

Synthesis and Energetic Characterization of Borane-Amines on High-Nitrogen Heterocycles

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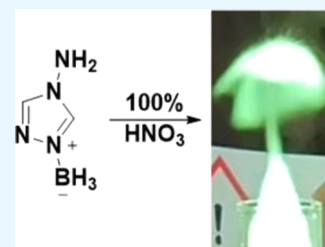
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ABSTRACT: Borane-amines have garnered attention over the last several decades in a variety of applications, ranging from hydrogen storage materials to hypergolic fuel systems. An investigation into the synthesis of borane-amines with high-nitrogen content heterocycles was undertaken in this work. Borane-amines were formed by the reaction of $\text{BH}_3 \cdot \text{Me}_2\text{S}$ in tetrahydrofuran (THF) with the requisite nitrogen-containing heterocycle and isolated by placing the crude reaction mixture in hexanes to precipitate the product. X-ray crystallography, thermogravimetric analysis (TGA), high resolution mass spectroscopy (HRMS), ^1H NMR, ^{13}C NMR, and ^{11}B NMR were utilized for product characterization, while impact and friction sensitivity testing were conducted to identify sensitivity in the synthesized compounds. Most isolated borane-amines, except one, were found to decompose in the atmosphere and were more sensitive to mechanical stimuli than their starting materials; however, all synthesized compounds were found to be hypergolic in the presence of white fuming nitric acid (WFNA).



INTRODUCTION

Few materials have demonstrated versatility in their use as boron. In its various chemical forms, it may be utilized as a dopant to yield thermal shock-resistant borosilicate glass,¹ a hydrogen source,^{2–4} detergents like borax, hypergolic fuels,^{5,6} and even act as essential nutrients for certain plant species.⁷ In chemistry, organoboron compounds, such as diborane and its derivatives, attract much attention for their versatility in synthetic applications.⁸ Additionally, boronic esters have found widespread use in Suzuki–Miyaura cross-coupling reactions for the C–C bond formation.⁹ Furthermore, boron finds use in the field of energetic materials, specifically in hypergolic fuels.

Boron-based hypergolic fuels have been a topic of interest over the last several decades due to their reduced toxicity relative to hydrazine-based binary propulsion systems.^{10–12} Hypergolic propulsion systems are an attractive option where reliability, simplicity, and reignitability are important as they only require valves to bring the hypergolic components together to achieve ignition.^{13,14} Accordingly, work has been conducted on boron-containing ionic liquids by Shreeve^{15–17} and hypergolicity studies of borane-amines with nonenergetic backbones by Ramachandran.^{5,6} However, comparatively little research has been conducted on borane-amines on high-nitrogen content heterocycles as hypergolic fuels.

In the field of energetic materials, there is a continued push for improved densities, detonation pressures, and combustion temperatures as these are the predominant indicators against which the energetic performance is measured. New heteroatoms other than carbon are desirable for investigation, as they may allow for higher-performing systems than those presently available. Boron is a highly sought-after heteroatom

as the bond dissociation energy (BDE) of B–O is 787 ± 42 kJ/mol, which is significantly greater than the BDE of the Al–O bond at 485 ± 8 kJ/mol.¹⁸ High BDEs translate to higher combustion temperatures, which are important in the performance of rocket motors. Accordingly, boron may be useful not only in high-explosive formulations but also in rocket motors, as it may have desirable characteristics in both areas.

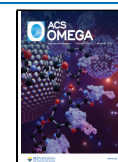
Although borane-amines seem to intersect the field of energetic materials quite well due to their hypergolic characteristics with white fuming nitric acid (WFNA) as well as the high-energy storage capability inherent in boron, there is comparatively little research on borane-amines with high-nitrogen content heterocycles. An article by Bélanger-Chabot et al.¹⁹ examined borane-trinitromethyltetrazole and related compounds, yet it remains one of the few papers that has investigated borane-amines on high-nitrogen content energetic materials. In contrast, zwitterionic *N*-oxides of high-nitrogen content heterocycles have been comparatively more widely investigated and shown to improve the properties of the parent energetic systems, with examples such as dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50),²⁰ 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105),²¹ nitrotetrazole-2*N*-oxide,²² and 3,6-diamino-1,2,4,5-tetrazine 1,4-dioxide (LAX-112).²³ In principle, N–BH₃ bonds may behave as zwitterions,

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which may yield a good comparison to N-oxides in energetic systems and possible related stabilization of such systems.^{24–26} Accordingly, we have attempted the synthesis and characterization of various borane-amines of high-nitrogen content heterocycles and evaluated their hypergolicity with WFNA.

EXPERIMENTAL SECTION

General Procedure for Addition of Borane. To an oven-dried three-neck round-bottom flask with a stir bar, 1 equiv of the relevant nitrogen-containing precursor was added. Next, the round-bottom flask was connected to a Schlenk line and purged with an inert gas atmosphere, typically neat N₂ or argon gas, using conventional Schlenk techniques. Tetrahydrofuran was then added to the reaction mixture, followed by 2.0 equiv of 9 M BH₃·Me₂S (BMS) to make a 0.5 M solution. The reaction mixture was then stirred for 3 h; however, precursors with low solubility in tetrahydrofuran (THF) were instead stirred for a total of 16 h. The reaction progress was monitored by ¹¹B NMR spectroscopy of the crude material. After the reaction was complete, the crude reaction mixture was then placed in hexanes, which precipitated the borane-amine product. The liquid organics were then removed by pipette, and the remaining solids were dried under vacuum, yielding the required borane-amine.

Procedure for Attempted Transamination of Borane-Ammonia with 19a. To an oven-dried three-neck round-bottom flask, 1 equiv of the precursor of 19a and 1 equiv of borane-ammonia were added and placed along with a stir bar. Next, the round-bottom flask was connected to a Schlenk line and purged with an atmosphere of neat N₂ using conventional Schlenk techniques. Then, 1 M tetrahydrofuran was added to the reaction mixture, and the mixture was stirred under reflux for 10 h. The reaction progress was monitored by ¹¹B NMR of the crude material. After the reaction was complete, the mixture was dried under vacuum, yielding a mixture of 19b and the parent compound, 19a. Isolation of 19b from 19a was not attempted, as the general procedure for borane-amines discussed previously yielded better results.

RESULTS AND DISCUSSION

The general procedure for the addition of borane via adduct exchange of BMS was followed for all compounds shown in Figures 1, 2, and 3, but did not demonstrate any detectable addition of borane by ¹¹B NMR for 1–14 (Figure 1). We also attempted an alternate method to synthesize the product compounds via the transamination of borane-ammonia²⁷ in a trial run with the parent compound 19a. While the expected N–BH₃ peak was detected in the ¹¹B NMR spectrum, noticeable amounts of the parent amine were also detected in the ¹H NMR spectrum. In the case of utilizing BMS as the borane source for 19a, primarily the product was observed. As such, despite the toxic and malodorous hazards associated with the dimethyl sulfide byproduct, the adduct exchange of BMS and the presented heterocycles was primarily used here as the relatively mild reaction conditions and straightforward isolation (compared to other methods like transamination) were found to be critical in handling these moisture-sensitive products.

Figure 1 shows the nitrogen-rich heterocycles that failed to form borane-amines. This also shows the difficulty of finding an acceptable backbone for forming a borane-amine with a high-nitrogen heterocyclic backbone, yet it is also a useful

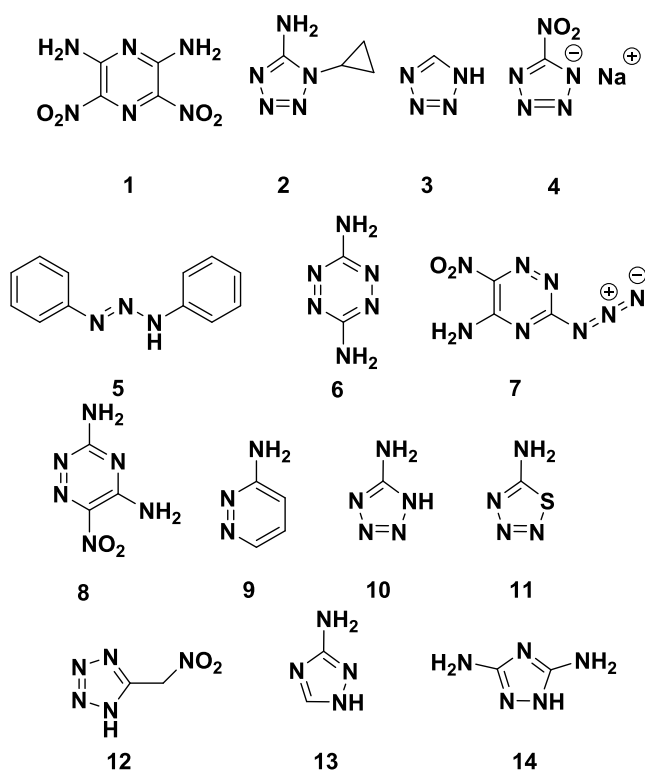


Figure 1. Nitrogen-rich compounds did not exhibit any detectable interactions with BH₃.

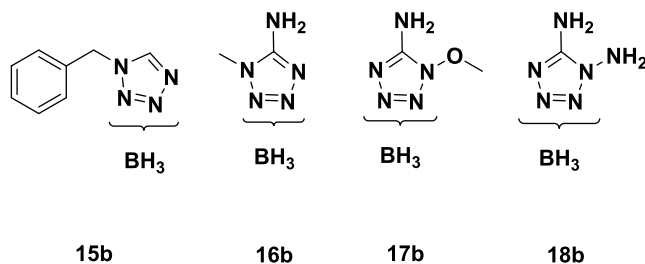


Figure 2. Transiently stable borane-amines.

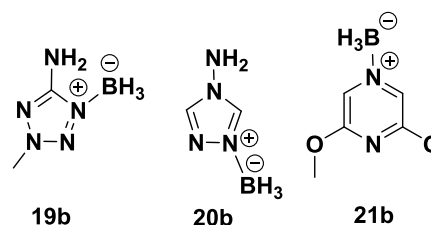


Figure 3. Examples of isolatable borane-amines, in which the Lewis acid–Lewis base pairs are presented as zwitterionic pairs.

guide for observing the failure patterns of borane addition. For example, no borane-amine was formed with any compounds that had an acidic proton or anion (3, 4, 5, 10, 12, 13, and 14). Of this group, it should be noted that the borane of 12 was not successfully synthesized, despite there being literature precedent for trinitro analogues successfully forming borane-amines.¹⁹ Additionally, it seems that tetrazoles with substitutions at one position do not form stable borane-amines, while substitutions at the two positions tend to allow for a transiently stable product, an unusual substitution pattern. Furthermore, heterocycles with nitro-substituents have never

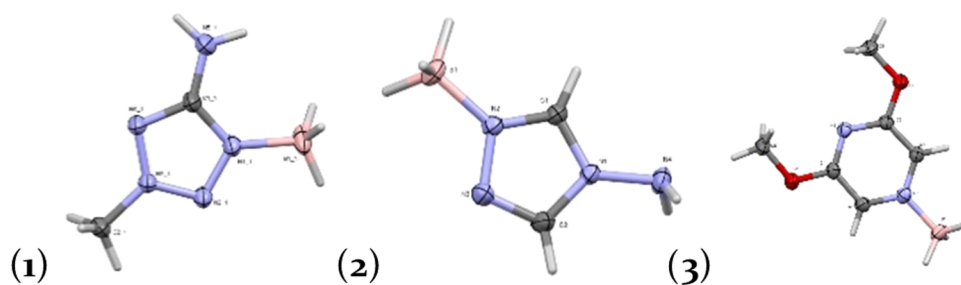


Figure 4. ORTEP representation of the molecular structures of **19b**, **20b**, and **21b** in the crystalline state. Non-H atomic displacement ellipsoids are shown at a 50% probability level.

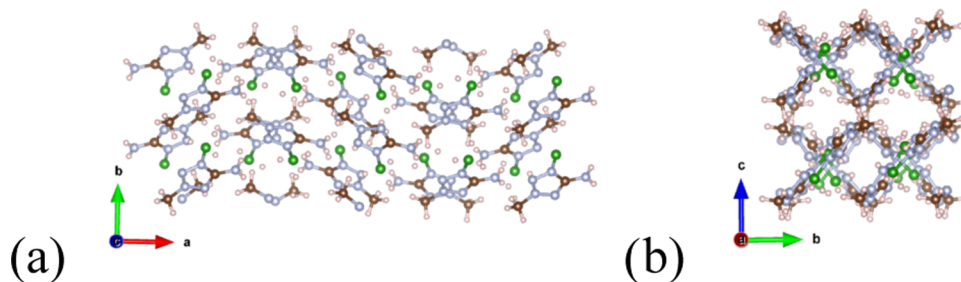


Figure 5. Unit cell packing of **19b**: (A) viewed along the *c*-axis and (b) viewed along the *a*-axis. Bond distances of 1.58 are observed for B–N bonds at 150 K.

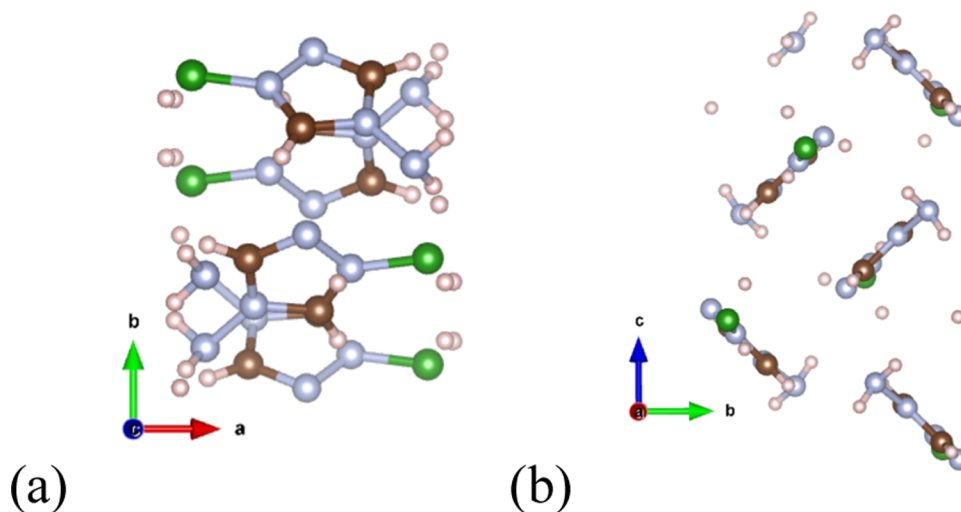


Figure 6. Unit cell packing of **20b**: (a) viewed along the *c*-axis and (b) viewed along the *a*-axis. Bond distances of 1.57 are observed for the B–N bonds at 150 K.

demonstrated successful borane-amine addition, which may be attributed to the deactivation of the ring's electrons by the electron-withdrawing nature of the nitro-substituents. Lastly, the N-oxide zwitterions of **1**,²¹ **4**,²² **6**,²³ and **8**²⁸ are all well-known and exhibit good performance as explosives; however, the corresponding N–BH₃ zwitterion was not detectable for any of these compounds, even in situ. Accordingly, it seems that a compound's proclivity for the addition of zwitterionic N-oxides is not to be considered a good predictor of how borane may add to the same high-nitrogen content backbone.

While the aforementioned compounds were unsuccessful coupling partners, other backbones yielded borane-amines that were transiently stable using the general procedure for borane addition (Figure 2). Oftentimes, a borane-amine was detected in the crude solution via ¹¹B NMR spectroscopy; however, upon attempted isolation of the borane-amine, the product

would decompose even under more gentle drying techniques such as vacuum drying. Of the transiently stable borane-amines, **15b** is the most stable. Nevertheless, **15b** shows visible signs of decomposition (the dry powdery solid turns into an oily solid) even under argon gas. In contrast, **16b**–**18b** are unstable in situ and decompose readily on their own.

Isolable borane-amines whose products are relatively stable are shown in Figures 3 and 4, along with their crystallographic unit cells in Figures 5, 6 and 7. Borane-amines **19b**, **20b**, and **21b** were the most stable and were successfully isolated and characterized by utilizing single-crystal X-ray diffraction (SCXRD). Of these, **21b** is by far the most stable and shows no signs of decomposition, even after two months of exposure to the atmosphere, unlike **19b** and **20b**. The B–N bond lengths of **19**, **20b**, and **21b** were found to be 1.58, 1.57, and 1.61, respectively, in single-crystal X-ray analysis at 150 K. The

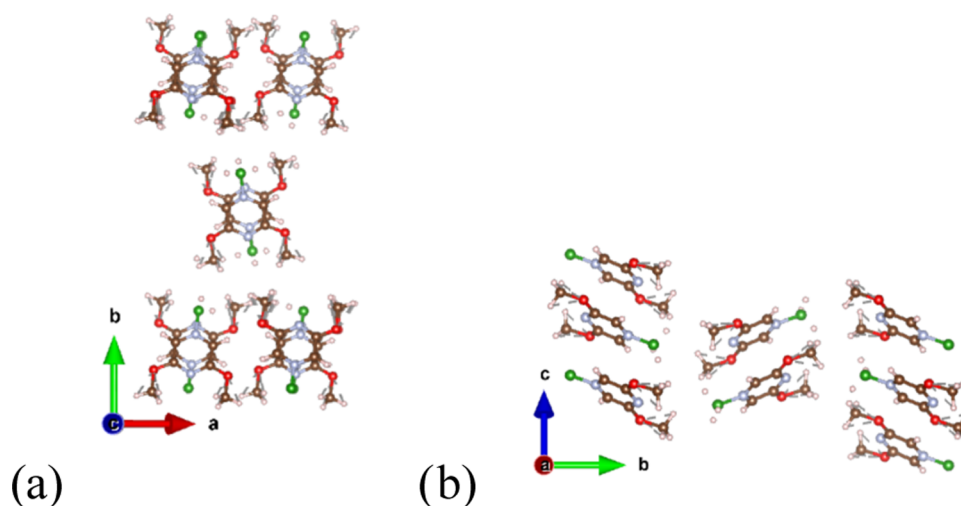


Figure 7. Unit cell packing of **21b**: (a) viewed along the *c*-axis and (b) viewed along the *a*-axis. Bond distances of 1.61 are observed for B–N bonds at 150 K.

B–N bond lengths of **19b** and **20b** are slightly shorter than the B–N bond length of tetragonal borane-ammonia (1.599 Å), while that of **21** is slightly longer (1.61 Å).²⁹ The B–H distances are all ≤ 1.11 , which is the usual B–H bond length of borane-amines (Table 1). The identified B–H bond lengths

Table 1. Comparison of the Crystallographic B–N and B–H Distances of **19b**, **20b**, **21b**, and Borane-Ammonia^a

Property	19b	20b	21b	Borane-Ammonia ^{29,30b}
B–N distance [Å]	1.58	1.57	1.61	1.60
B–H distance [Å]	1.10	1.11	1.09	1.11
ρ (g/cm ³)	1.232	1.270	1.224	0.78

^aDensities of **19b**, **20b**, and **21b** Originate from Single-Crystal X-ray Diffraction at 150 K while those of Borane-Ammonia Is Taken from 200 K.³⁰ ^bBond lengths for borane-ammonia are essentially unchanged from 90 to 298 K.

are significant as they were elucidated by HFIX/AFIX 138 constraints to allow for refinement of the B–H bond lengths. Notably, no intermolecular H-bonding was observed for **19b**, **20b**, and **21b** in their crystal structures. Furthermore, **21b** was the only long-term air-stable borane-amine, yet it possessed the longest B–N bond length of all synthesized compounds and was even longer than borane-amine's B–N bond.

Comparisons of the densities of the borane-amine products to the respective precursor molecules allow for the analysis of the energetic properties of borane-amines. Although the starting compounds range in density from 1.175 to 1.75 g/cm³, the crystalline density of all borane adducts is ~ 1.25 g/cm³. **21b** marginally increases in density when compared to its starting material, which is the only example of an increase in density during borane-amine formation in this work. In high explosives, density is the most important measure of performance, as a compound's density directly influences its detonation velocity and detonation pressure.^{31–33} Since the density of all the borane adducts is ~ 1.25 g/cm³, it is unlikely that the addition of borane groups is desirable for high-explosive formulations as acceptable densities are at least comparable to TNT at 1.65 g/cm³.

TGA analysis was used to determine the decomposition temperatures of borane-amines. For **19b** and **20b**, the

decomposition temperatures were recorded as 36.7 and 50.5 °C, respectively (Table 2). In contrast, **19a** and **20a** had

Table 2. Comparison of Select Physical and Chemical Properties of Successful Borane-Amine Products with a Comparison to Their Precursors, Where Applicable

	19b	20b	21b	TNT ³⁵	RDX ²⁰
density (g/cm ³) ^a	1.232	1.270	1.224	1.65	1.82
% N	61.9	57.1	18.2	18.5	37.8
T_{dec} (°C) ^b	36.7	50.5	108.0	295	210
precursor T_{dec} (°C)	84	159	N/A ^g	N/A	N/A
H_f , 298 K (kJ/mol) ^c	186.3	232.7	−293.1	−80.5	86.3
detonation velocity (m/s) ^d	7138	7379	5566	6880	8983
detonation pressure (GPa) ^d	14.5	15.9	9.66	19.5	38.0
impact sensitivity (J) ^e	30	1	>40	40	7.5
friction sensitivity (N) ^f	30	40	>360	360	120

^aDensities of **19b**, **20b**, and **21b** were identified from single-crystal X-ray crystallography values at 150 K. ^bDecomposition temperatures from TGA analysis are defined as the onset of mass loss. ^cSolid-state enthalpies of formation were calculated with Gaussian 16W. ^dCalculated using Explo5 V6.05.02. ^eImpact sensitivities performed according to STANAG 4489³⁶ with modifications to an OZM drop hammer by the BAM method according to instructions³⁷. ^fFriction sensitivity characterization was carried out as outlined in STANAG 4487³⁸ with modifications to instructions³⁹ on a BAM friction tester. ^gSublimates at room temperature.

decomposition temperatures of 84 and 159 °C, which are substantially higher than those of their borane-amine counterparts. As will be seen in future data, **21b** is an anomaly in the data set as its precursor, **21a**, sublimates under standard conditions, while its borane-amine, **21b**, decomposes at 108 °C. It should be noted that the decomposition temperature of **21b** is higher than that of borane-ammonias, which stands at 90 °C and is of interest for hypergolic fuel use.³⁴ While it seems that the stability of the formed borane-amine adduct increases with the basicity of the parent amine, the trend would need other examples to ensure the veracity of the observation.

The enthalpy of formation calculations were conducted with the Gaussian 16W package⁴⁰ using the previously described CBS-4 M methodology,⁴¹ which was initially developed by

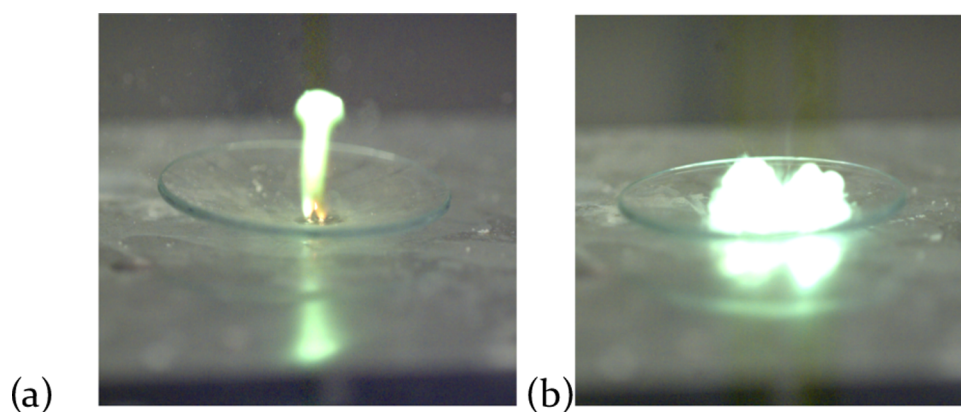


Figure 8. Images captured using a high-speed camera for hypergolic testing on **19b** (a) and **20b** (b) with white fuming nitric acid.

Petersson and co-workers.⁴² The method of the complete basis set (CBS) of Petersson and co-workers obtains accurate energies by using the known asymptotic convergence of pair natural orbital expressions to extrapolate via calculations of a finite basis set to the estimated complete basis limit.⁴³ First, CBS-4 uses an HF/3-21G(d) structure optimization, at which the zero-point energy is also computed. Next, a large basis set SCF calculation as a base energy and an MP2/6-31+G calculation are used with CBS extrapolation to correct the energy through the second order. Higher-order contributions are approximated with an MP4(SDQ)/6-31+(d,p) calculation. Presently, the modified CBS-4 M methodology (M is the use of minimal population localization) was used, which includes additional empirical corrections in addition to the reparameterization of the original CBS-4 M method. Optimized Gaussian structures are available in the [Supporting Information](#). Such methods are consistent with previous reports of the enthalpy of formation in the energetics literature.^{44–48}

Occasionally, computational calculations may result in overestimations; TKX-50 is a pertinent example.^{44,49,50} An alternative approach to identifying the enthalpy of formation for these materials is by group contribution calculations, which may be accomplished by subtracting the enthalpy of formation of a borane-amine from its free amine. For example, the enthalpies of borane-hydrazine ($\text{BH}_3\cdot\text{N}_2\text{H}_4$) and hydrazine (N_2H_4) are -42.68 ⁵¹ and 42.7 kJ/mol,⁵² respectively. Subtracting the enthalpy of formation of borane-hydrazine from that of hydrazine affords the group contribution of borane to the enthalpy of formation, which is -85.4 kJ/mol. Using 5-amino-2-methyl-tetrazole as an example, we subtract the enthalpy of formation of the borane group contribution (-85.4 kJ/mol) from the parent amine (206.8 kJ/mol),⁵³ and find the enthalpy of formation for **19b** to be 121.4 kJ/mol by the group contribution calculation. Such an estimation reveals that the enthalpy of formation for **19b** may be overestimated by the CBS-4 M methodology. Despite possibly overestimating the enthalpy of formation, CBS-4 M remains the standard method for reporting the enthalpy of formation in the literature on energetic materials.^{45–48,54}

The detonation properties were calculated with Explo5 V6.05.02⁵⁵ using the density from single-crystal X-ray diffraction and the previously calculated CBS-4 M solid-state enthalpies of formation. The calculations revealed that **21b** possessed the lowest performance of all three borane-amines with a detonation velocity of 5566 m/s and a detonation pressure of 9.66 GPa ([Table 2](#)). **20b** was found to be the best-

performing compound in this series with a detonation velocity of 7379 m/s and a detonation pressure of 15.9 GPa, **19b** was just behind **20b** in terms of its performance with a detonation velocity of 7138 m/s and a detonation pressure of 14.5 GPa. Energetic performance was generally greatest for compounds **19b** and **20b**, which boasted heats of formation of 186.3 and $23,278$ kJ/mol, respectively, and worst for **21b** with a heat of formation of -293.1 kJ/mol. For a summary of the energetic properties, see [Table 2](#).

Sensitivity testing of the borane-amines revealed that the addition of borane may act as a sensitizer in some of these systems. Free N-donor compounds **19a**, **20a**, and **21a** are all insensitive materials (>40 J impact, >360 N friction), but **19b** and **20b** became sensitized toward impact and friction with the addition of borane. **19b** had friction and impact sensitivities of 30 N and 30 J, respectively, and **20b** was found to possess impact and friction sensitivities of 1 J and 40 N, respectively. In contrast, **21b** remained insensitive with respect to both friction and impact stimuli. It is unknown why **19b** and **20b** became sensitive to impact and friction stimuli while **21b** did not.

Lastly, hypergolic testing was conducted on **19b–21b** and **15b** by dropping WFNA onto borane-amine powder. All **19b–21b** demonstrated hypergolicity with white fuming nitric acid, while **15b** only produced orange gas. Flames for boron combustion are generally vibrant green and can be seen clearly in [Figure 8](#). **15b** decomposed substantially prior to testing, as evidenced by its appearance, which was originally a white powder that became an oily solid after a couple of hours while still under argon gas. **19b** and **20b** are stable for at least several days, longer if under argon. **21b** was found to be air-stable for at least two months at the time of writing.

CONCLUSIONS

The synthesis of borane-amines was attempted with a wide variety of high-nitrogen content heterocycles. Although most borane additions failed, the information acquired from successful borane-amine syntheses provides valuable insights into the application of these compounds in energetic materials. N-oxide functionalization was found not to be a predictor of the successful addition of borane-amine. The synthesized borane-amine adducts were all air-sensitive, except **21b**, and most demonstrated sensitization to impact and friction stimuli with the addition of borane. The addition of borane to all amines resulted in a final borane-amine density of ~ 1.25 g/cm³, regardless of the density of the starting material. Accordingly, the use of borane-amines in highly explosive

formulations is likely unsuitable due to their low densities, poor energetic performance, decomposition from atmospheric moisture, and sensitization issues. There may be hypergolic applications, as they ignite upon contact with 100% nitric acid.

However, the use of **21b** as an additive in hypergolic propellant formulations may be beneficial for investigation. **21b** is more comparable to borane-ammonia than **19b** and **20b** because **21b** is air-stable, insensitive to friction and impact stimuli, possesses a superior decomposition temperature than borane-ammonia, and is hypergolic with WFNA. Perhaps most unusual for **21b** is that it has the highest decomposition point of all the synthesized borane-amines, higher than borane-ammonia, despite having a longer B–N bond length than borane-ammonia. Accordingly, **21** may serve as an alternative to borane-amine in hypergolic propellant systems and is likely worthy of further investigation.

■ WARNING

19b and **20b** are sensitive energetic materials. While no issues arose during our handling of these materials, appropriate personal protective equipment (face shield, body armor, Kevlar gloves) should be worn during the handling of these materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c09934>.

Experimental details, characterization data, and CIF files are available for **19b**, **20b**, and **21b** free of charge via the Internet (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

WFNA, white fuming nitric acid; RDX, 1,3,5-trinitro-1,3,5-triazinane; BMS, borane dimethyl sulfide

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