

Propellants

Amine–Boranes: Green Hypergolic Fuels with Consistently Low Ignition Delays

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Abstract: Complexation of amines with borane converts them to hypergols or decreases their ignition delays (IDs) multifold (with white fuming nitric acid as the oxidant). With consistently low IDs, amine–boranes represent a class of compounds that can be promising alternatives to toxic hydrazine and its derivatives as propellants. A structure–hypergolicity relationship study reveals the necessary features for the low ID.

Chemical rockets used in space and missile applications depend on propellants that react within a combustion chamber to form a very hot gas at high pressure, which, in turn, creates thrust.^[1] For nearly six decades, such rockets have used hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) as liquid hypergolic fuels that spontaneously ignite upon contact with oxidants, such as white fuming nitric acid (WFNA) (bipropulsion systems).^[2] Although their low ignition delays (IDs) and high specific impulse (Isp) are attractive features, they are more than offset by their toxicity, carcinogenicity, and high handling cost.^[2] These hypergolic propellants present the dual concerns of fire hazards and potential exposure of personnel to toxic, high vapor pressure liquids.

Viable replacements for hydrazine and its derivatives have been actively pursued for several decades.^[2b,3] However, the lack of a fundamental understanding of combustion kinetics and structure–hypergolicity relationship has adversely affected development of promising alternatives. The seminal work by Rapp and Strier, six decades ago, correlating the structure and hypergolicity of alkylamines, has received little attention.^[4] Simultaneously, Schalla and Fletcher reported that the spontaneous ignitibility of amines with WFNA is dependent on the syn-

ergetic influence of several reactions.^[5] Interestingly, recent reports have identified 3° amines such as *N,N,N',N'*-tetramethylethylenediamine or 1,4-dimethylpiperazine (DMPZ, **1o**), alone or mixed with azido compounds, as potential hypergolic fuels.^[6] A modern trend in propellant research considers ionic liquids (ILs) as future fuels for space applications.^[7] The incorporation of boron in the IL structure^[8] or as nanoparticle additives^[9] has provided new openings. IL solubilized boranes as hypergolic fluids have been recently reported by Shreeve and Gao.^[10] Their study identified triethylamine–borane as the most efficient “additive” for decreasing IDs of ILs.^[10b]

For nearly a decade, we have been investigating amine–boranes for a variety of applications.^[11] As part of this program, several efficient syntheses of amine–boranes have been described.^[11a,c,d] The history of boron hydride clusters as jet fuels,^[12] the aforementioned advantages of boron on propellants,^[8–10] and the known superior hypergolicity of 3° amines^[4] encouraged the examination of such amine–boranes as hypergols by themselves, without solubilizing in ILs. Support came from the fact that non-hypergolic NH₃^[13] (**1a**) is transformed into a hypergol by complexation with BH₃, albeit with an ID of 80 ms.^[10a] Accordingly, a series of amine–boranes were prepared from the corresponding amines and tested—as neat liquids or solids—with WFNA. The difference in the IDs of 3° amines, such as triethylamine (**1j**, 70 ms)^[4] and DMPZ (**1o**, 10 ms),^[6c] prompted a re-examination of the corresponding amines as well by using modern analytical tools.^[14] Our successful project identifying several promising amine–borane hypergols is discussed below.

The results from the drop test are summarized in Table 1. We initiated our study by examining the simplest amine–borane, ammonia borane (AB, **2a**), and were surprised at the short ID (2.0 ms, entry 1), in contrast to the 80 ms delay that has been reported.^[10a] Owing to the large discrepancy in ID values, the test was repeated with several batches of AB, and consistent results were obtained. A faint green light emission, indicative of ignition, is observed 2.0 ms after the oxidizer contacts AB (Figure 1). A light green flame envelops the powder and propagates outwards while an intense green flame is produced at the location where the fuel and oxidizer came in contact. The green flame, owing to the formation of boron combustion products, probably indicates the participation of borane in the initial hypergolic reaction.

Stimulated by the unexpected, remarkable success with AB, we evaluated 1° amine–boranes.^[15] Although 1-propanamine (**1b**) is not hypergolic,^[16] complexation with BH₃ converted it

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| Entry | Amine 1 | | Amine-BH ₃ | |
|-------|---------------------------|--|--------------------------|-------------------------|
| | Structure | ID [ms] ^[b] | 2/3 ^[c] | ID [ms] ^[b] |
| 1 | 1a NH ₃ | — ^[d,e] | 2a | 2.0 (80) ^[f] |
| 2 | 1b | — ^[d] (1730) ^[g] | 2b | 64.2 |
| 3 | 1c | 205.4 | 2c | 56.8 |
| 4 | 1d | 166.7 (90) ^[g] | 3d | 2.9 ^[j] |
| 5 | 1e | — ^[d] (450) ^[g] | 2e | 32.4 |
| 6 | 1f | 125.4 | 2f | 107.4 |
| 7 | 1g | 115.4 | 2g ^[h] | 21.6 |
| 8 | 1h | 211.4 | 2h | 47 |
| 9 | 1i | 102.2 | 2i | 15.4 |
| 10 | 1i | 102.2 | 3i | 17.3 |
| 11 | 1j | 18 (70) ^[g] | 2j | 3.4 |
| 12 | 1k | 41.8 | 2k | 4.0 |
| 13 | 1l | 74.4 | 2l | 18 |
| 14 | 1m | 80.8 | 2m | 9.4 |
| 15 | 1n | 115.7 | 3n ^[h] | 8.8 |
| 16 | 1o | 14.2 (10) ^[i] | 3o | 3.9 |

[a] Determined by using the drop test with WFNA as oxidant. [b] Average IDs from multiple runs. The values in parentheses are from literature. [c] 2 denotes amine-borane and 3 denotes diamine-bisborane. [d] Not hypergolic. [e] From ref. [13]. [f] From ref. [10a]. [g] From ref. [4]. [h] A mixture of diastereomers. [i] From ref. [6c]. [j] See ref. [18].

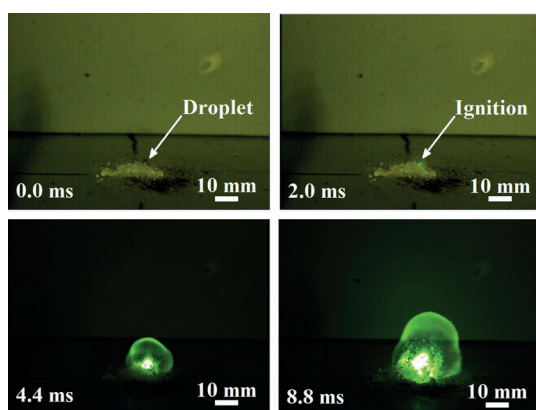


Figure 1. Drop test of AB (**2a**).

into a hypergol (**2b**, 64.2 ms, entry 2). Conversely, although cyclohexylamine (**1c**) is a hypergol (ID: 205.4 ms), borane complexation to **2c** shortened the ID to 56.8 ms (entry 3). Proceed-

ing to 2° amine-boranes, although the parent acyclic amine (diethylamine, **1e**) by itself is not hypergolic,^[16] the amine-borane (**2e**) revealed an ID of 32.4 ms (entry 5). Surprisingly, the ID of parent cyclic amine piperidine (**1f**, 125.4 ms) did not improve considerably upon complexation with BH₃ (**2f**, 107.4 ms, entry 6). However, this was not the case with *cis*-2,6-dimethylpiperidine (**1g**), morpholine (**1h**) and piperazine (**1i**), where we observed a 5–6-fold improvement owing to complexation (**2g**, **2h**, and **2i**, entries 7, 8, and 9). Thus, a fascinating trend of the effect of amine-borane structural features on hypergolicity begins to emerge (Figure 2). Comparing **2e** and **2f** shows a distinct advantage of using an acyclic system over a ring system. The steric environment around the amine-borane also appears to play a role, with **2g** having a much lower ID (21.6 ms, entry 7) than **2f**. Introduction of a heteroatom in the ring decreases ID times, with piperazine-monoborane (**2i**) exhibiting the shortest ID for a secondary amine-borane (15.4 ms, entry 9).

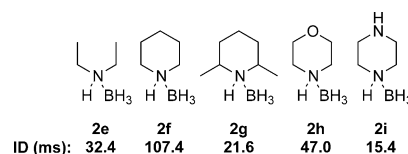


Figure 2. Structure-hypergolicity relationship of 2°-amine-boranes.

Trialkylamines possess the lowest IDs amongst the amines.^[4] Following this trend, the corresponding amine-boranes were expected to be superior hypergols, which turned out to be true. Indeed, our concern on the reported ID of *N,N,N*-triethylamine (**1j**) was also proven right with the observation of an ID of 18 ms (as against 70 ms).^[4] To our excitement, the corresponding amine-borane (**2j**) exhibited a short ID (3.4 ms, entry 11), close to that of hydrazine (3.1 ms).^[17] *N,N*-Diisopropylethylamine-borane (**2k**) displayed a similarly low ID (4 ms, entry 12), further confirming our hypothesis. Even cyclic 3° amine-boranes exhibited much shorter IDs compared with the corresponding cyclic 2° amine-boranes. Thus, *N*-ethylpiperidine-borane (**2l**) and *N*-methylpyrrolidine (**2m**) revealed IDs of 18 ms and 9.4 ms (entries 13 and 14), respectively. It is noteworthy that even among the 3° amine-boranes, acyclic ones were superior to their cyclic equivalents.

The success with piperazine-monoborane (**2i**) led to the bisborane adduct (**3i**), which revealed a similar short ID (17.3 ms, entry 10, Figure 3). The piperazine structure allowed us to examine a combination of 2° and 3° amine-boranes in the same molecule. *N*-Methylpiperazine-bisborane (**3n**) showed an ID of 8.8 ms (entry 15). On the basis of the results thus far with 3°

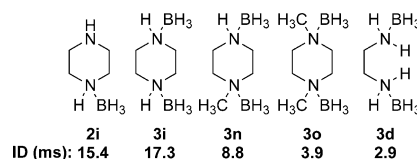


Figure 3. Structure-hypergolicity relationship of diamine-bisboranes.

amine–boranes, we expected the ID for *N,N'*-dimethylpiperazine–bisborane (**3o**) to be even shorter and the drop test confirmed it with a 3.9 ms interval between contact and ignition (entry 16). However, a question remained as to whether the low ID of **3o** was an artifact of the 3° amine or bisborane structure. The overriding effect of the latter was demonstrated when a bisborane (**3d**), prepared from 1° 1,2-diaminoethane (**1d**), displayed an ID of 2.9 ms (entry 4). Compared with **2a**, the initial green flames with **3d** are mixed with yellow flames as the reaction proceeds, characteristic of carbon combustion and soot formation (Figure 4). The delayed appearance of the yellow luminosity may suggest that borane is primarily involved in the ignition process.

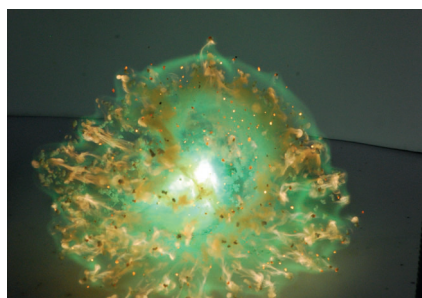


Figure 4. Flame characteristics of **3d**.

Most of the hypergolic amine–boranes evaluated (Table 1) are solids (see the Supporting Information), which provides a unique opportunity to study solid, air-breathing propulsion systems, or hybrid fuel rockets. Compared with solid-state or bipropellant systems, a hybrid propulsion system offers significant advantages.^[2a] Stable hypergolic hybrid fuels exhibiting IDs < 10 ms with WFNA are unknown thus far. We are currently examining the feasibility of some of the liquid amine–boranes as bipropellants and solid amine–boranes as hybrid rocket fuels.

In conclusion, we have prepared a series of 1°, 2°, and 3° amine–boranes and diamine–bisboranes and examined them for their hypergolicity. All of those investigated, solids and liquids, are hypergolic with WFNA with consistently shorter IDs compared with the corresponding amines. A structure–hypergolicity relationship has been established for the amine–boranes. The different dynamics controlling the solid and liquid systems make comparisons difficult; however, the extent of the drop in ID caused by the complexation with BH₃ is significant. Amine–boranes **2a**, **2j**, **2k**, **3d**, and **3o** have been targeted for further rocket propulsion study owing to their low ID values (≤ 4 ms).^[18]

The low volatility, cost-effective large-scale synthesis, safe transportation, and storage^[19] of environmentally benign amine–boranes, while meeting existing performance standards, make them attractive as green propellants.

Experimental Section

All of the necessary amines were purchased from commercial sources and converted to the corresponding amine–boranes (see the Supporting Information for details). Ammonia borane was prepared as described.^[11a] The IDs were determined by using a digital high speed color camera, Phantom v7.3 with a Nikon 28–105 mm lens attached, positioned to observe the hypergolic contact and ignition events (Figure 5). A small quantity of amine–borane was placed in a 1 dram vial, if liquid, or on a teflon sheet, if solid. The sample was illuminated with an array of LED lights and WFNA was dropped from a microsyringe mounted 5" above the sample. The interval between the contact of WFNA and amine–borane and the first sign of light generated from the reaction (ignition delay) was determined by analyzing the 5000 fps video.

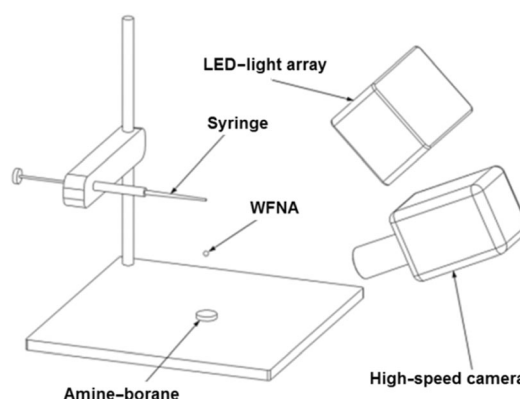


Figure 5. Drop test setup used to measure ID.

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- [15] Hydrazine–borane and its derivatives were not included in our study owing to the extreme carcinogenicity of the parent amines.
- [16] Rapp and Strier (ref. [4]) reported that **1b** and **1e** are hypergolic.
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- [19] Amine–boranes with different shelf-lives, up to 30 years, were used in our study and consistent results were obtained.

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