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ORIGINAL PAPER

Ab initio calculations on the thermodynamic properties of azaborospiropentanes

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Abstract Following our recent studies of the thermodynamic properties of azaspiropentane and borospiropentane, in consideration of their usefulness as new potential high energy materials, we follow up with ab initio calculations on the thermodynamic properties of azaborospiropentanes. Properties reported in this study include optimized structural parameters, vibrational frequencies, enthalpies of formation, specific enthalpies of combustion, proton affinities, and hydride affinities. Our results indicate that azatriborospiropentane gives off most energy when combusted, as evidenced by its specific enthalpy of combustion of about −52 kJ per gram.

Keywords Ab initio calculations · Azaborospiropentane · High energy materials

Introduction

Research involving the search for and synthesis of new high energy (HE) materials is an ongoing quest. There are certain bonding characteristics that commonly appear in HE materials, including strained ring structures, molecules that are metastable or unstable with respect to their combustion products, and relatively high nitrogen content [1]. Other studies offer additional characteristics, such as using boron and aluminum, due to the stability of their combustion products [2].

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Spiropentane is an organic molecule that is composed of two cyclopropane rings fused at a central carbon atom; this carbon atom is known in organic chemistry as the spiro carbon. Each molecule of spiropentane has large amounts of ring strain energy due to the two cyclopropane rings that compose it.

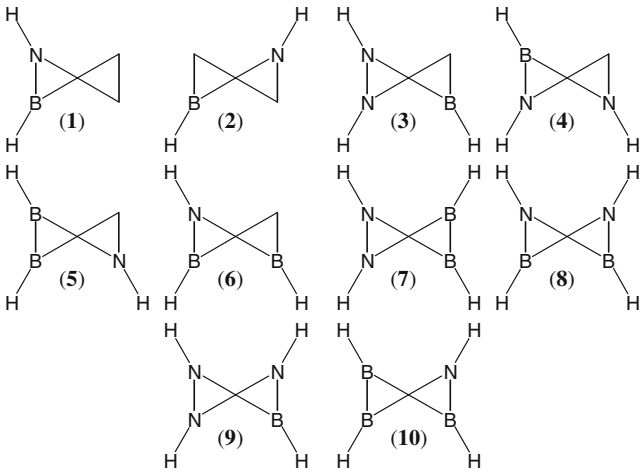
In our previous two studies, we examined the thermodynamic properties of boron [3] and nitrogen [4] derivatives of spiropentane with respect to their usefulness as new potential HE materials. Our results indicated that the inclusion of boron atoms caused the resulting molecules to give off up to about 24 kJ g^{-1} more energy than that given off by a spiropentane molecule without boron atoms [3]. Our study of nitrogen-containing spiropentane derivatives indicated that the inclusion of nitrogen atoms caused the resulting molecule to give off less energy then spiropentane alone, by as much as 28 kJ g^{-1} [4]. This unexpected result was rationalized in terms of the molecules' thermodynamic stabilities, and the amount of water molecules created when the molecules were combusted.

As a follow up study, we decided to consider the thermodynamic consequences of mixed azaborospiropentanes. Based on our previous two studies, we expect that the resulting molecules' usefulness as HE materials will depend largely on the amount of boron and nitrogen present in the molecules and the relative ratio of these amounts.

The most daunting feature of this system is the large number of isomers possible. Not accounting for chirality, there are a total of ten isomers, which are shown below as structures **1**–**10** (Scheme 1).

Structures 1–10

Structures **1**–**10** are 2-aza-3-borospiropentane (**1**), 2-aza-4-borospiropentane (**2**), 2,3-diaza-4-borospiropentane (**3**), 2,4-



Scheme 1 Structures **1**–**10**

diaza-3-borospiropentane (**4**), 2-aza-4,5-diborospiropentane (**5**), 2-aza-3,4-diborospiropentane (**6**), 2,3-diaza-,4,5-diborospiropentane (**7**), 2,4-diaza-3,5-diborospiropentane (**8**), 2,3,4-triaza-5-borospiropentane (**9**), and 2-aza-3,4,5-triborospiropentane (**10**), respectively . We were unable to locate a minimum energy structure for molecule (**5**), 2-aza-4,5-diborospiropentane, so it will not be considered further. Keep in mind that, for the most part, the two rings are perpendicular to each other, which makes the top and bottom positions, in the rings drawn above, degenerate; however, in some molecules the environment above the ring and below the ring is not the same, and in these cases there do exist additional isomers, which we have labeled with a 1 or a 2 arbitrarily. Analogous to our previous paper on azaspiropentanes [4], we have chosen to label chiral molecules using the R/S system from organic chemistry and include predicted data only for molecules that are expected to have different properties, namely diasteriomers and meso-compounds; thus, we have omitted data for one enantiomer of each enantiomeric pair, based on the assumption that the energy and thermodynamic data will be the same.

To our knowledge, none of the molecules considered in this study have been the subject of previous studies. Thus, for comparison, we will refer to our previous two studies and note similarities and differences that occur as a result of the nitrogen and boron atoms in the same spiropentane molecule.

Computational details

All calculations were performed on a personal computer using the Gaussian 03 [5] computational chemistry program. Minimum energy structures were located at two different levels of theory, the first being a density functional theory (DFT), which makes use of Becke's 3-parameter exchange functional plus the correlation functional of Lee, Yang, and Parr (B3LYP) [6, 7], with the second level of theory using second order Møller-Plesset (MP2) perturbation theory [8–12]. For both levels of theory, we used the 6–311G (d,p) [13] basis set with diffuse functions on heavy atoms and hydrogen atoms [14]. Vibrational frequencies were calculated at both levels of theory to ensure that optimized structures were indeed minimum energy structures. Single point energies of the optimized structures were calculated at both levels of theory and used to predict various thermodynamic properties; the results were in poor agreement and so a higher level of theory—the coupled cluster method with single, double, and selected triple substitutions [CCSD(T)] [15–19], using the same basis set—was employed on the optimized structures. The optimized structures and vibrational frequencies were visualized using the GaussView [20] program.

In order to calculate the enthalpy of formation for the 16 energetically different azaborospiropentane molecules, we used the following eight isodesmic reactions:

$$NBCH_4(g) + C_3H_6(g) \rightarrow NBC_3H_6(g) + CH_4(g) \quad (1)$$

$$NC_2H_5(g) + BC_2H_5(g) \rightarrow NBC_3H_6(g) + CH_4(g) \quad (2)$$

$$N_2CH_4(g) + BC_2H_5(g) \rightarrow N_2BC_2H_5(g) + CH_4(g) \quad (3)$$

$$NBCH_4(g) + NC_2H_5(g) \rightarrow N_2BC_2H_5(g) + CH_4(g) \quad (4)$$

$$BC_2H_5(g) + NBCH_4(g) \rightarrow NB_2C_2H_5(g) + CH_4(g) \quad (5)$$

$$2NBCH_4(g) \rightarrow N_2B_2CH_4(g) + CH_4(g) \quad (6)$$

$$N_2CH_4(g) + NBCH_4(g) \rightarrow N_3BCH_4(g) + CH_4(g) \quad (7)$$

$$2BC_2H_5(g) + NBCH_4(g) \rightarrow NB_3CH_4 + CH_4(g) + C_3H_6(g) \quad (8)$$

Isodesmic reactions are used because the number of each type of bond between different elements is the same for products and reactants, reducing certain types of computational error. Equation 6 was used for all isomers of diazadiborospiropentane because we were unable to locate a minimum energy geometry for the diboridine, B_2CH_4, molecule in gas phase. Similarly, Eq. 8 uses two boridine, BC_2H_5, molecules to avoid having to use a diboridine molecule. The enthalpies of formation of gaseous azaboridine

($NBCH_4$), azacyclopropane (NC_2H_5), diazacyclopropane (N_2CH_4), and boridine are 126.4 [21], 126.8 [22], 252.7 [23] and 183 [J. Hillegass Jr and D.W.B., unpublished results] kJ mol^{-1} respectively. All other enthalpies of formation were taken from the experimental data found in the NIST Chemistry Webbook website [24].

Once the enthalpies of formation have been calculated, it is possible to calculate the enthalpies of combustion using the general combustion reaction listed as Eq. 9:

$$N_xB_yC_zH_\sigma(g) + \psi O_2(g) \rightarrow 0.5xN_2(g) + 0.5yB_2O_3(s) + zCO_2(g) + 0.5\sigma H_2O(\ell) \quad (9)$$

where z, σ, and ψ are all functions of the number of boron and nitrogen atoms present within the starting azaborospiropentane, as given by Eqs.10, 11, and 12.

$$z = 5 - x - y \quad (10)$$

$$\sigma = 8 - x - y \quad (11)$$

$$\psi = 14 - 2.5x - y \quad (12)$$

Equation 9 assumes complete combustion, which is unlikely in reality but does provide a computational limit to the energy produced. After the enthalpies of combustion have been calculated, the results can be divided by the molar masses of the molecules, which yields the specific enthalpies of combustion for the molecules. This data is important because one important datum is the amount of energy produced per unit mass of HE material.

In order to better understand the reactivities of the molecules, we have calculated the proton affinities and hydride affinities of the various azaborospiropentanes. The proton affinity (PA) of a molecule is a measure of the Lewis basicity of a molecule, and is defined as the negative of the change in enthalpy of Eq. 13.

$$XN + H^+ \rightarrow XNH^+ \quad PA \equiv -\Delta H \quad (13)$$

where *X* is the particular molecule, and the binding site, a nitrogen atom, is shown explicitly.

In order to determine the Lewis acidity of the molecules, we have computed the hydride affinity (HA) of the various azaborospiropentanes using Eq. 14:

$$XB + H^- \rightarrow XBH^- \quad HA \equiv -\Delta H \quad (14)$$

Again *X* is the particular molecule, and the binding site, which in this case is a boron atom, is shown explicitly. Analogous to the PA, the HA is defined as the negative of the enthalpy of reaction of Eq. 14.

Both the PA and the HA are site-specific values and therefore must be calculated at each chemically different binding site in the molecule. This means that some molecules will have multiple PA and/or multiple HA values.

Results and discussion

Optimized geometries

Figure 1 shows the optimized geometries of the various azaborospiropentanes at the B3LYP level of theory; the MP2 level of theory predicts geometries that are nearly identical to the geometries predicted at the B3LYP level of theory, with one exception, which will be discussed below. The caption on Fig. 1 notes the two-dimensional molecule **1**–**10** that corresponds to the three-dimensional structure; because of stereochemistry, there may be more than one stereoisomer for some of the substituted spiropentane molecules. The optimized structural parameters for both levels of theory are located in supplementary materials Tables S1–S9. In the tables, a subscript "t" stands for terminal and is used to denote a carbon atom that is not the spirocarbon. When further clarification is necessary a subscript "B" or "N" is used, which stand for boron and nitrogen, respectively; these subscripts denote the other atom in the three-membered ring besides the spirocarbon. For example, C_N means the carbon atom in the spirocarbon-nitrogen-carbon ring. For S6 and S9, the numbers 1 and 2 denote the corresponding atoms in Fig. 1.

In general, for bond distances we see that the two optimization methods agree well with one another, with the B3LYP method tending to predict shorter bond distances than the MP2 method by about 0.01 Å. Trends in the values of the bond angles are harder to analyze because neither method consistently predicts smaller or larger bond angles than the other method; however, the bond angles tend to agree between methods to within about 1.0°.

Visually, the structures the two isomers of azaborospiropentane (**1** and **2**) are similar to one another, and Tables S1 and S2 confirm the similarity. An interesting point is that there are two isomers of the 2-aza-4-borospiropentane molecule (**2**) due to different environments above and below the nitrogen-containing ring plane, causing different chemical environments for the boron atom depending on whether it is above or below the ring. The most notable structural difference between the isomers is the presence of the dative boron–nitrogen bond in the 2-aza-3-borospiropentane molecule (**1**); this bond stabilizes the molecule significantly as evidenced by the enthalpies of formation presented later in this study.

The diazaborospiropentanes (**3** and **4**) structurally resemble the azaborospiropentanes; again, the predominant stabilizing feature of the molecules is the dative bond

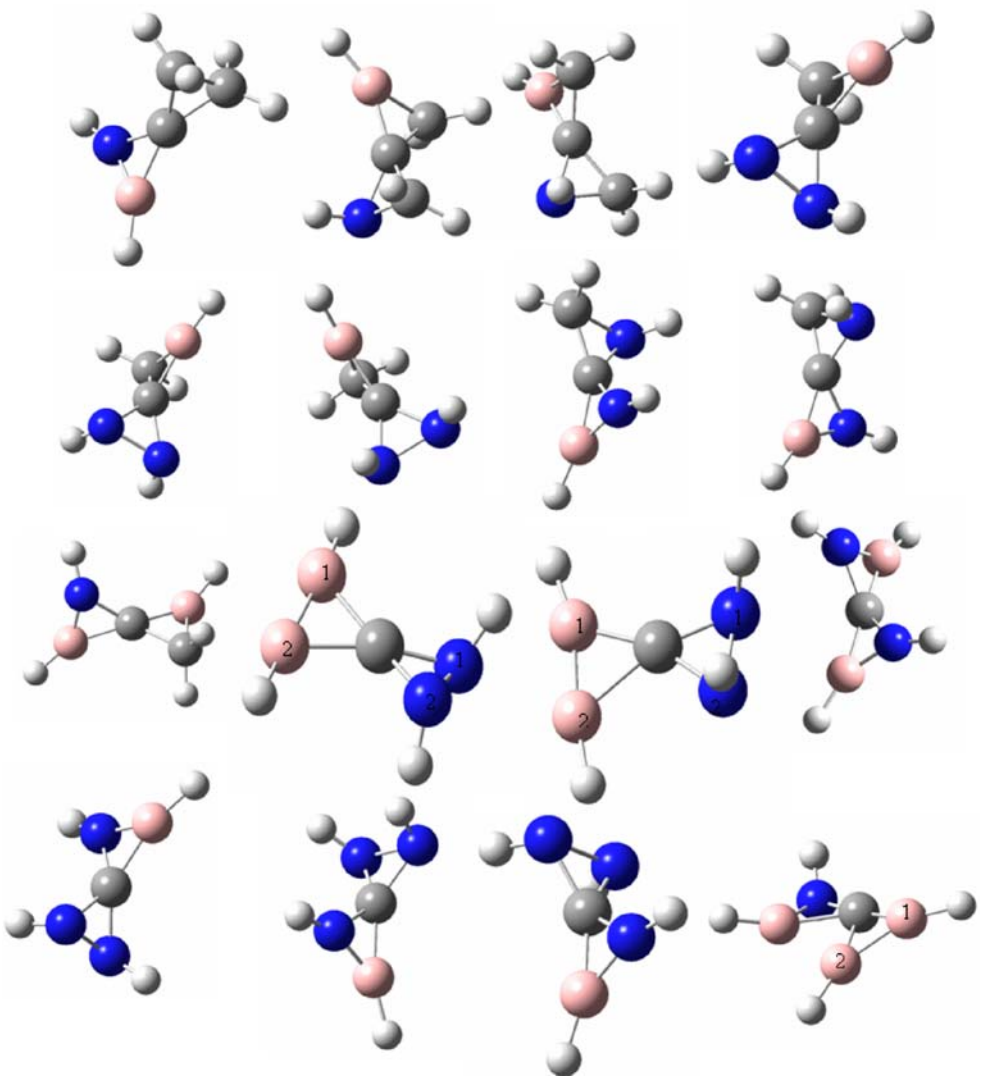


Fig. 1 Optimized geometries. **a** 2-Aza-3-borospiropentane (**1**), **b** R-2-aza-4-borospiropentane-1 (**2**), **c** R-2-aza-4-borospiropentane-2 (**2**), **d** R,R-2,3-diaza-4-borospiropentane (**3**), **e** R,S-2,3-aza-4-borospiropentane-1 (**3**), **f** R,S-2,3-aza-4-borospiropentane-2 (**3**), **g** R-2,4-diaza-3-borospiropentane-1 (**4**) and **h** R-2,4-diaza-3-borospiropentane-2 (**4**), **i** R-2-aza-3,4-diborospiropentane (**6**), **j** R,R-2,3-diaza-4,5-diborospiropentane (**7**), **k** R,S-2,3-diaza-4,5-diborospiropentane (**7**), **l** 2,4-diaza-3,5-diborospiropentane (**8**), **m** R,R-2,3,4-triaza-5-borospiropentane (**9**) and **n** R,S-2,3,4-triaza-5-borospiropentane-1 (**9**), **o** R,S-2,3,4-triaza-5-borospiropentane-2 (**9**), and **p** R-azatriborospiropentane (**10**)

between the boron and nitrogen atoms. Analogous to the azaborospiropentanes, the trigonal pyramidal geometry of the nitrogen atom causes the environments above and below the ring to be different.

The most intriguing aspect of the various azadiborspiropentane isomers (**5** and **6**) is the effect that the location of the two boron atoms has on the stability of the molecules. As mentioned in the Introduction, placing the boron atoms in the same ring causes the molecule to fall apart; however, when one boron atom was allowed to form a dative bond to the nitrogen atom, the molecule stabilized and we were able to locate a minimum energy structure.

The geometries of the diazadiborospiropentane isomers (**7** and **8**) are also dependent on the relative placement of the atoms. If the boron atoms are located next to one another, the geometry about the spirocarbon is essentially planar, as evidenced by the dihedral angles in Tables S6 and S7; if they are in opposite rings, then the structure is similar to the previous azaborospiropentanes (**1** and **2**), with the two three-membered rings almost perpendicular to each other. This is also due to the dative bond between the nitrogen and boron atoms. It is also apparent from Fig. 1 and Table S6 that when like atoms are in the same ring, the molecule distorts itself to minimize symmetry. This is particularly obvious when comparing the two different B–C bond lengths for 2,3-diaza-4,5-diborospiropentane (**7**), which differ by 0.1 to 0.2 Å, depending on the diasteriomer. One last point of interest for this group of molecules is the disagreement seen between the B3LYP and MP2 levels of theory about the exact structure of the optimized geometry for the R,S enantiomer. The MP2 level of theory predicts that the N1–C bond will be the longer N–C bond; the MP2 level of theory predicts that B1–C bond will be the longer B–C bond. This is the exact opposite of what the B3LYP level of theory predicts.

Triborospiropentane (**10**) is essentially flat about the spirocarbon and the B–C bonds are of different lengths; however, unlike the 2,3-diaza-4,5-diborospiropentanes (**7**), which triborospiropentane structurally resembles, there is a

dative bond that significantly stabilizes the molecule, as evidenced by the enthalpies of formation (see discussion below).

When this group of mixed azaborospiropentanes is compared to the azaspiropentanes and the borospiropentanes, several trends are noted. In our previous study on azaspiropentanes [4], we predicted N–N bond lengths in the range of about 1.53 to 1.56 Å; however, in this study we predict N–N bond lengths ranging from about 1.45 Å to about 1.56 Å. In both cases, the more nitrogen atoms in the molecule, the longer the N–N bond.

The B–B bond distances in our borospiropentane study [3] range from 1.50 Å to about 1.63 Å; here we see a range of 1.49 Å to about 1.61 Å. Based on the previous observation, one would have expected the bonds to have significantly lengthened, but instead the range is almost the same. In our previous study on borospiropentane [3], we noted that when two boron atoms are next to each other, a π system is created, which stabilizes the planar arrangement of the spirocarbon. In this case we see the same phenomenon leading to an overall planar geometry of the spirocarbon.

In summary, the optimized geometry of the azaspiropentanes is dependent largely on the relative amounts of nitrogen and boron atoms in the molecule and their location. When the number of nitrogen atoms is greater than the number of boron atoms we see results that are reminiscent of our previous study on azaspiropentanes [4]. The boron atom influence is apparent only when the boron atoms are present in the same ring. This causes the overall geometry to become planar, which makes the molecules similar to the planar molecules in our study on borospiropentane [3]. Whenever a nitrogen atom is located in the same ring as a boron atom a dative bond is formed, which causes the boron atom to be tetravalent (due to the presence of the fourth dative bond), and the resulting structure is similar to the azaspiropentane structures.

Vibrational frequencies

Vibrational frequencies were calculated for all molecules at the B3LYP and MP2 levels of theory to ensure that the optimized structures were minimum energy geometries. The predicted values of the vibrational frequencies and their approximate descriptions at both levels of theory are available as supplemental information. The vibrational frequency calculations confirmed that all structures were true minima in their potential energy curves.

For the sake of brevity, only a few points will be made regarding the vibrational frequencies. First, all of the molecules exhibit low symmetry and, as a result, all vibrational frequencies are predicted to be infrared active. Our results agree with this point; however, some of the vibrational frequencies are very weak, i.e., <0.1 km mol^{-1}. The second point is that the two levels of theory agree relatively well with one another, with the B3LYP tending to predict lower vibrational frequencies then the MP2 level of theory.

Enthalpies of formation

The enthalpies of formation for the 16 azaborospiropentanes are listed in Table 1. Despite the agreement between the two levels of theory in regards to the optimized geometries, there are seven azaborospiropentanes for which the B3LYP and MP2 levels of theory predict enthalpies of formation that differ by more than 100 kJ mol^{-1}. These seven are R-2-aza-4-borospiropentane, structures 1 and 2 (**2**); R,R-2,3-diaza-4-borospiropentane (**3**); R,S-2,3-diaza-4-borospiropentane,

Table 1 Enthalpies of formation for azaborospiropentanes (kJ mol^{-1})

Molecule	B3LYP	MP2	CCSD(T)/B3LYP	CCSD(T)/MP2
2-aza-3-borospiropentane (**1**)	255.2	253.8	257.2	256.1
R-2-aza-4-borospiropentane-1 (**2**)	376.8	520.4	378.0	376.1
R-2-aza-4-borospiropentane-2 (**2**)	386.1	528.9	386.3	384.5
R,R-2,3-diaza-4-borospiropentane (**3**)	515.1	660.8	517.0	515.0
R,S-2,3-diaza-4-borospiropentane-1 (**3**)	544.3	690.2	544.9	542.9
R,S-2,3-diaza-4-borospiropentane-2 (**3**)	527.6	675.6	530.5	528.4
R-2,4-diaza-3-borospiropentane-1 (**4**)	318.8	317.5	321.1	320.1
R-2,4-diaza-3-borospiropentane-2 (**4**)	306.5	304.6	308.9	308.0
R-2-aza-3,4-diborospiropentane (**6**)	370.8	513.9	371.8	369.9
R,R-2,3-diaza-4,5-diborospiropentane (**7**)	606.9	594.5	592.8	591.0
R,S-2,3-diaza-4,5-diborospiropentane (**7**)	630.4	620.5	618.5	616.7
2,4-diaza-3,5-diborospiropentane (**8**)	308.2	304.9	309.7	308.7
R,R-2,3,4-triaza-5-borospiropentane (**9**)	423.7	421.9	426.2	425.1
R,S-2,3,4-triaza-5-borospiropentane-1 (**9**)	457.3	456.5	459.0	457.7
R,S-2,3,4-triaza-5-borospiropentane-2 (**9**)	434.7	432.7	436.6	435.6
R-azatriborospiropentane (**10**)	397.9	654.0	376.5	373.9

structures 1 and 2 (**3**); R-2-aza-3,4-diborospiropentane (**6**); and R-azatriborospiropentane (**10**). For this reason, we also calculated the energies of the optimized geometries at the CCSD(T) level of theory. The enthalpies of formation calculated from the single point energy of the B3LYP optimized geometry at the CCSD(T) level of theory are listed in the column headed CCSD(T)/B3LYP in Table 1; analogously, the CCSD(T)/MP2 column in Table 1 lists the enthalpies of formation calculated from the single point energies of the MP2 geometry at the CCSD(T) level of theory. The enthalpies of formation values as calculated using CCSD(T) are within 3 kJ mol^{-1} of each other, a large improvement over the previously seen deficit. For six of the seven anomalous cases mentioned above, the CCSD(T) level of theory predicts enthalpies of formation that are within about 2 kJ mol^{-1} of the enthalpy of formation predicted by the B3LYP level of theory. The seventh case, R-azatriborospiropentane (**10**), has a difference of about 20 kJ mol^{-1}, but is still closer to the value predicted by the B3LYP level of theory. This strongly suggests that the MP2 level of theory is adequate for predicting the optimized geometries of azaborospiropentanes, but inadequate for predicting the energies of these molecules.

Analysis of the data listed in Table 1 alludes to several points regarding the enthalpies of formation for these molecules. The first point is that all of these molecules have large positive enthalpies of formation, ranging from about 255 kJ mol^{-1} for the least substituted molecule, 2-aza-3-borospiropentane (**1**), to about 620 kJ mol^{-1} for R, S-2,3-diaza-4,5-diborospiropentane (**7**). For comparison, spiropentane in its hydrocarbon form has an enthalpy of formation of 185.1 kJ mol^{-1} [24]. We conclude that all of these azaborospiropentanes are significantly less thermodynamically stable then the parent hydrocarbon, spiropentane.

The next point is that the presence of a dative bond between the nitrogen and boron atoms in a molecule significantly lowers the enthalpy of formation for the molecule. For example, the isomer of azaborospiropentane that has the dative bond has an enthalpy of formation that is roughly 100 kJ mol^{-1} lower then the two isomers that do not have the dative bond. Another trend is that the inclusion of boron atoms raises the enthalpy of formation more than the inclusion of nitrogen atoms. For example, adding a boron atom into the other ring of 2-aza-3-borospiropentane (**1**) creates 2-aza-3,4-diborospiropentane (**6**), which has an enthalpy of formation that is roughly 120 kJ mol^{-1} higher then 2-aza-3-borospiropentane. Analogously, the addition of a nitrogen atom into 2-aza-3-borospiropentane creates 2,4-diaza-3-borospiropentane (**4**), which has an enthalpy of formation that is only roughly 50–70 kJ mol^{-1} higher, depending on the created isomer, than 2-aza-3-borospiropentane.

Previously, in our azaspiropentane study [4], we saw that azaspiropentane has an enthalpy of formation of about 253 kJ mol^{-1}. In our borospiropentane study [3] we saw that borospiropentane has an enthalpy of formation of roughly 300 kJ mol^{-1}. This is consistent with our results that the inclusion of boron atoms in the molecules raises the enthalpy of formation more than the inclusion of nitrogen atoms. What is particularly interesting is that 2-aza-3-borospiropentane (**1**) has an enthalpy of formation of about 255 kJ mol^{-1}, which is very close to the enthalpy of formation of azaspiropentane. Again, this is further testament to the stabilizing effects of the dative bond between the boron and nitrogen atoms. One last point regarding the enthalpies of formation is that the range seen for this study is roughly equal to the range of enthalpies of formations seen in the other two studies, which are 300–525 kJ mol^{-1}, and 250–600 kJ mol^{-1} for the studies on borospiropentane

Table 2 Specific enthalpies of combustion for azaborospiropentanes (kJ g^{-1})

Molecule	B3LYP	MP2	CCSD(T)/B3LYP	CCSD(T)/MP2
2-aza-3-borospiropentane (**1**)	−43.8	−43.8	−43.8	−43.8
R-2-aza-4-borospiropentane-1 (**2**)	−45.6	−47.8	−45.6	−45.6
R-2-aza-4-borospiropentane-2 (**2**)	−45.8	−47.9	−45.8	−45.7
R,R-2,3-diaza-4-borospiropentane (**3**)	−39.1	−41.2	−39.1	−39.1
R,S-2,3-diaza-4-borospiropentane-1 (**3**)	−39.5	−41.7	−39.5	−39.5
R,S-2,3-diaza-4-borospiropentane-2 (**3**)	−39.3	−41.5	−39.3	−39.3
R-2,4-diaza-3-borospiropentane-1 (**4**)	−36.2	−36.2	−36.2	−36.2
R-2,4-diaza-3-borospiropentane-2 (**4**)	−36.0	−36.0	−36.1	−36.0
R-2-aza-3,4-diborospiropentane (**6**)	−48.6	−50.8	−48.6	−48.6
R,R-2,3-diaza-4,5-diborospiropentane (**7**)	−43.3	−43.1	−43.1	−43.1
R,S-2,3-diaza-4,5-diborospiropentane (**7**)	−43.7	−43.5	−43.5	−43.5
2,4-diaza-3,5-diborospiropentane (**8**)	−38.8	−38.7	−38.8	−38.8
R,R-2,3,4-triaza-5-borospiropentane (**9**)	−29.4	−29.4	−29.4	−29.4
R,S-2,3,4-triaza-5-borospiropentane-1 (**9**)	−29.9	−29.9	−29.9	−29.9
R,S-2,3,4-triaza-5-borospiropentane-2 (**9**)	−29.6	−29.5	−29.6	−29.6
R-azatriborospiropentane (**10**)	−52.4	−56.5	−52.0	−52.0

Table 3 Proton affinities for azaborospiropentanes (kJ mol^{-1})

Nitrogen number	2		3		4	
Molecule	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
2-aza-3-borospiropentane (**1**)	878.6 (881.7)	871.3 (881.2)				
R-2-aza-4-borospiropentane-1 (**2**)	915.3 (921.0)	910.5 (920.1)				
R-2-aza-4-borospiropentane-2 (**2**)	924.6 (929.4)	919.0 (928.5)				
R,R-2,3-diaza-4-borospiropentane (**3**)	866.5 (872.1)	859.6 (870.3)	872.8 (877.7)	865.8 (876.0)		
R,S-2,3-diaza-4-borospiropentane-1 (**3**)	895.7 (900.0)	888.9 (898.2)	895.7 (900.0)	888.9 (898.2)		
R,S-2,3-diaza-4-borospiropentane-2 (**3**)	885.2 (891.3)	880.5 (889.5)	885.2 (891.3)	880.5 (889.5)		
R-2,4-diaza-3-borospiropentane-1 (**4**)	833.2 (834.8)	823.1 (834.4)			948.9 (952.5)	943.6 (951.8)
R-2,4-diaza-3-borospiropentane-2 (**4**)	936.7 (940.3)	930.8 (939.7)			844.6 (846.5)	834.8 (846.3)
R-2-aza-3,4-diborospiropentane (**6**)	881.5 (886.0)	881.8 (886.7)				
R,R-2,3,4-triaza-5-borospiropentane (**9**)	880.2 (883.8)	872.9 (882.5)	892.8 (896.4)	886.2 (895.1)		
R,S-2,3,4-triaza-5-borospiropentane-1 (**9**)	913.8 (916.6)	907.5 (915.2)	913.8 (916.6)	907.5 (915.2)	775.6 (778.7)	765.0 (778.0)
R,S-2,3,4-triaza-5-borospiropentane-2 (**9**)	903.8 (906.8)	897.0 (905.6)	903.8 (906.8)	897.0 (905.6)	799.6 (801.5)	787.8 (801.5)

[3] and azaspiropentane [4], respectively. Note that the borospiropentane range only goes up to triborospiropentane, and if a minimum energy geometry could have been located for tetraborospiropentane, it would have been expected to make the range extend past 600 kJ mol^{-1}.

Enthalpies of formation

Table 2 shows the specific enthalpies of combustion for the molecules. Because the specific enthalpies of combustion are derived from the enthalpies of formation, similar trends are present. The parent hydrocarbon spiropentane has a specific enthalpy of formation of about −48 kJ g^{-1} [24]. With two exceptions (azatriborospiropentane (**10**) and 2-aza-3,4-diborospiropentane (**6**)) all of the molecules considered in this study give off less energy per gram than spiropentane. 2-Aza-3,4-diborospiropentane gives off roughly the same amount of energy, and azatriborospiropentane gives off about 4 kJ g^{-1} more energy. This can be explained, in part, in terms of the combustion reaction stoichiometry. Each additional nitrogen and boron atom decreases the number of hydrogen atoms in the molecule by 1, which thus decreases the number of water molecules produced by half a molecule. The thermodynamic instability caused by the substitution of a nitrogen or a boron atom does not fully compensate for the lost water molecule as a combustion product, and the resulting specific enthalpies of combustion are lower. However, it should be noted that all of these specific enthalpies of combustion are higher then those of some of the most commonly used HE materials such as RDX (cyclotrimethylenetrinitramine), which has a specific enthalpy of combustion of −7.4 kJ g^{-1} [24].

Azatriborospiropentane gives off the most energy per gram of the molecules considered here, about −52 kJ g^{-1}. This is just short of the specific enthalpy of combustion for methane, which is −55.7 kJ g^{-1} [25]. Although these values suggest

Table 4 Hydride affinities for azaborospiropentanes (kJ mol^{-1})

Boron number	3		4		5	
Molecule	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
2-aza-3-borospiropentane (**1**)	282.0 (260.8)	247.7 (259.3)				
R-2-aza-4-borospiropentane-1 (**2**)			350.8 (331.8)	319.8 (329.9)		
R-2-aza-4-borospiropentane-2 (**2**)			353.9 (334.2)	322.3 (332.4)		
R,R-2,3-diaza-4-borospiropentane (**3**)			382.3 (362.2)	350.7 (360.4)		
R,S-2,3-diaza-4-borospiropentane-1 (**3**)			387.6 (366.5)	355.5 (364.9)		
R,S-2,3-diaza-4-borospiropentane-2 (**3**)			380.9 (362.1)	350.8 (360.1)		
R-2,4-diaza-3-borospiropentane-1 (**4**)	298.0 (276.5)	262.9 (275.1)				
R-2,4-diaza-3-borospiropentane-2 (**4**)	288.6 (266.7)	266.6 (265.3)				
R-2-aza-3,4-diborospiropentane (**6**)	332.1 (325.3)	322.2 (325.2)	N/A	N/A		
2,4-diaza-3,5-diborospiropentane (**8**)	279.6 (252.8)	238.41 (251.9)			279.6 (252.8)	238.41 (251.9)
R,R-2,3,4-triaza-5-borospiropentane (**9**)					310.9 (287.7)	273.3 (286.5)
R,S-2,3,4-triaza-5-borospiropentane-1 (**9**)					319.7 (296.9)	283.5 (295.8)
R,S-2,3,4-triaza-5-borospiropentane-2 (**9**)					301.0 (276.9)	262.0 (275.6)

that the molecules studied here would make good HE materials, the usefulness of any of these molecules as new HE materials will depend on other properties such as their phase, density, velocity of detonation, and ease of synthesis.

The proton and hydride affinities of the various azaborospiropentanes were calculated to determine the extent of the Lewis basicity and Lewis acidity of the molecules, respectively. The PA and HA values are given in Table 3 and Table 4, respectively. For both tables, the values listed in parentheses are the values calculated at the CCSD(T) level of theory for the structure optimized at the column heading level of theory. In both tables there are several molecules that are not listed; when a molecule was not listed in Table 3 it is because protonation at the nitrogen atom caused the ring to open; when a molecule was not listed in Table 4 it is because attachment of the hydride ion caused the ring to open or the hydride ion became a bridging hydrogen between two boron atoms.

For comparison, ammonia has a PA of 851.4 kJ mol^{-1} [26] and borane has an HA of 306 kJ mol^{-1} [27]. Comparing these values to the PA values listed in Table 3 and the HA affinities in Table 4 indicates that, in general, the nitrogen atoms in these molecules behave as stronger bases than ammonia while the boron atoms' behavior varies with the location of the boron atom. The boron atoms located in dative bonds behave as less acidic than borane and those not located in a dative bond tend to be more acidic than borane; this behavior is simple to explain in the sense that the boron atoms in a dative bond are already accepting an electron pair from the nitrogen atoms and are less likely to accept another electron pair from an attacking hydride ion then boron atoms not in a dative bond. These PA and HA values suggest that the nitrogen and boron sites in these molecules should react similarly to ammonia and borane.

Conclusions

In this study we have considered a series of mixed azaborospiropentanes for their use as new potential high energy (HE) materials. We were able to locate 16 minimum energy geometries, as supported by the lack of negative vibrational frequencies. We have noted that the presence of a dative bond between a nitrogen atom and a boron atom significantly stabilizes the molecule. The conditions under which the spirocarbon adopts a planar geometry and the conditions under which it adopts a tetrahedral geometry were also noted. It is also apparent that the inclusion of nitrogen and boron atoms into spiropentane raises the enthalpy of formation; however, this increase in instability is not always great enough to compensate for the loss of water molecules when the combustion reactions are considered. Thus, only two molecules give off energy equal to or greater then spiropentane. Of all of these molecules, R-azatriborospiropentane gives off the most energy as indicated by its large negative specific enthalpy of combustion of −52 kJ mol^{-1}. The usefulness of any of these molecules as new potential HE materials will depend on additional properties such as phase, density, velocity of detonation, and ease of synthesis. The proton and hydride affinities for these molecules suggest that the nitrogen atoms will behave chemically similar to the nitrogen atom in ammonia, and that the boron atoms will behave chemically similar to the boron atom in borane.

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