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Isomers and Conformers of H(NH₂BH₂)ₙH Oligomers: Understanding the Geometries and Electronic Structure of Boron−Nitrogen−Hydrogen Compounds as Potential Hydrogen Storage Materials

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Boron−nitrogen−hydrogen (BNH$_x$) materials are polar analogues of hydrocarbons with potential applications as media for hydrogen storage. As H(NH₂BH₂)ₙH oligomers result from dehydrogenation of NH₃BH₃ and NH₄BH₄ materials, understanding the geometries, stabilities, and electronic structure of these oligomers is essential for developing chemical methods of hydrogen release and regeneration of the BNH$_x$-based hydrogen storage materials. In this work we have performed computational modeling on the H(NH₂BH₂)ₙH ($n = 1-6$) oligomers using density functional theory (DFT). We have investigated linear chain structures and the stabilizing effects of coiling, biradicalization, and branching through Car−Parrinello molecular dynamics simulations and subsequent geometry optimizations. We find that the zigzag linear oligomers are unstable with respect to the coiled, square-wave chain, and branched structures, with the coiled structures being the most stable. Dihydrogen bonding in oligomers, where protic $H^{\delta+}(N)$ hydrogens interact with hydridic $H^{\delta-}(B)$ hydrogens, plays a crucial role in stabilizing different isomers and conformers. The results are consistent with structures of products that are seen in experimental NMR studies of dehydrogenated ammonia borane.

Introduction

On-board hydrogen storage (HS) is one of the major technological bottlenecks in developing a hydrogen economy.[1−4] Boron−nitrogen−hydrogen (BNH$_x$) materials such as ammonia borane, NH₃BH₃, are potentially important candidates for chemical hydrogen storage because of their high gravimetric and volumetric densities of hydrogen.[5−11] One of the key challenges in investigating BNH$_x$ is to understand the geometric and electronic factors that govern the stabilities, reactivities, and inter- and intramolecular interactions. Computational modeling is uniquely suited to provide a molecular-level understanding of the electronic structure and stabilities of these materials.

There are many theoretical studies of the gas-phase geometry and electronic structure of the NH₃BH₃ ($n = 1$) monomer, which is known to have a staggered structure as the most stable conformation.[12−15] Due to Pauli exchange repulsion, the eclipsed gas-phase conformer has a slightly longer B−N distance (∼0.03 Å) and is energetically higher in energy, by a few kilocalories/mole. From our PW91 calculation, the rotation barrier from the staggered to the eclipsed conformation is 1.94 kcal/mol, in excellent agreement with the experimental value of 2.07 kcal/mol.[16] The H(NH₂BH₂)ₙH oligomers ($n \geq 2$), which are products of n consecutive dehydrocoupling reactions involving NH₃BH₃ molecules, are good starting points for understanding the structures and stabilities of the partially dehydrogenated material.

There are theoretical calculations on infinite polyaminoborane (NH₂BH₂)∞ polymers,[17,18] but little is understood of the structures and the stabilities of the finite BNH$_x$ oligomers. The only previous theoretical effort to understand the electronic structure of these oligomers is a recent study on the properties of four types of selected linear chain structures.[19] It is not clear if these structures are the most stable or if other nonchain structures are stable as well. Therefore, an in-depth theoretical investigation is necessary to explore the geometries, stabilities, and electronic structure of these oligomers.

Because of significant differences in the electronegativities and the number of valence electrons in B and N, the −BH₂ and −NH₂ groups are electron-deficient and electron-rich, respectively. As a result, the H(NH₂BH₂)ₙH oligomers, with the Lewis structures of H-(H₂B←:NH₂)ₙ-H, have large dipole moments if they adopt linear chain configurations. These configurations would become less stable as the oligomer chains grow longer because the dipole moment increases as n increases. Isomerization, conformational changes, and ground-state spin crossing of the oligomers are possible pathways to transform linear chain oligomers into more stable species with smaller dipole moments.

Here we report a computational investigation of the oligomeric molecules H(NH₂BH₂)ₙH ($n = 1-6$) using DFT methods with Slater-type and planewave basis sets. In particular, we investigate the stabilities of oligomers with respect to conformational and isomeric degrees of freedom. In addition to coiling and branching, we also consider biradicalization via electron transfer from the negative to the positive charge end of the closed-shell H(NH₂BH₂)ₙH molecule. We probe the energetics of this pathway via the singlet−triplet energy splitting. We will show that the oligomers energetically prefer coiled structures,

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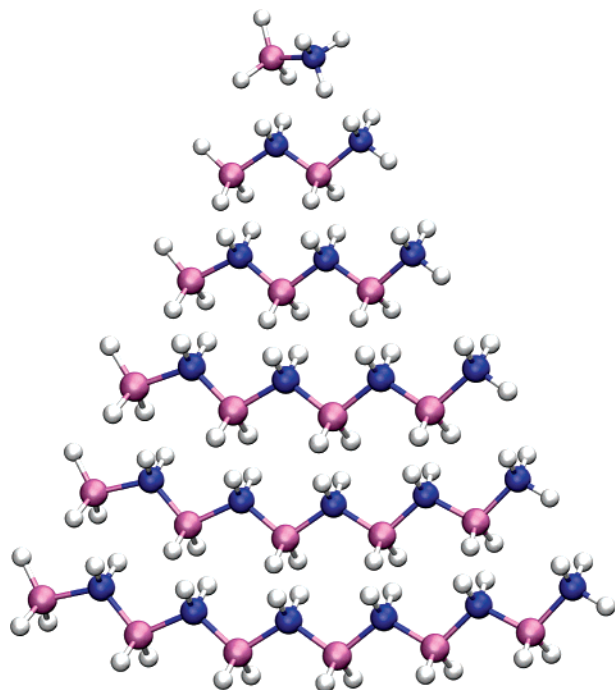§ Heriot-Watt University.
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Figure 1. The optimized zigzag (ZZ) linear chain structures of H(BH$_2$-NH$_2$)$_n$H ($n = 1-6$) (B, magenta; N, blue; H, white).

Figure 2. The optimized square-wave (SW) linear chain structures of H(BH$_2$NH$_2$)$_n$H ($n = 1-6$) (B, magenta; N, blue; H, white).

Figure 3. The optimized coiled structures of H(BH$_2$NH$_2$)$_n$H ($n = 1-6$). The dihydrogen bonds are orange (B, magenta; N, blue; H, white).

with the branched and square-wave chain structures being slightly higher in energy. All the zigzag linear chain and biradical structures lie much higher in energy.

Computational Methods

As the NH$_3$BH$_3$ monomer adopts staggered conformations, we started from "zigzag" (ZZ) linear chain structures of H(NH$_2$-BH$_2$)$_n$H with C_s symmetry (Figure 1), in which both the $-$(BH$_2-$NH$_2$)$_n-$ unit and the interconnect sections have a staggered, i.e., a trans$-$trans, conformation. The ZZ structure was previously used in ab initio study of polyaminoborane [BNH$_4$]$_\infty$.[17,18] We also investigated "square-wave" (SW) linear chain structures that have a staggered conformation within the $-$(BH$_2-$NH$_2$)$-$ unit but an eclipsed conformation between the $-$(BH$_2-$NH$_2$)$-$ units, i.e., a trans$-$cis conformation (Figure 2). These ZZ and SW structures were named trans-transoid and trans-cisoid, respectively, in the literature.[19] Due to the accumulated dipole moment of the repeating units, these chain structures might be affected by electrostatic instability if the electronic structure is restricted to closed-shell states. For this reason we explored how conformational relaxation away from the chain structures (e.g., coiling) affects the stability of singlet states. These calculations for H(NH$_2$BH$_2$)$_n$H ($n = 1-6$) oligomers were performed in two steps.

The first step was a simulated annealing (SA) search[20] for global minima using Car$-$Parrinello molecular dynamics (CP-MD).[21] We used norm-conserving pseudopotentials of Hamman for all B, N, and H atoms.[22] These calculations were performed by using the NWPW module of the plane-wave supercell DFT method implemented in NWChem 4.7.[23] The SA calculations were performed within the local density approximation (LDA)[24] with use of a 30 × 30 × 30 bohr^3 simple cubic lattice and a 48 × 48 × 48 grid for discretization along lattice vector directions, which yields a 12.663 hartree (~344.6 eV) plane-wave cutoff energy. The oligomers were thermally equilibrated at 1000 K with use of constant temperature simulations and then annealed with a time step of 5 au (2.419 × 10^{-5} ps). In a few cases, in which the molecular structure dissociated, the initial temperature
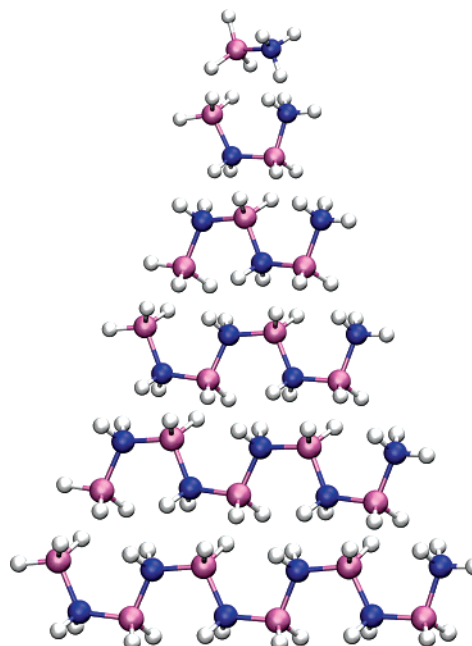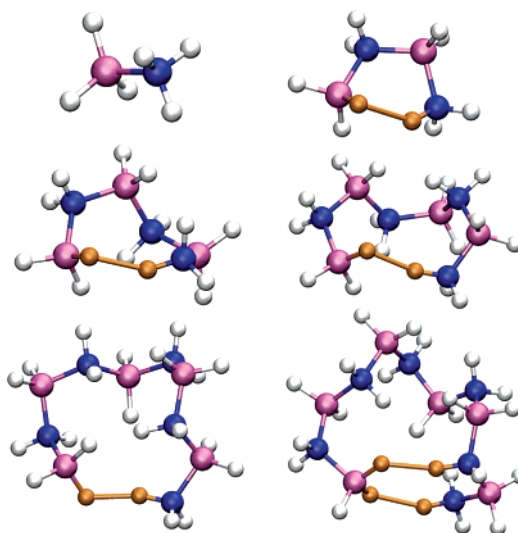
was reduced to 500 K. Both simulation steps were carried out for 2.419 ps with a final temperature of less than 90 K after annealing.

Next, we performed molecular DFT geometry optimizations for these CPMD-SA structures as well as for the zigzag and square-wave chain structures (Figures 1 and 2). The optimized geometries of the CPMD-SA singlet structures resulted in coiled configurations (Figure 3). These structures display characteristic dihydrogen bonds between protic H$^{\delta+}$(N) and hydridic H$^{\delta-}$(B) hydrogens,[25,26] which are shown in orange in Figure 3. The geometry optimizations and electronic structure calculations were performed by using the generalized gradient approximation (GGA) with the exchange-correlation functional of Perdew$-$Wang (PW91).[27] Uncontracted Slater basis sets of triple-ζ quality plus two polarization functions (TZ2P) were employed, which include d- and f-type polarization functions for B and N, and p- and d-type polarization functions for H. To obtain accurate geometries, high numerical accuracy was used for the integrations (integration = 8.0)[28] and all geometries were fully

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TABLE 1: Total Energies (E_{tot}), Relative Energies (ΔE), and Dipole Moment (μ) of H(NH$_2$BH$_2$)$_n$H Oligomers ($n = 1 - 6$) in Singlet States[a]

| | coiled C_1 | | square-wave | | | | zigzag C_s | |
| | | | C_s | | C_1 | | | |
n	μ	E_{tot}	μ	ΔE	μ	ΔE	μ	ΔE
1	5.3	−854.5	5.3	0.0	5.3	0.0	5.3	0.0
2	3.8	−1567.0	3.7	0.6	3.8	0.0	10.6	13.0
3	1.6	−2280.9	7.8	6.4	8.1	5.4	16.4	24.6
4	1.3	−2993.8	8.8	9.2	7.8	8.0	22.6	33.4
5	4.5	−3703.6	12.6	9.1	8.7	8.4	28.7	38.2
6	3.0	−4415.4	14.5	10.5	12.6	9.6	34.7	44.4

[a] The total energies E_{tot} are the ADF "binding energies" of atomic fragments. The relative energies ΔE are referenced to the total energy of the coiled structure. All the energies are in kcal/mol and the dipole moments are in D. The PW91 results were obtained with the ADF code, using integration = 8.0.

optimized until the energy gradients converged to within 10^{-4} au. Vibrational frequencies were calculated to determine the nature of the stationary points. In some cases, where small imaginary frequencies might exist due to numerical inaccuracies, the energy gradients were converged to within 10^{-5} au. These results were obtained with the Amsterdam Density Functional (ADF) code (version 2005.01).[28] All these calculations were accomplished with the HP Itanium2 Linux cluster MPP2 in the Molecular Science Computing Facility in the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory.

Results and Discussion

The computational results will be presented in four sections: (1) zigzag (ZZ) and square-wave (SW) linear chain structures, (2) biradicalization of the linear chain oligomers, (3) coiling stabilization, and (4) branching stabilization. We note that the calculated dipole moment of the staggered NH$_3$BH$_3$ molecule, 5.3 D, is close to the experimentally measured value in the gas phase, 5.216 D,[29] and the optimized B−N bond length, 1.65 Å, is also close to the gas-phase experimental distance of $r_0 =$ 1.6722 Å.[16] The optimized structures of the singlet-state ZZ and SW oligomers are shown in Figures 1 and 2. The total energies and dipole moments of the "coiled" structures in ground electronic (singlet) states are presented on the left side of Table 1. The singlet-state zigzag and square-wave "linear chain" structures are characterized on the right side of this table with their relative energies being defined with respect to the coiled structures.[30] The calculated dipole moments of the ZZ and SW linear chain structures in triplet states and the relative energies referenced to the coiled singlet states are listed in Table 2. Our estimates of the relative stabilities in Tables 1 and 2 are based on electronic energies. As our interest lies in the trend of relative stabilities, corrections for zero-point vibration energies were not included in these tables, as they typically have almost no impact on the relative stability of various conformers and isomers,[19] particularly when the energy differences between different geometries are large.

I. Zigzag and Square-Wave Linear Chain Structures of H(NH$_2$BH$_2$)$_n$H ($n = 1-6$). The −NH$_2$BH$_2$− unit can adopt staggered or eclipsed conformers, which possess different B−N bond lengths. As expected, when the chain grows longer the B−N distances alternate when starting from the BH$_3$ end ("head") to the NH$_3$ end ("tail"). For example, in the ZZ linear chain structures, the distances alternate as (1.67 Å, 1.54 Å) for the $n = 2$ oligomer, as (1.66 Å, 1.56 Å) for the $n = 3$ oligomer, and as (1.63 Å, 1.57 Å) for the $n = 6$ oligomer. As the chains

TABLE 2: Relative Energies (ΔE) and Dipole Moment (μ) of H(NH$_2$BH$_2$)$_n$H Oligomers ($n = 1 - 6$) in Triplet States[a]

| | square-wave | | | | zigzag C_s | |
| | C_s | | C_1 | | | |
n	μ	ΔE	μ	ΔE	μ	ΔE
1	5.5	102.6	5.5	102.6	5.5	102.6
2	2.2	117.1	1.4	110.2	1.7	114.4
3	7.4	106.8	7.5	102.6	2.8	119.5
4	8.8	110.0	8.2	104.8	5.5	125.9
5	6.1	200.8	13.5	97.4	8.4	129.5
6	23.8	160.9	15.7	106.8	11.0	134.4

[a] All the energies (in kcal/mol) are referenced to the total energy of the singlet coiled structures listed in Table 1. The dipole moments are in D. The PW91 results were obtained with the ADF code, using integration = 8.0.

grow longer, the bond lengths tend to converge to a B−N bond distance that is even shorter than in the monomer, which bears a resemblance to the B−N bond in these donor−acceptor complexes being considerably shorter in the crystal than in the gas phase.[31] The tendency in bond length change is consistent with previous calculations.[19]

For the ZZ chain structures with C_s symmetry (see Figure 1), the calculated dipole moments for $n = 2, 4, 6$ are very close to those calculated previously.[19] The dipole moment of the singlet states increases as $\mu_n \approx n \times \mu_0$, where μ_0 is the dipole moment of NH$_3$BH$_3$ and n characterizes the length of the oligomer. The situation is analogous to polar slabs of ionic materials, in which one surface of the slab is populated by anions and the other by cations. Polar slabs are inherently unstable.[32] They reduce this instability via electronic relaxation, formation of defects, adsorption of counterions, or geometric reconstruction. As we will show below, coiling provides an efficient avenue to greater stability for the H(NH$_2$BH$_2$)$_n$H oligomers. From Table 1, the calculated energies of the singlet states of the ZZ chain structures all lie much higher than the SW structures and the coiled structures. Therefore the ZZ chain structures are not the most stable configurations for the boron−nitrogen−hydrogen oligomers.

For the SW structures, the differences between the neighboring B−N units are smaller than those in the ZZ structures, with all the B−N distances being around 1.57 Å, except the B−N distance in the head and tail units (1.63 Å). Consistent with previous findings,[19] the SW structures are much more stable than the ZZ structures due to shorter and stronger B−N bonds. Our calculations on the SW structures started with planar structures (C_s symmetry), considering that in such planar structures two dihydrogen bonds can be formed between the two separated −NH$_2$BH$_2$− units (see Figure 2). However, the calculations reveal that these SW structures with C_s symmetry are transition-state structures. By allowing the BH$_2$ and NH$_2$ groups to rotate, minimum-energy SW chain structures have been identified. These distorted SW structures with C_1 symmetry have slightly lower energy than the planar SW structures, because they have shorter dihydrogen bond distances. The SW structures have smaller dipole moments than those of the ZZ linear chain structures due to partial cancellation of the bond dipole moments. Whereas the SW structures are much more stable than the ZZ linear chain structures, they are still higher in energy than the coiled structures by some 5−10 kcal/mol for $n = 3−6$.

II. Biradicalization of the Linear Chain Oligomers. Biradicalization of closed-shell oligomers is analogous to electronic relaxation of polar slabs. It might provide additional stabilization of the ZZ structures when the oligomer chains become suf-

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ficiently long. Electron transfer from the negative to the positive side of the dipole might quench the dipole moment and provide additional stabilization. The formation of a biradical •H(NH$_2$-BH$_2$)$_n$H• molecule in a triplet electronic state can be envisioned as such a procedure. The calculated dipole moments of the ZZ and SW linear chain structures and the relative energies referenced to the coiled singlet states are listed in Table 2. All these triplet state energies are obtained by geometry optimization, using the singlet geometries as initial structures.

We considered two types of triplet states for the ZZ and SW linear chain structures with C_s symmetry: (1) the $(a'')^1(a')^1$ configuration with overall $^3A''$ symmetry, and (2) the $(a')^1(a')^1$ configuration with overall $^3A'$ symmetry. In the latter the two unpaired electrons are both in hydrogen-based orbitals, whereas in the former one electron occupies an out-of-plane boron 2p orbital with a'' symmetry. The optimized geometries of these $^3A'$ biradical structures are similar to those of the singlet states structures shown in Figures 1 and 2. Some of the $^3A''$ states are difficult to converge or optimizations of their geometries lead to cleavage of B−H bonds. The calculated energies of these two states are not too far from each other when comparing with the singlet states, so only the energies of the $^3A'$ states are listed in Table 2. For the structures with C_1 symmetry, only the lowest triplet states are calculated.
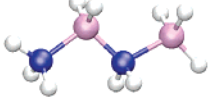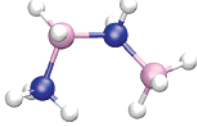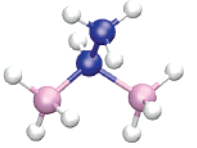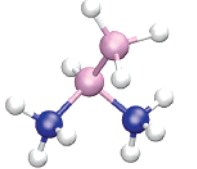
From Table 2, it is clear that biradicalization of these linear chain structures is not sufficient to suppress the intrinsic instability of the ZZ and SW linear chain structures. Even for $n = 6$, the triplet state of the ZZ structure is still less stable than the linear singlet state by 90.0 kcal/mol. Similarly, the triplet SW structure for $n = 6$ is 97.2 kcal/mol above its singlet counterpart. The results show, however, that for linear chain structures the singlet−triplet gap decreases as n increases. This indicates that ground singlet states of linear chain oligomers will have some biradical (multiconfigurational) character when n is sufficiently large. We also report that dipole moments of the ZZ triplet states are much smaller than those of the ZZ singlet states, which is consistent with the electron-transfer model.

III. Coiling Stabilization of H(NH$_2$BH$_2$)$_n$H ($n = 1$−6). Coiling and branching are analogous to reconstruction of polar slabs. As we have already pointed out, the coiled conformations were located as the most stable structures from the CPMD simulated annealing simulations. These structures are likely the global minima of the H(NH$_2$BH$_2$)$_n$H oligomers, and they are more stable than the helicoidal and partially coiled structures located in the previous calculations.[19] The coiled structures obtained from geometry optimizations with use of PW91 exchange-correlation functional are shown in Figure 3. In these structures, the B−N distances are around 1.61 Å in the head and the tail units, but are around 1.57−1.59 Å in the internal units, which are similar to those in the SW structures. The mean B−N distances are 1.650 ($n = 1$), 1.608 ($n = 2$), 1.601 ($n = 3$), 1.598 ($n = 4$), 1.596 ($n = 5$), and 1.596 Å ($n = 6$). As expected, the B−N bond lengths decrease as the oligomer chains grow longer, and gradually converge to a distance that is close to the B−N distance in the NH$_3$BH$_3$ crystal, 1.58 ± 0.02 Å, as is revealed in a recent neutron diffraction experiment.[33]

As shown in Table 1, the coiled structures not only have smaller dipole moments than the ZZ and SW linear chain structures but they are also much more stable based on the calculated total energies. The relative stability of the coiled structures with respect to the ZZ linear chain structures increases as the chain grows longer, consistent with the reduced strain energies upon coiling. Interestingly, all these coiled structures

TABLE 3: The Optimized Geometries, Relative Energies (kcal/mol), and Dipole Moments (D) of Branched H-(NH$_2$BH$_2$)$_2$-H^a

type	structure	μ(D)	ΔE
ZZ chain		10.5	12.3
Coiling/ SW chain		3.8	0.00
N@N		7.0	69.6
B@B		8.5	41.2

^{a} All the energies (in kcal/mol) are calculated with ADF PW91/TZ2P (integration = 8.0) and are relative to the coiled structures. Zero-point energy corrections are included.

adopt a staggered conformation along the −BH$_2$−NH$_2$− chains. Their high stability is further enhanced by dihydrogen bonds between protic and hydridic hydrogens located at the neighboring −BH$_2$−NH$_2$− unit and at the head and tail groups. The dihydrogen bonds are shown in orange in Figure 3. The coiled structures are more stable than the SW structures because in the former all the −BH$_2$−NH$_2$− units have stable staggered conformation. In addition, the head-to-tail dihydrogen bonds stabilize the coiled structures.

IV. Branching as an Alternative to Coiling. In hydrocarbons, chain-like and branched isomers are usually comparable in stability. As H(NH$_2$BH$_2$)$_n$H oligomers are isoelectronic with H(CH$_2$CH$_2$)$_n$H alkanes, another possibility of stabilizing the linear chain structures of the boron−nitrogen−hydrogen oligomers is to form branched isomers. We have adopted the naming convention that, for instance, N@B denotes a branched structure where a NH$_3$ group is branched at a B atom. We have investigated all possible branched structures of the H(NH$_2$-BH$_2$)$_n$H ($n = 2$−4) oligomers following the same procedure as described earlier, i.e., the CPMD simulated annealing using LDA followed by molecular DFT geometry optimizations. The branched structures were re-optimized from the structures rendered by CPMD SA by using the ADF code and the PW91 functional with the TZ2P basis sets. The optimized structures, their relative energies referenced to the singlet states of the coiled structures, and dipole moments for the $n = 2, 3, 4$ oligomers are summarized in Tables 3−5 The vibrational frequency calculations indicate that all these structures listed in Tables 3−5 are minima on the potential energy surfaces, except that the ZZ linear chain structures for $n = 3$ and 4 are transition states. Because the energy differences between some of these branched structures and their coiled counterparts are

TABLE 4: The Optimized Geometries, Relative Energies (kcal/mol), and Dipole Moments (D) of Branched H-(NH$_2$BH$_2$)$_3$-H[a]

type	structure	μ(D)	ΔE
ZZ chain		16.4	23.5
SW chain		8.0	5.0
coiling		1.6	0.0
N@B		7.6	9.4
B@N		3.7	7.6
N@N		3.0	63.9
B@B		4.4	33.9

TABLE 5: The Relative Energies (kcal/mol) and Dipole Moments (D) of Branched H-(NH$_2$BH$_2$)$_4$-H[a]

type	Structure	μ(D)	ΔE
ZZ chain		22.5	31.6
SW chain		7.8	7.1
coiling		1.3	0.0
N@B		6.0	6.7
B@N		6.6	11.5
BN@B		6.8	8.3
NB@N		5.4	6.5

relatively small, we also included the zero-point-energy (ZPE) corrections in the relative energies listed in Tables 3−5. As we discussed earlier, the ZPE effects are indeed small for these isomers or conformers.

From Table 3, the coiled structure is much more stable than the two branched structures, which tend to have very large dipole moments when NH$_3$ is connected to an N atom (N@N) or when BH$_3$ is connected to a B atom (B@B). In fact, these N@N and B@B structures are even higher in energy than the ZZ linear chain structure. The instabilities of the B@B and N@N branched structures are not surprising from the point of view of electronegativity and Lewis valence structures.

For $n = 3$ (Table 4), while the coiled structure is still the most stable, the structures resulting from branching of NH$_3$ at the B site (N@B) and BH$_3$ at the N site (B@N) are only a few kilocalories/mole less stable than the SW chain structure. Again, the structures with NH$_3$ at the N site (N@N) or BH$_3$ at the B site (B@B) are significantly higher in energy than the coiled structure, and even higher than the ZZ linear chain structure. The dipole moments of the B@N and N@B branched structures are much smaller than those of linear chain structures, indicating that branching is indeed an effective way to reduce the dipole

moments of these strongly polar oligomers. Because of small DFT energy differences between the coiled and some branched structures, additional ab initio calculations were needed to determine the relative stabilities of these isomers. We therefore re-optimized the structures at the level of MP2/6-31++G(d,p) using NWChem 4.7[23] Our MP2 calculations, without including the 1s^2 cores of B and N in the electron correlation, reveal that for $n = 3$ the coiled structures are more stable than the N@B and B@N structures by 5.8 and 7.4 kcal/mol, respectively, confirming the above conclusion that the coiled structures are indeed more stable than the branched structures in the gas phase.

As the N@N and B@B branched structures are not stable, we did not include them in the calculations for $n = 4$. As shown in Table 5, the coiled structure is again the most stable, and the SW, N@B, NB@N, and BN@B structures are some 6−8 kcal/mol less stable than the coiled structure. The B@N structure lies slightly higher in energy than these isomers. In fact, a recent ^{11}B NMR experiment seems to confirm the formation of BN@B-like branched structures in ionic liquid.[34] All these branched structures are significantly more stable than the ZZ linear chain structures.

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We conclude that branching is a viable method of reducing electrostatic instability for the linear chain structures. At 0 K, the branched structures are slightly less stable than the coiled structures, but the difference is relatively small. We believe that the thermolysis of NH$_3$BH$_3$ proceeds through the coiled oligomers, even though environmental and kinetic effects can favor branched dehydrogenated products. Indeed, it was experimentally observed that the kinetics and thermodynamics of hydrogen release is different for neat NH$_3$BH$_3$ and solid NH$_3$BH$_3$ encapsulated in nanoporous scaffolds.[8] It might be that the structure of the polymeric product (NH$_2$BH$_2$)$_n$ is influenced by the nanoporous environment. Recent NMR experiments[8,34] seem to provide evidence for some of the stable structures explored in the current work. In our future study we will compare the calculated NMR properties of the most stable oligomers with the available experimental spectra.

Conclusions

We have performed density functional studies of the geometric and electronic factors that influence the stability of the H(NH$_2$BH$_2$)$_n$H oligomers. We have demonstrated that the coiled structures are much more stable than the zigzag linear chain structures, and they are also more stable than the square-wave linear chain structures at 0 K. The coiled structures are characterized by short B—N bonds and multiple intramolecular dihydrogen bonds. Branching is also an effective mechanism to stabilize oligomers, with the branched structure of −NH$_2$ at the B site or −BH$_2$ at the N site being particularly stable. We believe that environmental and kinetic effects will govern whether the thermolysis of NH$_3$BH$_3$ proceeds through the coiled or branched or even the square-wave linear chain oligomers. Biradicalization is the least efficient mechanism of stabilization of linear chain structures, at least for the range of oligomers considered.

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