

**BH₃-Amine and B(CH₃)₃-Amine Adducts as Additives for
Liquid/Gel Hypergols and Solid Hybrid Rocket Motor
Fuels: Property and Performance Predictions**

by Michael McQuaid and Chiung-Chu Chen

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December 2013

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14. ABSTRACT BH ₃ -amine and B(CH ₃) ₃ -amine adducts were investigated as potential additives for rocket-propellant formulations. The investigation included the calculation of property predictions for a variety of known and notional adducts. Property predictions were based on results from quantum chemistry methods. Predicted gas-phase properties included B-N bond dissociation energies (BDEs) and enthalpies of formation at 298 K [$\Delta_f H_g(298)$]. Predicted condensed-phase properties included enthalpies of sublimation [$\Delta H_s(298)$], enthalpies of formation at 298 K [$\Delta_f H_c(298)$], and densities (ρ). Values for these properties that were derived from measured data or higher-level computational methods were also obtained from open literature sources. In the course of the literature search, assessments of the thermal and/or air stabilities of some adducts were identified, and an attempt was made to correlate them with B-N BDEs. The $\Delta_f H_c(298)$ estimates were employed as input for thermochemical code-based calculations of the specific impulse that adducts could potentially generate when combined with inhibited red fuming nitric acid. Results from the study indicate that several BH ₃ -amine adducts warrant further investigation as additives for liquid/gel hypergols or for solid fuels for hybrid concepts.					
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Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Literature Search for Adduct Properties	6
3. Computational Methods	6
3.1 Gas-Phase Equilibrium Geometries and Bond-Dissociation Energies.....	6
3.2 Gas-Phase Enthalpies of Formation at 298 K [$\Delta_f H_g(298)$].....	7
3.3 Condensed-Phase Property Estimates	7
3.4 Specific Impulse (I_{sp}) and Adiabatic Temperature Predictions	8
4. Results	8
4.1 Gas-Phase Properties.....	8
4.2 Condensed-Phase Properties	13
4.3 Specific Impulse and Adiabatic Temperature Predictions	17
5. Summary and Conclusions	19
6. References	21
List of Symbols, Abbreviations, and Acronyms	29
Distribution List	30

List of Figures

Figure 1. Geometric structures for BH ₃ -amine adducts.....	9
Figure 2. Correlation between $MW/Vol_{0.001}$ and densities for BH ₃ -amine adducts.....	15
Figure 3. Comparison of measured ΔH_s values for B(CH ₃) ₃ -amine adducts and their estimation using equation 3.	17
Figure 4. I_{sp} predictions as a function of Φ for various fuels in combination with IRFNA.	19

List of Tables

Table 1. Amines considered in this study: names and stoichiometries.....	6
Table 2. BH ₃ -amine adduct gas-phase properties: estimates from the current work, benchmark values, and stability assessments.....	10
Table 3. B(CH ₃) ₃ -amine adduct gas-phase properties: estimates from the current work, benchmark values, and stability assessments.....	11
Table 4. BH ₃ -amine adduct condensed-phase properties: estimates from the current work and benchmark values.....	14
Table 5. B(CH ₃) ₃ -amine adduct condensed-phase properties: estimates from the current work and benchmark values.....	15
Table 6. ΔH_s values derived from vapor pressure measurements and parameters of the 0.001 electron/bohr ³ isosurface of electron density for BH ₃ -amines.....	16
Table 7. Maximum theoretical I_{sp} and adiabatic temperature (T_{ad}) predictions for fuels combined with IRFNA.....	18

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1. Introduction

The U.S. Army is interested in developing propulsion systems for tactical missiles that can be throttled (or turned off and restarted) and are less vulnerable to external threats than currently fielded systems. Motor types with the potential to achieve both of these objectives include concepts fueled with hypergolic liquid/gel bipropellants or solid-liquid/gel (hybrid) combinations. In both cases, thrust is modulated by controlling the flow rate of a pumpable fuel and/or oxidizer. Increasing targeting options and range, the integration of such motor types into tactical missiles would increase their lethality while reducing the vulnerability of their launch platforms. In addition, because the fuel and oxidizer are stored separately in these motor types, they are inherently insensitive to a variety of stimuli that can produce catastrophic events in solid-(mono)propellant-fueled rocket motors.

A hypergolic propulsion system concept that is capable of being integrated into Army tactical missiles has been demonstrated. The concept is referred to as the impinging stream vortex engine (ISVE) (Wilson and Connaughton, 1967; Michaels and Wilson, 1995). For a recently completed development effort, it was fueled with a hydrazine-alternative hypergol (called TEDMAZ) and inhibited red fuming nitric acid (IRFNA). TEDMAZ is a blend of tetramethylethylenediamine (TMEDA) and 2-azido-N, N-dimethylethanamine (DMAZ), and the fuel's qualifications for the application have been established (McQuaid, 2009; Mathis et al., 2008). Individually, both TMEDA-IRFNA and DMAZ-IRFNA showed some promise as candidates. Testing of TMEDA-IRFNA dates back to the 1950s, and it was successfully fired in an engine. DMAZ's potential as a hypergol was identified by the U.S. Army Aviation and Missile Research Development and Engineering Center (AMRDEC) in the 1990s (Thompson, 2000), but the ignition delay of DMAZ-IRFNA was slightly too long to make it a viable option. The potential of TMEDA-IRFNA was rediscovered by AMRDEC in the course of attempts to address this issue. Blending DMAZ and TMEDA produces several benefits (Stevenson et al., 2008). For one, blends have shorter ignition delays with IRFNA than either fuel alone. Also, compared to TMEDA-IRFNA, TEDMAZ-IRFNA combusts more cleanly and has a higher theoretical density*specific impulse ($\rho * I_{sp}$). There is, however, some concern about the aging characteristics of DMAZ. Thus, an additive that would provide the benefits of DMAZ and not have this potential drawback would be preferred.

Compared to hypergolic liquid/gel propulsion technology, hybrid rocket motor technology is much less mature and has yet to find a role within the Department of Defense (DOD). Concluding in the early 1980s, a more than decade-long development program called the High Altitude Supersonic Target (HAST), Teledyne Ryan successfully flew a recoverable target drone (AQM-81) with a ram-air augmented hybrid rocket motor. However, a follow-on contract for production of the missile was not awarded (Parsch, 2002). Parsch presumes this decision was

made because the AQM-81 was more expensive than the expendable drone (AQM-37) it was to replace. We could find no other DOD-sponsored hybrid motor development program that approached the AQM-81's level of maturity.

A recently discontinued AMRDEC effort highlights some of the difficulties faced in developing hybrid propulsion systems for tactical missiles. The primary issue is that the amount of thrust that can be developed depends upon the rate at which the fuel grain can be made to regress, and the regression rates found for the (storable) fuel-oxidizer combinations that have been studied to date are fairly limited. Therefore, the solid (grain) must have a relatively large exposed surface area for thrust to reach required levels. To obtain the required surface area, (empty) space must be created in the (volume-limited) combustion chamber, reducing the loading density. AMRDEC attempted to address this issue by using IRFNA in combination with a fuel grain composed of hydroxy-terminated polybutadiene (HTPB) and an additive (at high concentrations) that promoted reactivity (IRFNA was also employed in the AQM-81, but we were unable to find a characterization of the composition of its fuel grain). While the combination tested by AMRDEC did demonstrate a restart capability, measured I_{sp} efficiencies were significantly lower than standards set by liquid/gel bipropellants and solid monopropellants. In a related approach, DeSain et al. (2007) added the strong reducing agent lithium aluminum hydride (LiAlH_4) to paraffin to achieve higher regression rates. The group reported that the LiAlH_4 , which in neat form is highly reactive with water, was "suitably stable" when mixed with the highly hydrophobic paraffin. However, we are skeptical about the feasibility of employing LiAlH_4 in fuel grain formulations for tactical missiles. Studies of other "hypergolic" hybrid combinations have also been reported in the open literature (Jain, 1995). None of these combinations appear to remain of interest to researchers in the field.

Because IRFNA will react rapidly with any number of materials, it is not a challenge to find compounds that can be combined with it to yield required regression rates. Indeed, it is not even necessary to employ an oxidizer as aggressive as IRFNA; many compounds (like LiAlH_4) will react spontaneously with just water or O_2 (in air). However, such compounds could represent a greater threat to safety than IRFNA. Handling procedures would be onerous, and any penetration of the motor housing (e.g., by fragment impact) could lead to a catastrophic event. The challenge is to identify fuels that are thermally stable, are highly reactive with storable oxidizers, age well, can be formulated into grains with good mechanical properties, and do not pose undue risk to human health and the environment. In addition, although the risks associated with IRFNA are considered acceptable, the best fuel candidates would be highly reactive with an oxidizer that is less aggressive, such as hydroxylammonium nitrate (HAN).

Although there would seem to be an almost unlimited number of possibilities that one might propose as candidates for fuels in hypergolic liquid/gel or hybrid rocket motors, once some basic screening criteria are invoked—namely, that the materials consist of molecular entities with low atomic weight atoms (for better performance) and have no multiple order C-C bonds (to avoid aging problems), yet nonetheless react readily with fieldable oxidizers—one is led to hydrides or

organic compounds of aluminum (Al) and boron (B). Having a relatively low atomic weight and (at a molecular level) making strong bonds with oxygen atoms, Al (metal) is often added to rocket propellant formulations to increase their energy density/performance. However, “pure” powders of Al metal have an attendant oxide coat that is both a parasitic (nonperforming) mass and an inhibitor of the powders’ initial reactivity. Theoretically, boron, which is in the same column of the periodic table as Al, has even greater performance potential than Al, but that has been difficult to achieve in practice (see, for example, Clark [1972]). In addition, its metal powders also have a parasitic oxide coat that limits their initial reactivity. In contrast, the hydrides of these metals [alane (AlH_3) and borane (BH_3)] and their alkylated derivatives—including trimethylaluminum [$\text{Al}(\text{CH}_3)_3$] and trimethylborane [$\text{B}(\text{CH}_3)_3$]—are pyrophoric (i.e., they will ignite when exposed to ambient air). They will also react spontaneously and violently with water.

The pyrophoricity of AlX_3 and BX_3 compounds, where X can be an H-atom, a halogen atom, or an alkyl group, is related to the fact that they are strong Lewis acids and O_2 and H_2O have donatable lone-pair electrons.* Moreover, their pyrophoricity has been exploited for rocket propulsion applications. For example, a triethylaluminum-trimethylborane [$\text{Al}(\text{CH}_2\text{CH}_3)_3\text{-B}(\text{CH}_3)_3$] mixture is used as a first-stage igniter for the SpaceX Falcon 9 rocket (Clark, 2010). In a research effort for another application, Young et al. (2010) found that regression rates for AlH_3 -loaded HTPB fuel grains oxidized by O_2 were comparable to, or better than, the baseline HTPB grain; and that the performance of such grains was better than those loaded with micron- or nano-sized aluminum. However, the thermal stability of AlH_3 is insufficient for it to be employed as a propellant ingredient for tactical missile applications (Ishmail and Hawkins, 2005). And even if that issue could be overcome (Petrie et al., 2001), given their pyrophoricity, in neat form on a battlefield, AlX_3 and BX_3 compounds would be a vulnerability waiting to be exploited.

The foregoing considerations led us to ask whether derivatives of AlX_3 and BX_3 compounds might have the requisite combination of reactivity and stability. The study summarized here was motivated by the idea that the prereaction of AlX_3 or BX_3 with a weak base to form a Lewis adduct might be analogous to reacting highly corrosive nitric acid (HNO_3) with ammonia (NH_3). The $\text{NH}_3 + \text{HNO}_3$ reaction produces a noncorrosive material (i.e., the fertilizer ammonium nitrate) that, nonetheless, releases considerable energy if appropriately stimulated in the right environment. Being well-known weak bases and having shown promise as hypergolic fuels, alkyl amines (like TMEDA) were obvious candidates to pair with AlX_3 and BX_3 . Moreover, unlike ammonium nitrate and other energetic salts that have the potential to detonate because the

*Lewis acids are molecular entities/chemical species that can accept an electron pair. (Chemical species with molecular formulae BX_3 and AlX_3 are textbook Lewis acids.) Lewis bases are molecular entities/chemical species that can donate an electron pair. If the reaction of a Lewis acid with a Lewis base produces a single product, the term “dative” is employed to describe the (single) bond that forms and the product is referred to as an adduct.

cation and anion are fuel and oxidizer components, respectively; AlX_3 -amine and BX_3 -amine adducts with X equal H or CH_3 would be pure fuels.

Focused initially on $\text{Al}(\text{CH}_3)_3$ -amine adducts, a literature search performed in 2010 identified that a number of such compounds had been made and characterized in the early 1960s at the Naval Ordnance Laboratory (Fetter and Bartocha, 1961; Fetter et al., 1963; Fetter and Moore, 1964). Although the application for these compounds was not mentioned in the cited publications, the researchers later patented syntheses involving the reaction of $\text{Al}(\text{CH}_3)_3$ with various hydrazines and listed propellants and explosives as potential uses for the products (Fetter and Bartocha, 1967). However, it was reported that all the compounds reacted vigorously to violently with water and decomposed in air. Moreover, the only Lewis adduct of the patented group of compounds [$\text{Al}(\text{CH}_3)_3$ - $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$] was observed to be among the most reactive. Thus, the idea looked as though it had already been investigated and lacked promise.

Reconsidering the idea in 2012, we performed another literature search and identified a recently commercialized adduct (named DABAL-Me3) that suggested further investigation was warranted. Advertised to be stable in low-humidity air for short periods of time (Sigma-Aldrich, 2013); DABAL-Me3 is formed from $\text{Al}(\text{CH}_3)_3$ and 1,4-diazabicyclo[2.2.2]octane (also commonly referred to as DABCO, or triethylenediamine). The adduct is referred to here as $2\text{Al}(\text{CH}_3)_3$ -DABCO. Bradford et al. (1992) published a study of its properties, reporting it to be a solid that decomposed/melted at $230\text{ }^\circ\text{C}$. Benefiting from its stability relative to other organoaluminum-based catalysts, academic researchers have employed it to cross-methylate aryl and vinyl halides (Biswas et al., 2005). At the same time, $2\text{Al}(\text{CH}_3)_3$ -DABCO will produce explosive gases if exposed to (liquid) water or acids (Sigma-Aldrich, 2013). Taken together, the information suggested that $2\text{Al}(\text{CH}_3)_3$ -DABCO might have the balance between stability and reactivity that is required for an adduct to be a viable fuel additive.

The identification of a potentially promising $\text{Al}(\text{CH}_3)_3$ -amine adduct led to a literature search for the properties of BX_3 -amine adducts. As highlighted by several recent reviews (see, for example, articles by Lane [2006] and by Staubitz et al. [2010a and 2010b]), an extensive variety of BX_3 -amine adducts have been studied. Moreover, many are commercially available. Reports of BX_3 -amine adducts date from 1809, and a spectroscopic characterization of BH_3 - $\text{N}(\text{CH}_3)_3$ was made in 1937 (Bauer, 1937). Chew et al. (1979) proposed employing BH_3 -amine adducts as solid propellants for H_2 generation, envisioning their use as a fuel for laser weapons. The potential of BH_3 -amine adducts as hydrogen storage media for fuel cells has led to a tremendous amount of research into their properties. BX_3 -amine adducts are also being exploited for the production of B-N ceramics and films (see, for example, the article by Frueh et al. [2011]).

Gatti and Wartik (1966b) discuss the preparation of 2BH_3 -DABCO, stating “this white, crystalline, air-stable compound was nonvolatile and did not melt at temperatures up to $350\text{ }^\circ\text{C}$, but darkened slightly above $300\text{ }^\circ\text{C}$.” Monoalkylborane-DABCO adducts have also been reported to be air stable (Brown et al., 1979). Additionally, Yang et al. (2012) report the

synthesis of a poly(methyl acrylate)-BH₃-N(CH₃)H₂ composite, which suggests that mechanically viable propellant grains could be formulated with such adducts. Aluminum borohydride [Al(BH₄)₃]-amine adducts (referred to as Hybalines) have been investigated as (liquid) hypergols (see Clark, 1972). A paper by Weismuller et al. (2010) was the only one found in which an adduct was employed as a hybrid fuel additive. It reports that a 10-weight-percent (wt%) addition of BH₃-NH₃ to paraffin increased the paraffin's regression rate, but that the addition of larger weight fractions decreased it. As an example of the potential of the approach to regression enhancement that is considered here, this result is encouraging. However, because it decomposes at 68 °C (Sigma-Aldrich, 2013), BH₃-NH₃ would not be suitable for tactical missile applications, regardless of the optimum performance increase achievable with it.*

To determine if AlX₃-amine or BX₃-amine adducts warranted further investigation as additives for hypergols and/or hybrid rocket motor fuels, a search of open literature sources was performed to identify other application-relevant properties. In addition, computational chemistry methods were employed to obtain estimates for properties that are needed to predict their performance potential. Many of the amines that were considered have been previously investigated to establish their potential as hypergolic fuels (Stevenson et al., 2008). (Table 1 lists the amines that were considered and the shorthand that is used to name them in this report.) Results for AlX₃-amine adducts were published previously (McQuaid and Chen, 2013). Property estimates and performance predictions for BX₃-amine adducts are presented here. Gas-phase property estimates that are presented include: B-N bond lengths, B-N bond dissociation energies (BDEs), and adduct enthalpies of formation at 298 K [$\Delta_f H_g(298)$]. Condensed-phase property estimates that are presented include: enthalpies of sublimation [$\Delta H_s(298)$], enthalpies of formation at 298 K [$\Delta_f H_c(298)$], and densities (ρ). Values derived from measured data or higher-level computational methods were identified in open literature sources, and they were employed both to develop and to validate the estimation methods utilized in the study. Assessments of the thermal and air stability of some adducts were also identified in the course of the search, and their correlation with estimated B-N BDEs was assessed. The $\Delta_f H_c(298)$ estimates were employed as input for thermochemical code-based calculations of specific impulse (I_{sp}). On the basis of the results, further investigation of some adducts is recommended.

*For a compound to qualify as a propellant ingredient for a tactical missile propulsion system, it must be able to be held (isothermally) at 75 °C for 24 hours (h) and retain more than 99% of its mass. If, as indicated by visual inspection in the course of a melting point determination, a compound decomposes at a temperature below 75 °C, it will obviously not meet this standard. The converse, however, cannot be assumed to be true (i.e., a compound will pass the criterion if a higher decomposition temperature has been reported for it on the basis of visual inspection). As discussed by McQuaid and Drake (2011), if techniques that are more sensitive to product decomposition (e.g., differential scanning calorimetry) are employed, a decomposition temperature below 150 °C will usually be taken to indicate that a compound will not meet the primary standard. Thus, if during a melting point determination a compound is observed to decompose at a temperature below 150 °C, it is assumed that it is unlikely to have thermal stability sufficient for it to be a propellant ingredient.

Table 1. Amines considered in this study: names and stoichiometries.

Shorthand	Name	Stoichiometry
ABCO	1-azabicyclo[2.2.2]octane or quinuclidine	C ₇ H ₁₃ N
azetidine	azetidine	C ₃ H ₇ N
DABCO	1,4-diazabicyclo[2.2.2]octane or triethylenediamine	C ₆ H ₁₂ N ₂
DBN	1,5-diazabicyclo[4.3.0]non-5-ene	C ₇ H ₁₂ N ₂
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene	C ₉ H ₁₆ N ₂
DMA	N-methylmethanamine or dimethylamine	C ₂ H ₇ N
DMP	1,4-dimethylpiperazine	C ₆ H ₁₄ N ₂
HMTA	hexamethylenetetramine	C ₆ H ₁₂ N ₄
HTBN	1,5,7-triazabicyclo[4.3.0]non-6-ene	C ₆ H ₁₁ N ₃
MMA	methanamine or monomethylamine	CH ₅ N
NH ₃	ammonia	H ₃ N
piperidine	piperidine	C ₅ H ₁₁ N
pyridine	pyridine	C ₅ H ₅ N
pyrrolidine	pyrrolidine	C ₄ H ₉ N
TMA	N,N-dimethylmethanamine or trimethylamine	C ₃ H ₉ N
TMEDA	tetramethylethylenediamine	C ₆ H ₁₆ N ₂
TMH	tetramethylhydrazine	C ₄ H ₁₂ N ₂
TMMA	tetramethylmethylenediamine	C ₅ H ₁₄ N ₂
TMTZ	1,3,5-trimethyltriazine	C ₆ H ₁₅ N ₃

2. Literature Search for Adduct Properties

The search for species properties that was performed for this study was primarily conducted via the Cambridge Structural Database (Conquest Version 1.15, Cambridge Crystallographic Data Center) and two Web sites: SciFinder (<https://scifinder.cas.org>, last accessed Aug. 2013) and Web of Knowledge (<http://apps.webofknowledge.com>, last accessed Aug. 2013). Another important source of information was the Sigma-Aldrich Web site (<http://www.sigmaaldrich.com>, last accessed Aug. 2013).

3. Computational Methods

3.1 Gas-Phase Equilibrium Geometries and Bond-Dissociation Energies

Predictions for the molecular properties of species considered in this report were obtained from quantum-chemistry models. The models were implemented via the Gaussian09 suite of codes (Frisch et al., 2013). The B3LYP density functional (Becke, 1993; Lee et al., 1988; Vosko et al., 1980; Stephens et al., 1994) with 6-31+G(d,p), 6-31G(d,p), or 6-31G(d) basis sets (Petersson et al., 1988; Petersson and Al-Laham, 1991; Clark et al., 1983) was employed to predict geometric parameters for equilibrium configurations that isolated molecules could acquire. Although it is

well known that the lengths (r_e) and BDEs of dative bonds are better predicted by MP2-based models (Gilbert, 2004), Potter et al. (2010) observed that B-N bond lengths found with B3LYP and MP2 models agreed to within 0.020 Å. Moreover, Potter et al. observed that when coupled with correlated methods, B-N BDEs obtained with B3LYP-based geometries were only 2–4 kcal/mol larger than those derived from benchmark CCSD(T)/CBS-based calculations. Given that the discrepancies are relatively small, and assuming that the energy bias is relatively consistent, we assumed they would be ameliorated via the use of isodesmic reaction schemes. Therefore, the less computationally expensive approach was employed. As will be shown, this decision was validated.

Starting structures for the geometry optimizations were constructed with Gaussview 5.0 (Gaussian, Inc.). The convergence criteria employed for the optimizations were: max. force ≤ 0.000450 hartree/bohr; root mean square (RMS) force ≤ 0.000300 hartree/bohr; max. displacement ≤ 0.001800 bohr; and RMS displacement ≤ 0.001200 bohr. For all structures meeting these criteria, normal mode analyses were conducted to establish that they had no imaginary frequencies, and thus were indeed equilibrium structures.

3.2 Gas-Phase Enthalpies of Formation at 298 K [$\Delta_f H_g(298)$]

$\Delta_f H_g(298)$ estimates were derived from enthalpy-of-reaction estimates [$\Delta H_r(298)$] for (hypothetical) isodesmic reactions for which established $\Delta_f H_g(298)$ values for all species except the target moiety were available. The gas-phase enthalpy of each molecule in a given reaction was computed based on results from G3MP2B3 (Baboul et al., 1999), G4 (Curtiss et al., 2007), CBS-4M (Montgomery et al., 2000), and CBS-QB3 (Montgomery et al., 2000) models. For all molecules/compounds except $x\text{BH}_3\text{-HMTA}$ and $x\text{B}(\text{CH}_3)_3\text{-HMTA}$ ($x = 3\text{--}4$), the nominal values presented here are the average of values derived from results produced by the G3MP2B3, G4, and CBS-QB3 models. (Results from these three models are expected to be more accurate than those from the CBS-4M model.) For $x\text{BH}_3\text{-HMTA}$ and $x\text{B}(\text{CH}_3)_3\text{-HMTA}$ ($x = 3\text{--}4$), the values are based on CBS-4M results; calculations required by the other three models proved to be impractical for these cases.

3.3 Condensed-Phase Property Estimates

To obtain estimates for adduct densities (in grams/centimeter³), constants a and b for empirical relationships with the form

$$\rho = a(\text{MW}/\text{Vol}_{0.001}) + b \quad (1)$$

where MW is an adduct's molecular weight (in atomic mass units) and $\text{Vol}_{0.001}$ is the volume enclosed by its 0.001 electron/bohr³ isosurface (in Å³), were derived from least squares fits to (very limited) sets of measured densities that were found in open literature sources.

Enthalpy of phase-change estimates were sought in order to produce condensed-phase enthalpy of formation estimates [$\Delta_f H_c(298)$] from corresponding $\Delta_f H_g(298)$ estimates. Since most of the

known Lewis adducts considered in this study are solids at 298 K, it was assumed that notional adducts will be as well. Thus, ΔH_s was considered to be the required parameter. Another reason for employing ΔH_s estimates instead of enthalpy of vaporization (ΔH_v) estimates was that ΔH_s values tend to be larger than ΔH_v values. Therefore, even if a compound should prove to be a liquid (at 298 K), the use of ΔH_s for producing a $\Delta_f H_c(298)$ estimate would likely yield a conservative I_{sp} estimate.

Based on the success Rice et al. (1999) had in developing a correlation between ΔH_s values and B3LYP-based predictions for properties of the 0.001 electron/bohr³ isosurface of electron density of compounds containing only C, H, N, and O atoms, the same approach was attempted for the compounds considered here. The functional form of the equation Rice et al. employed was:

$$\Delta H_s = a(SA)^2 + b(\sigma^2 * \nu)^{1/2} + c \quad (2)$$

where SA is the surface area (in \AA^2); σ^2 is the (dimensionless) variance of the electrostatic surface potential; ν is the (dimensionless) degree of balance between positive and negative charge. The constants a , b , and c were derived from least squares fits.

3.4 Specific Impulse (I_{sp}) and Adiabatic Temperature Predictions

Estimates for the I_{sp} and adiabatic temperatures the adducts will produce in combination with IRFNA were obtained with the “infinite area” combustor model and thermodynamic database provided in CEA2 (Gordon and McBride, 1996). The chemical composition of the IRFNA employed in the calculations was the CEA2 default specification. The chamber pressure was specified to be 70 atm (1029 psia), and the properties were calculated for an expansion to 1 atm (14.7 psia). Because the fuel-air equivalence ratio (Φ) can vary significantly over the course of a hybrid rocket motor firing, predictions were obtained for a wide range of ratios.

4. Results

4.1 Gas-Phase Properties

Figure 1 presents the (gas-phase) molecular structures that were produced for BH_3 -amine adducts. The orientations of the acids and bases in the analogous $\text{B}(\text{CH}_3)_3$ -amine adducts are similar. For all the species whose structures have been characterized via x-ray crystallography, the bond angles and dihedral angles of the corresponding gas-phase structure are similar.

Tables 2 and 3 list predicted gas-phase properties for various BH_3 -amine and $\text{B}(\text{CH}_3)_3$ -amine adducts. The properties include B-N bond lengths (r_e), B-N BDEs, and $\Delta_f H_g(298)$. Values derived from measured data or higher-level computational methods are included for comparison. Because it was hypothesized that the thermal stability and possibly the air stability of adducts might correlate with B-N BDEs, the compounds in each table are ordered according to the BDE estimates we obtained for them. For some adducts, the tables also include a distillation of

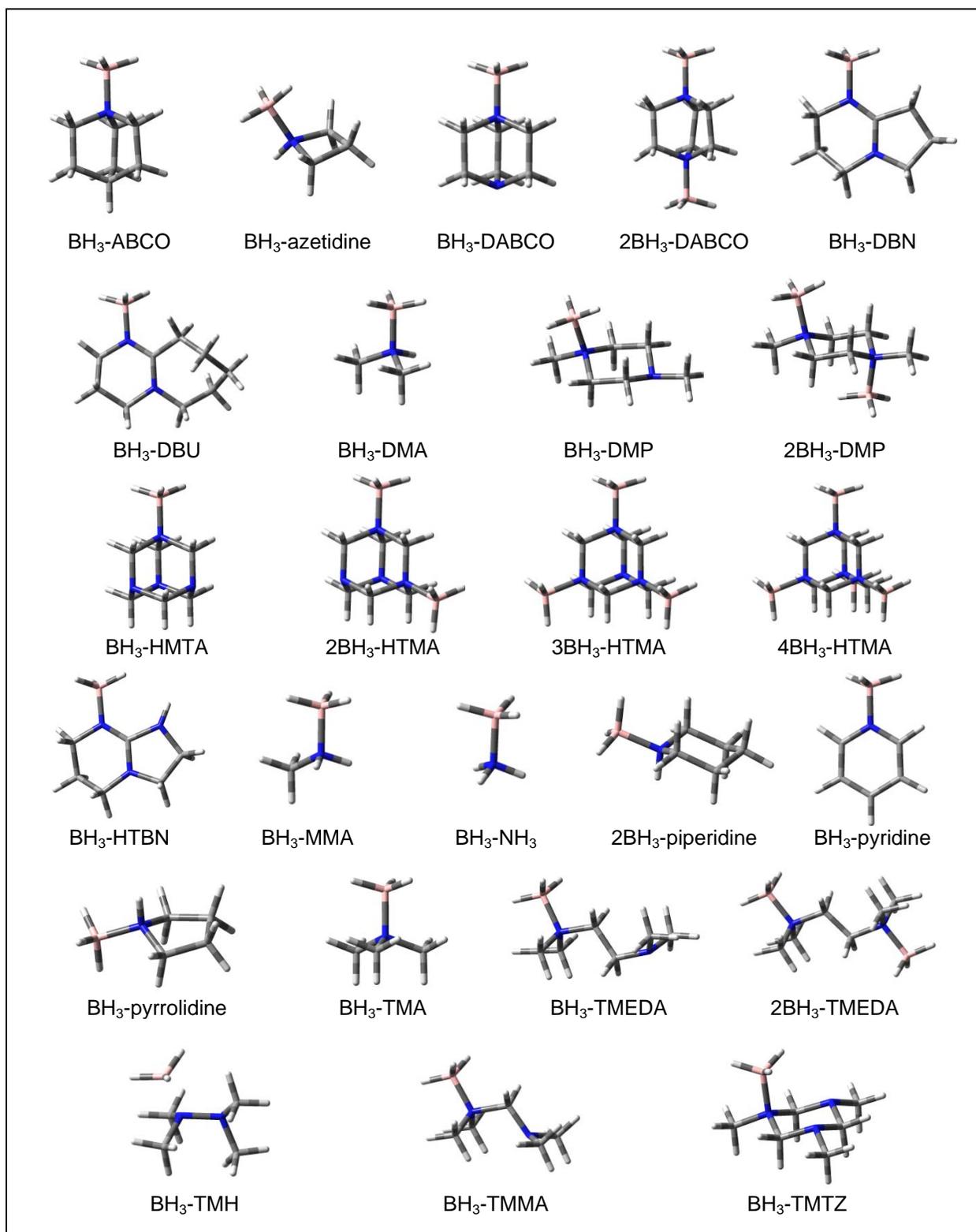


Figure 1. Geometric structures for BH₃-amine adducts.

Table 2. BH₃-amine adduct gas-phase properties: estimates from the current work, benchmark values, and stability assessments.^a

	$r_e(\text{B-N})$ (Å)		BDE(B-N) (kcal/mol) ^b		mp (C)	T _d (C)	Air Stable?	$\Delta_f H_g(298)$ (kcal/mol)	
	This work	Other	This work	Other				This work	Other
BH ₃ -NH ₃	1.669	1.658 ^d	27.4	31.1 ^e , 27.7 ^{f,g} , 31.0 ^m		68 ^h		-12.9	-13.5 ⁱ
BH ₃ -TMH	1.677		31.9					12.1	
BH ₃ -pyridine	1.620		32.6	33.4 ^g	11	50 ^h	N ^g	25.2	
BH ₃ -MMA	1.654	1.602 ^j	33.1	35.0 ^e , 33.4 ^f		<100 ^k		-12.8	
BH ₃ -DMA	1.654	1.615 ^j	34.1	36.4 ^e , 36.7 ^f			N ^h	-15.0	-15.1 ⁱ
BH ₃ -TMEDA	1.665		34.6			-1 ^c		-13.1	
BH ₃ -DMP	1.668		35.3					-10.4	
BH ₃ -pyrrolidine	1.639		36.7					-12.4	
BH ₃ -piperidine	1.647		36.7	38.0 ^g				-23.6	
BH ₃ -TMTZ	1.680		36.8					3.4	
BH ₃ -azetidide	1.634		37.3					11.8	
BH ₃ -TMA	1.660	1.656 ^l , 1.623 ^j	37.4	34.8 ^e , 37.8 ^f , 38.2 ⁿ		>172 (?) ⁿ		-18.4	-20.3 ^o , -20.4 ^p
BH ₃ -DBU	1.615		37.8					-9.7	
BH ₃ -HMTA	1.630		38.8			>300 ^q		29.8	
BH ₃ -DABCO	1.648		38.8		167(dec) ^{r,s}		Y ^r	7.4	
BH ₃ -ABCO	1.647		38.9					-14.5	
BH ₃ -DBN	1.600		39.3					-3.4	
BH ₃ -TMMA	1.655		40.6					-13.4	
BH ₃ -HTBN	1.598		40.9					3.7	
2BH ₃ -TMMA	1.693		25.0					-12.8	
2BH ₃ -TMH	1.675		30.9			60 ^t		6.7	
2BH ₃ -HMTA	1.645		34.4				Y	20.9	
2BH ₃ -DMP	1.662		36.1		178(dec) ^r		Y ^r	-21.0	
2BH ₃ -TMEDA	1.668		36.3		182 ^{s,u}			-23.9	
2BH ₃ -DABCO	1.651		36.9			>300 ^{r,s}	Y ^r	-4.0	
3BH ₃ -HMTA	1.660		30.5					15.9	
4BH ₃ -HMTA	1.671		27.0			25 ^v		14.4	

^a See text for a discussion of the T_d values and air stability assessments shown in this table. ^b For xBH₃-amine adducts (x > 1), the value for the first B-N bond dissociation is given. ^c Gatti and Wartik, 1966a. ^d Thorne et al., 1983. ^e Haaland, 1989. ^f CCSD(T); Grant et al., 2009. ^g G3MP2: Potter et al., 2010. ^h Sigma-Aldrich, 2013. ⁱ CCSD(T): Dixon and Gutowski, 2005. ^j Aldridge et al., 2009. ^k Bowden et al., 2008. ^l Iijima et al., 1984. ^m Calorimetry and vapor pressure data: see Potter et al., 2010. ⁿ Reported as the compound's boiling point (Sigma-Aldrich, 2013). ^o Wagman et al., 1982. ^p Cox and Pilcher, 1970. ^q Tayler, 1962. ^r Gatti and Wartik, 1966b. ^s Brown and Singaram, 1980. ^t Noth, 1960. ^u Miller and Muertertities, 1964. ^v Riley and Miller, 1974.

Table 3. B(CH₃)₃-amine adduct gas-phase properties: estimates from the current work, benchmark values, and stability assessments.^a

	$r_e(\text{B-N})$ (Å)		BDE(B-N) (kcal/mol) ^b		mp (C)	Air Stable?	$\Delta_f H_f(298)$ (kcal/mol)	
	This work	Other	This work	Other			This work	Other
B(CH ₃) ₃ -TMH	1.939		9.6		-16 ^c		-15.6	
B(CH ₃) ₃ -NH ₃	1.710	1.672 ^d	14.8	13.8 ^e , 14.5 ^f			-50.2	-54.1 ^g , -51.5 ^f
B(CH ₃) ₃ -TMEDA	1.806		16.4				-44.9	
B(CH ₃) ₃ -DBU	1.718		18.1				-39.8	
B(CH ₃) ₃ -pyridine	1.694		18.5	17.0 ^h			-10.7	
B(CH ₃) ₃ -MMA	1.711		19.4	17.6 ^e			-49.1	
B(CH ₃) ₃ -TMA	1.789	1.701 ⁱ	19.6	17.6 ^e			-50.6	-52.6 ^j
B(CH ₃) ₃ -HMTA	1.751		20.5				-1.9	
B(CH ₃) ₃ -DMA	1.737	1.656 ^k	20.6	19.3 ^e			-49.3	
B(CH ₃) ₃ -DBN	1.694		21.3				-35.3	
B(CH ₃) ₃ -DABCO	1.771		21.8				-25.6	
B(CH ₃) ₃ -TMMA	1.786		22.1				-44.8	
B(CH ₃) ₃ -ABCO	1.766		22.8	19.9 ^l			-48.3	
2B(CH ₃) ₃ -TMMA	1.874		5.8		35 ^m		-75.0	
2B(CH ₃) ₃ -HMTA	1.790		16.9				-43.2	
2B(CH ₃) ₃ -TMEDA	1.816		18.1		105 ^m		-87.5	
2B(CH ₃) ₃ -DABCO	1.774		20.4				-70.4	
3B(CH ₃) ₃ -HMTA	1.830		15.5				-83.2	
4B(CH ₃) ₃ -HMTA	1.893		12.7				-120.4	
B(CH ₂ CH ₃) ₃ -DBU	1.784		15.0			Y ⁿ	-43.5	

^aSee text for a discussion of the mp values and air stability assessments shown in this table. ^bFor xB(CH₃)₃-amine adducts (x>1), the value for the first B-N dissociation is given. ^cNoth 1960. ^dMP2: Grant et al., 2009. ^eBrown et al., 1944. ^fCCSD(T); Grant et al., 2009. ^gWagman, 1982. ^hBrown and Barbaras, 1947. ⁱKuznesof and Kuczowski, 1978. ^jGuest et al., 1969. ^kOuzounis et al., 1987. ^lBrown and Sujishi, 1948. ^mStorr and Thomas, 1970. ⁿMoren, 2001.

published remarks and/or data pertaining to their thermal and/or air stability. Although these assessments tend to be fairly qualitative, they nevertheless serve to identify the unsuitability of some compounds for propellant applications and provide some indication as to whether it is possible to predict an adduct's thermal stability on the basis of an estimate for its (gas-phase) B-N BDE.

As discussed in the section on computational methods, the lengths of dative bonds are not well-predicted by B3LYP-based models. For the four BH₃-amine adducts for which a gas-phase spectroscopy-based B-N bond length could be found, the length is overpredicted, with differences ranging from 0.004–0.052 Å. The predicted lengths of the B-N bond in B(CH₃)₃-amine species are also longer than values derived from gas-phase spectroscopic data, with differences ranging from 0.038–0.088 Å. Part of the discrepancies may be due to the fact that the definition of the bond length (parameter) derived from computational results (r_e) is different from the definitions of the parameters derived from gas-phase electron diffraction (GED) experiments (r_a , r_g , r_{hl} and $r_{a3,1}$) and from microwave spectroscopy (MWS) experiments (r_o and r_s) (see Aldridge et al., 2009). Regardless, as will be shown, the molecular structures produced by the B3LYP-based models proved adequate as bases for calculating BDEs when coupled with composite methods. Since B-N bond lengths were only of minor interest, no reason was seen to incur the added computational expense that would have been required to employ an MP2-based model.

Tables 2 and 3 show that the B-N BDE estimates produced by the methods employed in this study are in reasonable agreement with values derived from measured data or higher-level computational methods. Most estimates are within ± 2 kcal/mol of their respective benchmark, and no difference exceeds ± 4 kcal/mol. Since the geometries of the notional adducts suggest that steric hindrance will not have an impact on the B-N BDEs predictions, the accuracy of the predictions for notional adducts is believed to approach ± 2 kcal/mol.

A correlation between B-N BDEs and the thermal and air stabilities of BH₃-amine adducts is suggested by the data in table 2. All compounds with T_d values indicated to be above 150 °C have B-N BDEs ≥ 35 kcal/mol. Three of the four air stable compounds also have this property, and the fourth has a B-N BDE that is predicted to be 34.4 kcal/mol. None of the compounds with a T_d below 150 °C has a B-N BDE ≥ 35 kcal/mol. The implied (35 kcal/mol) threshold is greater than the 30 kcal/mol threshold Rahm and Brinck (2010) propose for predicting whether a compound will be thermally stable enough for a propellant application.

No quantitative data could be found regarding the thermal stabilities of B(CH₃)-amine adducts. In addition, no B(CH₃)₃-amine adducts were identified as air stable in the literature. (Moren [2001] claims B(CH₂CH₃)₃-DBU is air stable, but we are skeptical.) Coupled with the results presented in table 3, which indicate that none of the B(CH₃)₃-amine adducts have a BDE greater than 23 kcal/mol, the prospects for finding B(CH₃)₃-amine adducts that are stable enough for propellant applications appear to be remote.

Tables 2 and 3 also compare $\Delta_f H_g(298)$ estimates produced in this study with values derived from measured data and higher-level computational methods. In all but one case, the values agree to within ± 2 kcal/mol. The similarity of this degree of accuracy to that found for the BDE estimates reflects the fact that the potential sources of error in the two calculations are effectively the same. Thus, like the BDE estimates, the accuracy of the $\Delta_f H_g(298)$ estimates for all the adducts considered in this study is believed to approach ± 2 kcal/mol.

4.2 Condensed-Phase Properties

Tables 4 and 5 list predicted and measured values for ΔH_s , $\Delta_f H_c(298)$, and ρ . In the case of BH_3 -amine adduct densities, a reasonable correlation between $MW/Vol_{0.001}$ and measured values were found (see figure 2). A least squares fit of the data yielded,

$$\rho = 1.6823*(MW/Vol_{0.001}) - 0.0264 \quad (3)$$

and its R^2 value equals 0.975. Thus, it was employed to estimate densities for adducts for which measured densities could not be found. Another general observation is that 1-acid:1-base adduct densities are higher than those of their respective amine (base) substituent, with the difference decreasing as the density of the substituent goes up. For example, the density of TMEDA is 0.775 g/cc and the density of BH_3 -TMEDA is 0.96 g/cc, while the density of ABCO is 0.97 g/cc and the density of BH_3 -ABCO is 1.035 g/cc. In contrast, the densities of $x\text{BH}_3$ -amines adducts ($x \geq 2$) are slightly lower than their corresponding $(x-1)$ BH_3 -amine adduct.

An attempt to derive a correlation between measured BH_3 -amine ΔH_s values and properties of the adducts' 0.001 electron/bohr³ isodensity surfaces was not successful. Table 6 shows the data that were employed to derive a relationship with the functional form of equation 2. Unlike the relationship derived by Rice et al. (1999), in which ΔH_s was found to increase with increases in both SA and $(\sigma^2 * v)^{1/2}$, the data in table 6 does not support such a correlation. If BH_3 -piperidine is excluded from the group, the data generally supports a positive proportional relationship between ΔH_s and $(\sigma^2 * v)^{1/2}$, but an inverse relationship between SA and ΔH_s is observed. The latter result may be related to a reduction in an adduct's ionic character as the (molecular) size of the base increases, but it was concluded that the effort necessary to investigate this hypothesis was not warranted at this time. Regardless, with respect to molecular size, the BH_3 -piperidine adduct is more similar to the rest of the adducts characterized in this study than the other compounds in table 6. Thus, it was not considered prudent to exclude from the development of a relationship for density the datum associated with it.

Table 4. BH₃-amine adduct condensed-phase properties: estimates from the current work and benchmark values.

	$r_e(\text{B-N})$ (Å)	ρ (g/cc)		ΔH_s (kcal/mol)	$\Delta_f H_c(298)$ (kcal/mol)	
		This work	Other		This work ^t	Other
BH ₃ -NH ₃	1.601 ^d , 1.585 ^c	0.73	0.74 ^f , 0.78 ^e , 0.761 ^d	23.1 ^g	--	36.6 ^h
BH ₃ -TMH		0.96			-8.9	
BH ₃ -pyridine		1.07 ^s	0.92 ^{i,s}		4.2	
BH ₃ -MMA	1.594 ^j	0.79	0.830 ^j	18.8 ^k	--	32.2 ^l
BH ₃ -DMA	1.597 ^j	0.83	0.804 ^j	18.5 ^k	--	-37.0 ^u
BH ₃ -TMEDA		0.96			-34.1	
BH ₃ -DMP		1.02			-31.4	
BH ₃ -pyrrolidine	1.591 ^b	0.95	0.923 ^b		-33.4	
BH ₃ -piperidine		0.97		21.0 ^q	--	-44.6 ^u
BH ₃ -TMTZ	1.623 ^r	1.05	1.027 ^r		-17.6	
BH ₃ -azetidine		0.86		16.2 ^q	--	-44.0 ^u
BH ₃ -TMA	1.617 ^j	0.87	0.864 ^j	13.6 ^k	--	-33.8 ^l
BH ₃ -DBU		1.10			-30.7	
BH ₃ -HMTA	1.661 ^m	1.23	1.26 ^m		8.8	
BH ₃ -DABCO	1.598 ⁿ	1.09	1.082 ⁿ		-13.6	
BH ₃ -ABCO	1.608 ^o	1.05	1.035 ^o		-35.5	
BH ₃ -DBN		1.10			-24.4	
BH ₃ -TMMA		0.95			34.4	
BH ₃ -HTBN	1.566 ^p	1.14	1.169 ^p		17.3	
2BH ₃ -TMMA		0.93			33.8	
2BH ₃ -TMH		0.94			14.3	
2BH ₃ -HMTA		1.16			0.1	
2BH ₃ -DMP		0.99			42.0	
2BH ₃ -TMEDA	1.622 ^a , 1.617 ^b	0.93	0.928 ^a , 0.945 ^b		44.9	
2BH ₃ -DABCO	1.631 ^c	1.04	1.02 ^c		25.0	
3BH ₃ -HMTA		1.10			5.1	
4BH ₃ -HMTA		1.06			6.6	

^aMal'tseva et al., 1999. ^bChitsaz, 2002. ^cMal'tseva et al., 1995. ^dBoese et al., 1991. ^eKlooster et al., 1999. ^fSorokin et al., 1963.

^gMatus et al., 2007. ^hBaumann, 2003; Wolf, 2005. ⁱSigma-Aldrich, 2013. ^jAldridge et al., 2009. ^kAlton et al., 1959. ^lGuest et al., 1969.

^mHanic and Subrtova, 1969. ⁿArduengo, 1992. ^oWann, 2007. ^pSchulenberg et al., 2009. ^qAcree and Chikos, 2010. ^rFlores-Parra et al., 1999. ^sThis value appears to be an outlier and was not employed in deriving the relationship developed to estimate adduct densities.

^tBased on subtracting 21 kcal/mol from the $\Delta_f H_g$ estimate presented in table 2. ^uBased on subtracting the measured ΔH_s value from the $\Delta_f H_g$ estimate presented in table 2.

Table 5. B(CH₃)₃-amine adduct condensed-phase properties: estimates from the current work and benchmark values.

	$r_e(\text{B-N})$ (Å)	ρ (g/cc)		ΔH_f (kcal/mol)		$\Delta_f H_c(298)$ (kcal/mol)	
		Other	This work	Other	This work	Other	
B(CH ₃) ₃ -TMH			16.5		-32.1		
B(CH ₃) ₃ -NH ₃	1.648 ^a	0.849 ^a	12.8	13.9 ^b	-63.0		
B(CH ₃) ₃ -TMEDA			23.0		-67.9		
B(CH ₃) ₃ -DBU			22.7		-62.5		
B(CH ₃) ₃ -pyridine	1.664 ^c	1.033 ^c	16.8	16.9 ^d	-27.5		
B(CH ₃) ₃ -MMA			13.8	13.1 ^b	-62.9		-64.3 ^e
B(CH ₃) ₃ -TMA			14.4	15.1 ^b	-65.0		-66.6 ^e
B(CH ₃) ₃ -HMTA			20.6		-22.5		
B(CH ₃) ₃ -DMA	1.656 ^f	0.89 ^f	14.4	13.0 ^b	-63.7		
B(CH ₃) ₃ -DBN			23.2		-58.5		
B(CH ₃) ₃ -DABCO			17.8		-43.4		
B(CH ₃) ₃ -TMMA			18.2		-63.0		
B(CH ₃) ₃ -ABCO			19.7	19.0 ^g	-68.0		
2B(CH ₃) ₃ -HMTA			26.3		-69.5		
2B(CH ₃) ₃ -TMEDA	1.737 ^a	0.955 ^a	29.1		-116.6		
2B(CH ₃) ₃ -DABCO			24.9		-95.3		
3B(CH ₃) ₃ -HMTA			38.0		-121.2		
4B(CH ₃) ₃ -HMTA			46.8		-167.2		

^aBoese et al., 1991. ^bBrown et al., 1944. ^cKaszynski et al., 2009. ^dBrown et al., 1947. ^eGuest et al., 1969.

^fOuzounis et al., 1987. ^gBrown and Sujishi, 1948.

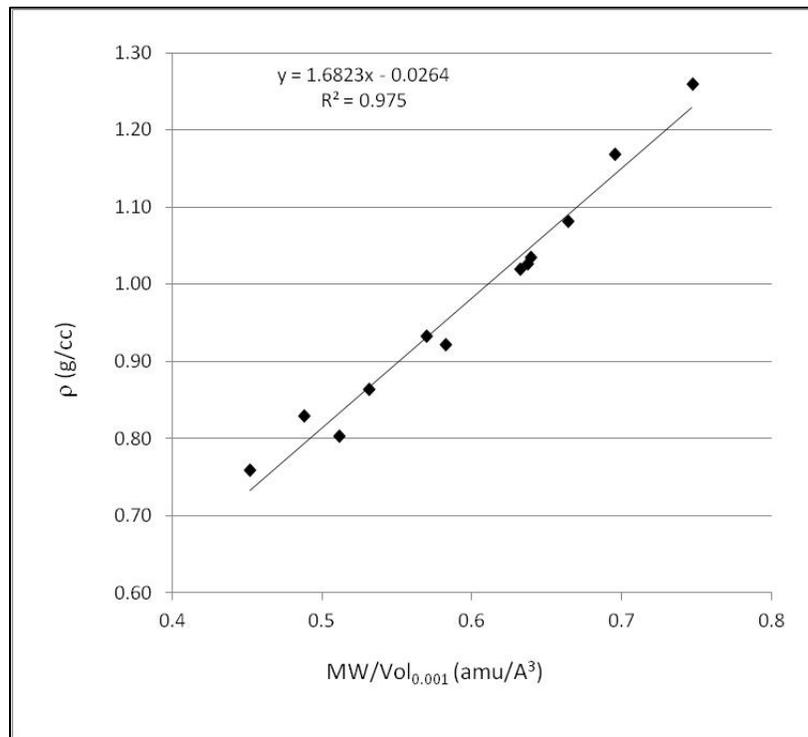


Figure 2. Correlation between $MW/Vol_{0.001}$ and densities for BH₃-amine adducts.

Table 6. ΔH_s values derived from vapor pressure measurements and parameters of the 0.001 electron/bohr³ isosurface of electron density for BH₃-amines.

	ΔH_s^a kcal/mol	SA Å ²	v	σ^2	$(\sigma^2*v)^{1/2}$
BH ₃ -NH ₃	23.1	86.5372546	0.224441	289.797209	8.1
BH ₃ -piperidine	21.0	165.7957310	0.175692	155.794618	5.2
BH ₃ -N(CH ₃)H ₂	18.8	107.7996105	0.243495	242.137756	7.7
BH ₃ -N(CH ₃) ₂ H	18.5	125.4371055	0.241111	178.724254	6.6
BH ₃ -azetidine	16.2	134.0133402	0.242317	187.810773	6.7
BH ₃ -N(CH ₃) ₃	13.6	139.5255518	0.146642	137.127478	4.5

^a See table 4 for the source of these values.

Rather, what appears to be more important than the parameters listed in table 6 is whether the amine group is primary, secondary, or tertiary, with $\rho(\text{primary}) > \rho(\text{secondary}) > \rho(\text{tertiary})$. Since most of the adducts considered in the study involve relatively large tertiary amines and piperidine is a relatively large secondary amine, it was surmised that the measured ΔH_s value for BH₃-piperidine is greater than, or similar to, those of the BH₃-amine adducts for which measured ΔH_s values could not be found. Therefore, we decided to employ the measured ΔH_s value for BH₃-piperidine as a nominal estimate for the latter. Admittedly speculative, particularly for xBH₃-amine adducts ($x > 1$), both this estimate and an estimate that is 10 kcal/mol larger was employed to derive nominal and lower bound $\Delta_f H_c$ estimates to use as input for I_{sp} predictions.

For the B(CH₃)₃-amine adducts, the correlation between $MW/Vol_{0.001}$ and measured densities proved to be poor. Coupled with the fact that the stabilities of these compounds were expected to be insufficient for them to be propellant ingredients; we decided to end the effort to predict their densities. Rather, it is noted that, as was observed for BH₃-amine adducts, compared to the density of their amine, the densities of 1-acid:1-amine adducts are higher.

The effort to develop a correlation between B(CH₃)₃-amine ΔH_s values and properties of the adducts' 0.001 electron/bohr³ isosurface was more successful than was the case for BH₃-amine adducts. A least squares fit of equation 2 to the data in table 5 yielded:

$$\Delta H_s = 0.000219 \text{ (kcal/mol-Å}^4\text{)}*(SA)^2 + 0.9125 \text{ (kcal/mol)}*(\sigma^2*v)^{1/2} + 3.668 \text{ (kcal/mol)}. \quad (4)$$

A plot of the fit ($R^2 = 0.86$) is shown figure 3. The ΔH_s estimates listed in table 5 are based on equation 4. Because no measured ΔH_s values for xB(CH₃)₃-amine adducts ($x > 1$) could be found, the applicability of equation 4 to them is somewhat speculative. We believe it is valid because there are no strong intermolecular interactions (e.g., hydrogen bonding) that are produced or eliminated by the addition of more B(CH₃)₃ groups.

Tables 4 and 5 list $\Delta_f H_c(298)$ estimates calculated by subtracting ΔH_s estimates from the $\Delta_f H_g(298)$ estimates listed in tables 2 and 3. However, establishing meaningful error limits for these estimates is problematic. We consider it reasonable to assume that the $\Delta_f H_g(298)$ estimates are within 5 kcal/mol of their actual value. Likewise, we expect the nominal ΔH_s estimates to be

no more than 5 kcal/mol too positive and no more than 10 kcal/mol too negative. Because I_{sp} decreases with decrease in $\Delta_f H_c(298)$, from the standpoint of screening an adduct's performance potential, the negative bound is the one of concern. Per the preceding discussion, it is considered to be 15 kcal/mol.

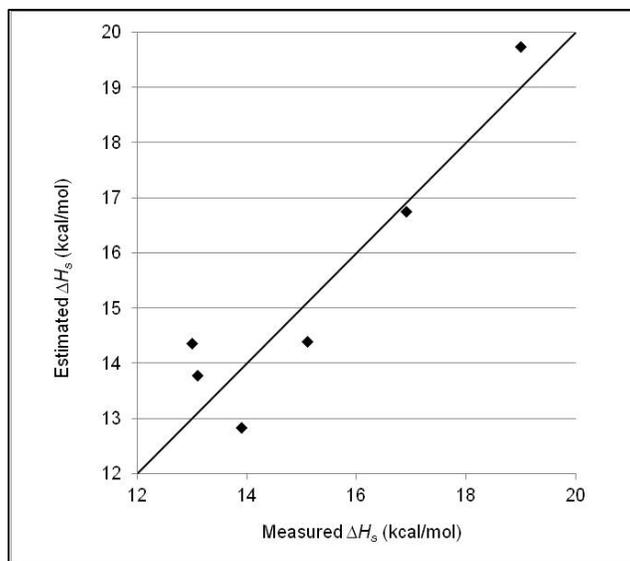


Figure 3. Comparison of measured ΔH_s values for $B(CH_3)_3$ -amine adducts and their estimation using equation 3.

4.3 Specific Impulse and Adiabatic Temperature Predictions

Based on the literature search and the low B-N BDE estimates produced for the $B(CH_3)_3$ -amine adducts, we were/are skeptical that any will be found to have the thermal and air stability required for tactical missile applications. Therefore, only I_{sp} predictions for BH_3 -amine adducts were calculated. Table 7 lists maximum theoretical I_{sp} and adiabatic temperature (T_{ad}) predictions for $[BH_3\text{-amine}]\text{-IRFNA}$ systems. Analogous predictions for HTPB-IRFNA, DMAZ-IRFNA, and TMEDA-IRFNA are shown for comparison. Maximum I_{sp} predictions based on nominal $\Delta_f H_c(298)$ estimates for the $[BH_3\text{-amine}]\text{-IRFNA}$ systems exceed those of HTPB-IRFNA and are competitive with TMEDA-IRFNA and DMAZ-IRFNA. The I_{sp} predictions calculated on the basis of $\Delta_f H_c(298)$ values that were 15 kcal/mol more negative than the nominal estimates are also presented. Except for the case of $BH_3\text{-NH}_3$, where the decrease is fairly significant, the maximum I_{sp} values decrease approximately 1%. The adiabatic temperatures of the $[BH_3\text{-amine}]\text{-IRFNA}$ systems are generally comparable to the one predicted for TMEDA-IRFNA. As such, they are not considered cause for concern.

Table 7. Maximum theoretical I_{sp} and adiabatic temperature (T_{ad}) predictions for fuels combined with IRFNA.^a

	Φ	I_{sp} (sec)		T_{ad} (K)
		$\Delta_f H_c(298)_{nom}$	$\Delta_f H_c(298)_{nom} -15$	$\Delta_f H_c(298)_{nom}$
BH ₃ -NH ₃	2.50	279	266	1430
BH ₃ -TMH	1.25	272	269	1690
BH ₃ -pyridine	1.25	263	260	1810
BH ₃ -MMA	1.25	272	267	1700
BH ₃ -DMA	1.25	269	266	1670
BH ₃ -TMEDA	1.00	267	266	1990
BH ₃ -DMP	1.00	266	264	2000
BH ₃ -pyrrolidine	1.25	266	264	1676
BH ₃ -piperidine	1.00	265	263	2010
BH ₃ -TMTZ	1.00	266	265	1990
BH ₃ -azetidine	1.00	264	262	1980
BH ₃ -TMA	1.25	269	267	1670
BH ₃ -DBU	1.00	263	262	2030
BH ₃ -HMTA	1.00	264	263	2010
BH ₃ -DABCO	1.25	265	264	1690
BH ₃ -ABCO	1.00	264	263	2040
BH ₃ -DBN	1.00	263	261	2030
BH ₃ -TMMA	1.00	268	266	1980
BH ₃ -HTBN	1.00	262	261	2000
2BH ₃ -TMMA	1.25	272	270	1720
2BH ₃ -TMH	1.25	275	273	1770
2BH ₃ -HMTA	1.25	267	266	1730
2BH ₃ -TMEDA	1.25	270	268	1700
2BH ₃ -DMP	1.00	268	266	1980
2BH ₃ -DABCO	1.25	268	267	1750
3BH ₃ -HMTA	1.25	270	269	1780
4BH ₃ -HMTA	1.25	273	272	1830
HTPB	1.00–1.25	262		1700
TMEDA	1.00	267		1960
DMAZ	1.25	270		1690

^a Results from an infinite area combustor rocket problem. Chamber pressure = 70 atm. Exit pressure = 1 atm.

Because Φ can vary significantly over the course of a hybrid rocket motor firing, we were also interested in determining how I_{sp} predictions changed as a function of this variable. I_{sp} predictions for [2B(CH₃)₃-DABCO]-IRFNA are compared to predictions for HTPB-IRFNA, TMEDA-IRFNA and DMAZ-IRFNA in figure 4. It is observed that I_{sp} predictions for Φ ranging from 0.2–1.0 are fairly similar for all four cases. However, as Φ increases above 1.0, the values for 2BH₃-DABCO fall much less quickly than those for HTPB-IRFNA and TMEDA-IRFNA; and they exceed values for DMAZ-IRFNA for $\Phi \geq 1.67$. This behavior would be advantageous in a hybrid rocket motor application.

Figure 4 also shows a plot of I_{sp} values for [2BH₃-DABCO]-IRFNA that were calculated assuming the fuel's $\Delta_f H_c(298)$ is 15 kcal/mol more negative than the nominal estimate. (It is

labeled [2BH₃-DABCO(-15)]-IRFNA.) It is observed that there is less than 1% difference between the two cases for Φ up to about 2.5. Differences for Φ greater than 2.5 are slightly larger, but they do not change the overall conclusions regarding the performance potential of this system versus the three standards. Also, given that 2BH₃-DABCO is denser than HTPB, TMEDA, or DMAZ, it would appear to warrant further study as a fuel additive. Of particular interest is a quantification of its reactivity with IRFNA and other oxidizers such as HAN and hydrogen peroxide. Drop-into-drop ignition delay experiments would undoubtedly be instructive.

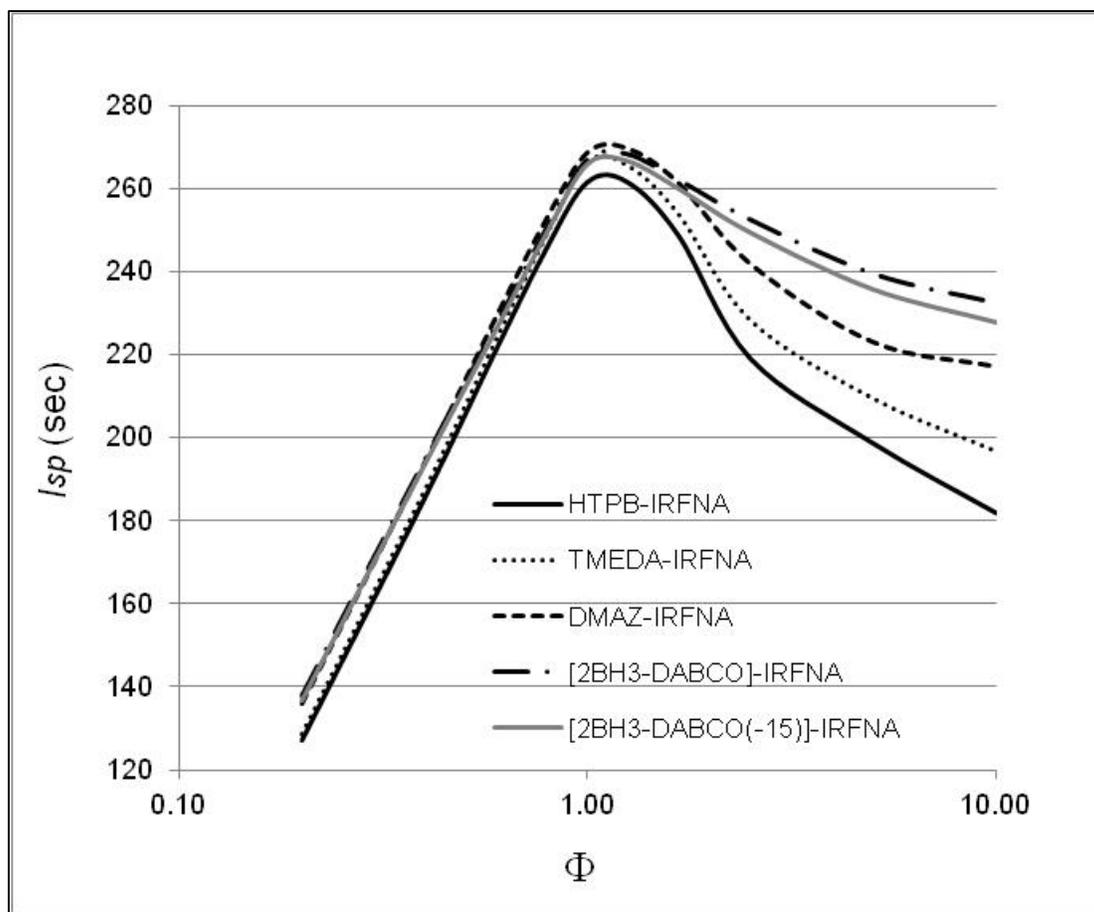


Figure 4. I_{sp} predictions as a function of Φ for various fuels in combination with IRFNA.

5. Summary and Conclusions

BH₃-amine and B(CH₃)₃-amine adducts were investigated as potential additives for liquid/gel or solid (hybrid) rocket motor fuels. The investigation included an extensive literature search and the calculation of property predictions for a variety of known and notional adducts. Gas-phase and condensed-phase property predictions were derived from results obtained from quantum chemistry methods. B-N bond dissociation energies and adduct enthalpies of formation at 298 K

were among the gas-phase properties predicted. Condensed-phase properties that were predicted included: enthalpies of sublimation, enthalpies of formation at 298 K [$\Delta_f H_c(298)$], and densities. Values for these properties that were derived from measured data or higher-level computational methods were also found in open literature sources. The literature-based data were utilized both to develop and to validate the estimation methods employed in this study.

General observations of the thermal and/or air stabilities of some adducts were also found in open literature sources, and they suggest that several BH_3 -amine adducts have stabilities that are sufficient for tactical rocket propellant applications, with the stability of 2BH_3 -DABCO being notable. Moreover, there appears to be a correlation between observed stabilities and B-N BDEs, the results indicating that B-N BDEs ≥ 35 kcal/mol are required for the adducts to have the requisite stabilities. A number of BH_3 -amine adducts have B-N BDEs that exceed 35 kcal/mol, but all the $\text{B}(\text{CH}_3)_3$ -amine adducts that were considered were found to have B-N BDEs ≤ 24 kcal/mol. Therefore, $\text{B}(\text{CH}_3)_3$ -amine adducts are considered unlikely to be viable candidates for the proposed applications.

The $\Delta_f H_c(298)$ estimates for BH_3 -amine adducts were employed as input for predicting the specific impulse (I_{sp}) each could potentially generate when combined with inhibited red fuming nitric acid. All adducts produced maximum theoretical values that are competitive with hypergolic/hybrid combinations that the Army has considered for tactical missile applications, and their values fall off less rapidly than the standards at nonoptimal equivalence ratios. On the basis of the study's findings, 2BH_3 -DABCO warrants further investigation as an additive for the proposed applications. 2BH_3 -dimethylpiperazine (2BH_3 -DMP) and BH_3 -trimethylamine (BH_3 -TMA) also appear to warrant further study. (BH_3 -TMA is commercially available.) The next step would be to perform simple screening tests that would quantify their reactivity with IRFNA and other liquid oxidizers, such as HAN and hydrogen peroxide.

6. References

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List of Symbols, Abbreviations, and Acronyms

AMRDEC	U.S. Army Aviation and Missile Research Development and Engineering Center
ARL	U.S. Army Research Laboratory
BDE	bond dissociation energies
DMAZ	2-azido-N, N-dimethylethanamine
DOD	Department of Defense
GED	gas-phase electron diffraction
h	hours
HAN	hydroxylammonium nitrate
HAST	High Altitude Supersonic Target
HTPB	hydroxy-terminated polybutadiene
IRFNA	inhibited red fuming nitric acid
ISVE	impinging stream vortex engine
MWS	microwave spectroscopy
RMS	root mean square
TMEDA	tetramethylethylenediamine
wt%	weight-percent

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