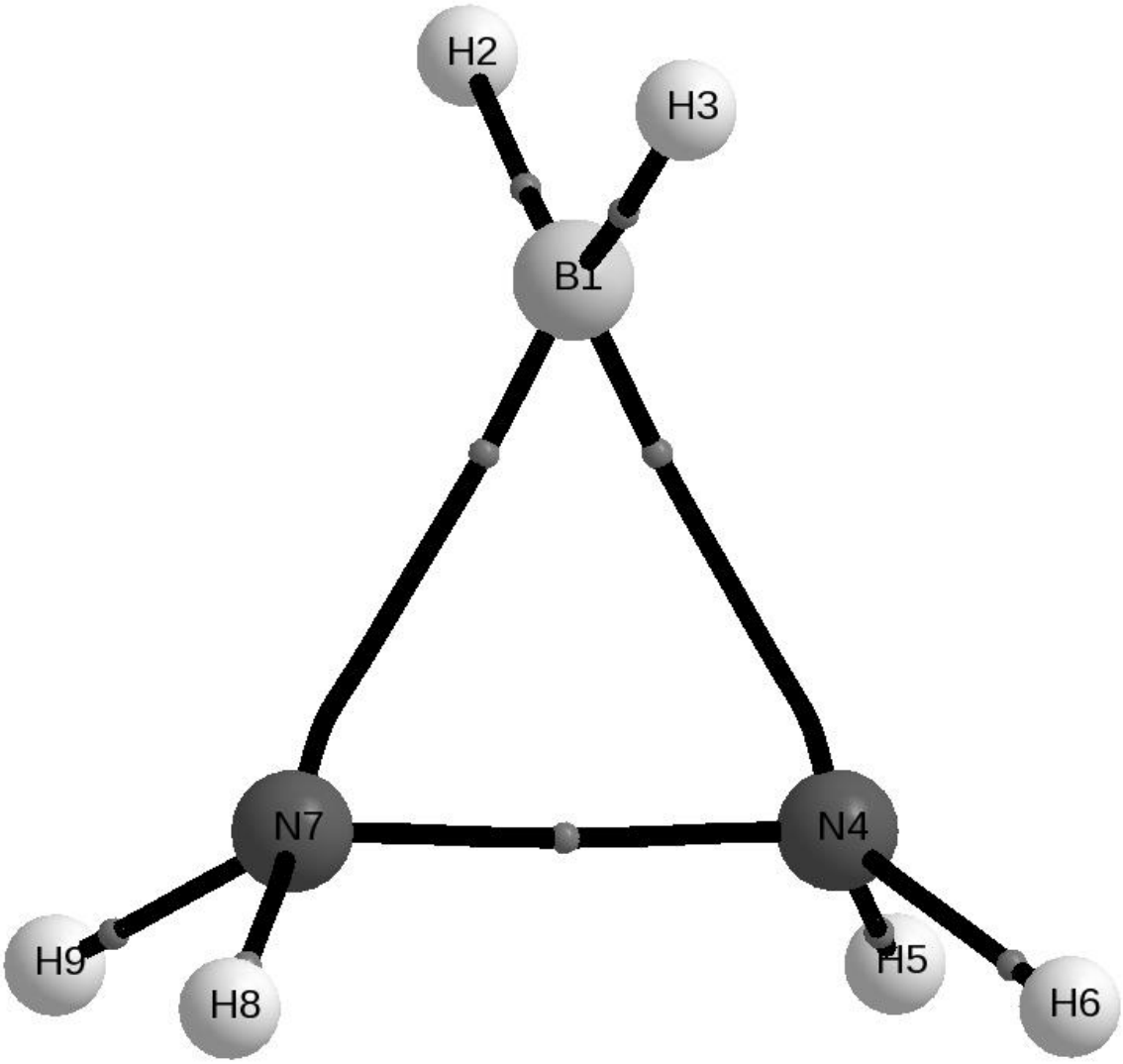

Figure 5. Product of the protonation of hydrazine-bisborane after H2 release

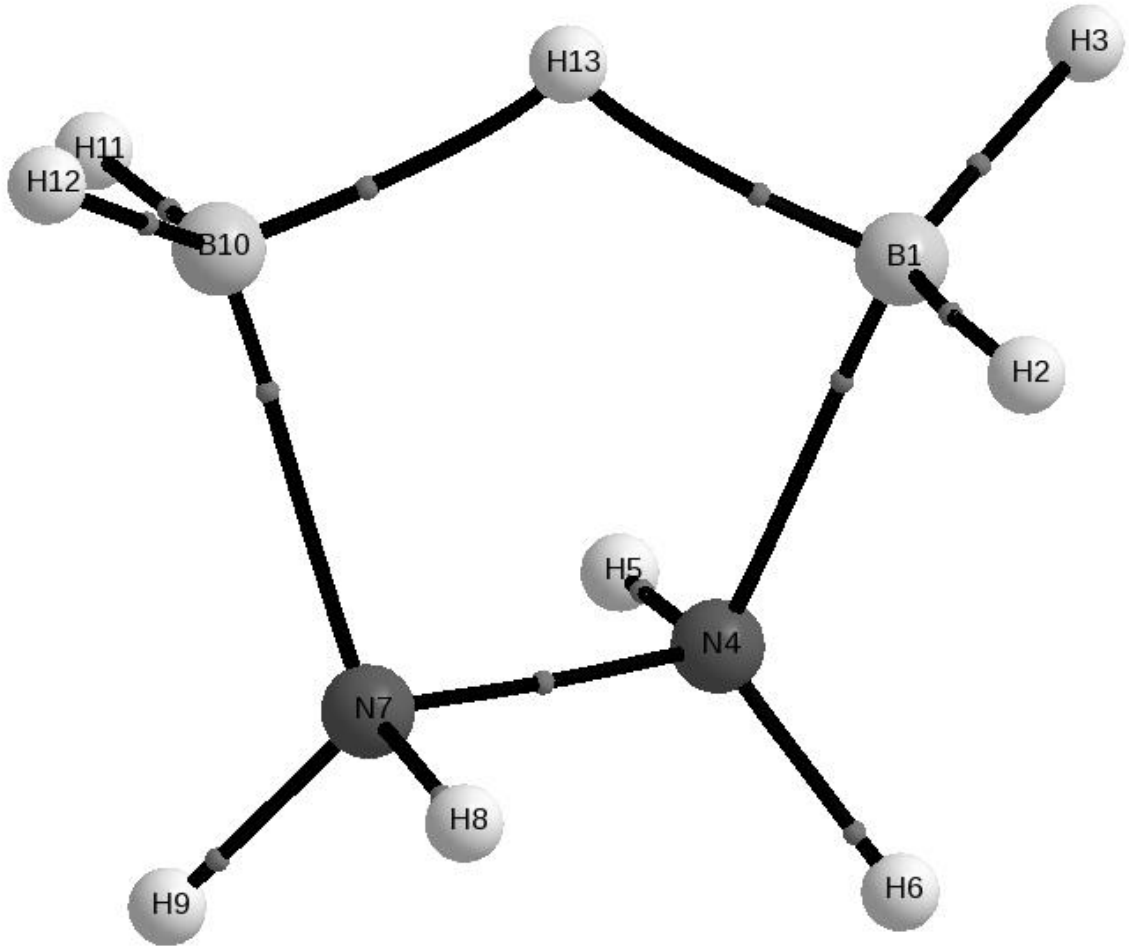

Figure 6. Protonated hydrazine-bisborane after H2 release