Energetic Materials

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Ammonia–(Dinitramido)boranes: High-Energy-Density Materials

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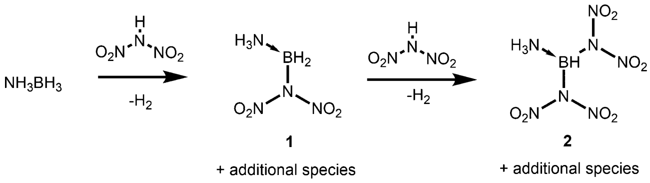
In memory of Robert Williams

Abstract: *Two ammonia–(dinitramido)boranes were synthesized by the reaction of dinitroamine with ammonia–borane. These compounds are the first reported examples of (dinitramido)boranes. Ammonia–mono(dinitramido)borane is a perfectly oxygen-balanced high-energy-density material (HEDM) composed of an ammonia–BH_2 fuel group and a strongly oxidizing dinitramido ligand. Although it is thermally not stable enough for practical applications, its predicted specific impulse as a solid rocket propellant would be 333 s. Its predicted performance as an explosive matches that of pentaerythtritol tetranitrate (PETN) and significantly exceeds that of trinitrotoluene (TNT). Its structure was established by X-ray crystallography and vibrational and multinuclear NMR spectroscopy. Additionally, the over-oxidized ammonia-bis(dinitramido)borane was detected by NMR spectroscopy.*

The dinitroamide anion (DN^-), discovered in 1971 by Luk'yanov et al.[1] and independently in the 1980s by Bottaro et al.,[2] is a powerful highly energetic oxidizing anion and its ammonium salt (ADN) is an important ionic high-energy-density material (HEDM). Although the existence of several covalent dinitramido compounds of elements of Groups 14–17 has been established,[3] no compounds with Group 13 elements have so far been structurally characterized. The ongoing work on boron-derived green energetic materials[4] in the Christe–Haiges group[5] prompted the exploration of the synthesis of dinitramido-substituted boron compounds. Our previous work on (trinitromethyl)trihydroborate suggested that even compounds containing presumably incompatible reducing and oxidizing groups could be surprisingly stable. Moreover, it has been shown that BH_3-derived (dinitramido)borate complexes are more stable than the corresponding compounds derived from boron trihalides.[6] It was therefore interesting to explore whether a neutral (dinitramido)borane could exist at room temperature, either in solution or even as a solid. Dinitramido derivatives of ammonia–borane, in particular, were of interest because ammonia–mono(dinitramido)borane is a perfectly oxygen-balanced propellant [Eq. (1)]. Herein the reaction chemistry of dinitroamine, $HN(NO_2)_2$ (HDN), with ammonia–borane is reported.

$$2\,H_3N\cdot BH_2N(NO_2)_2 \rightarrow 5\,H_2O + 4\,N_2 + B_2O_3 \qquad (1)$$

^{14}N and ^{11}B NMR spectra show that, in glyme or acetonitrile solution, the reaction of one equivalent of dinitroamine (HDN) with ammonia–borane yields a mixture of products (Scheme 1). The most dominant signals, a ^{11}B NMR signal at $\delta = -9$ ppm (triplet) and a sharp ^{14}N NMR signal at $\delta = -34$ ppm, were assigned to $NH_3{\cdot}BH_2DN$ (**1**). This assignment was further confirmed by a broad quartet at $\delta = 2.77$ ppm with $^1J(^1H\text{-}^{11}B) = 111$ Hz and a broad triplet at 4.69 ppm with $^1J(^1H\text{-}^{14}N) = 50$ Hz in the ^1H NMR spectrum, consistent with a deshielded BH_2 group and a deshielded boron-coordinated ammonia ligand, respectively. Variable amounts of ammonium dinitramide were also formed, depending on the reaction conditions (see the Supporting Information).



Scheme 1. Reaction of ammonia–borane with dinitroamine in glyme or acetonitrile at room temperature.

When three to four equivalents of HDN were reacted with ammonia–borane for several days at room temperature, the formation of additional species could be detected by NMR spectroscopy (Scheme 1). Two new species were seen in the ^{11}B NMR spectra as doublets at $\delta = -0.7$ and 1.6 ppm, respectively, indicating that a second hydrido ligand at the boron atom had been replaced. The only ^{14}N NMR signal which had a sufficiently high intensity comparable to that of the new ^{11}B NMR resonances at $\delta = -0.7$ ppm was found at -32.7 ppm, suggesting the presence of a $BH(DN)_2$ group. Furthermore, a new set of resonances was found at higher field in the ^1H NMR spectrum at 3.8 ppm (qt, $^1J(^1H\text{-}^{11}B) = 143$ Hz) and 5.3 ppm (t, $^1J(^1H\text{-}^{14}N) = 45$ Hz). These resonances are all consistent with $NH_3{\cdot}BH(DN)_2$ (**2**). The boron species displaying a ^{11}B NMR signal at 1.6 ppm could not be

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correlated to a new ^{14}N NMR signal and is therefore most likely not associated with a nitro-containing fragment.

After several days of reaction between ammonia–borane and an excess of dinitroamine, **1** and **2** disappeared and a new signal appeared in the ^{11}B NMR spectrum at $\delta = 20.6$ ppm. The presence of this signal, characteristic of a tricoordinate boron, and of a ^{1}H NMR signal at circa $\delta = 6$ ppm strongly indicates the formation of boric acid, suggesting that the expected $B(DN)_3$ or $NH_3{\cdot}B(DN)_3$ species are unstable and decompose quickly after being formed.

The isolation of $NH_3{\cdot}BH_2DN$ (**1**) was studied under various conditions. When HDN and ammonia–borane were reacted in stoichiometric amounts in glyme between −60 °C and ambient temperature, **1** was formed in circa 60 mol% yield, with ammonium dinitramide and several unidentified species accounting for the rest of the mixture. Evaporating the solvent under vacuum between 0 and 20 °C and extracting the products with dichloromethane afforded a solution containing only **1** (circa 80 mol%) and unidentified species with two overlapping ^{11}B NMR signals at approximately $\delta = -4$ ppm and a ^{14}N NMR signal at −29.6 ppm. When the solution was evaporated, colorless crystals formed on the walls of the vessel, which were identified as **1** by single-crystal X-ray diffraction. The isolated solid residue was not completely soluble in CD_3CN, indicating that some decomposition may have occurred during the isolation process. Because the major unidentified side products could not be removed by recrystallization and the purity of **1** significantly decreased during isolation attempts, we did not seek to obtain it in higher purity.

Since a significant excess of HDN was required to form $NH_3{\cdot}BH(DN)_2$ (**2**) at a reasonable rate, and because concentrating solutions containing excess dinitroamine can lead to explosions,[6b] the isolation of **2** was not pursued any further.

The dinitramido ligand could be attached to boron either through its amidic N atom or an oxygen atom. Using solvent-corrected coupled-cluster calculations (CBS-QB3 + SMD-M06-2X/cc-pVTZ), it was found that the B–N isomer is favored by circa 1.6 kcal mol^{-1} over the lowest energy B–O isomer (Figure 1). This was experimentally confirmed by the fact that only one major sharp -NO_2 ^{14}N NMR signal was found for **1** and for **2**, respectively, indicating the presence of only the B–N isomers.

The predicted NMR chemical shifts for **1** are in excellent agreement with the major species detected for all three nuclei (Table 1). The vibrational spectra of the isolated compounds, known to contain significant amounts of ammonium dinitramide, also agree well with the predicted data (Supporting Information). The good agreement between predicted and observed vibrational and NMR data establishes that the major compound detected by NMR is identical to the one found by X-ray diffraction (Figure 2).

Table 1: Predicted ^{1}H, ^{11}B, and ^{14}N NMR chemical shifts for the B–N and B–O isomers of **1**.[a]

Species	Predicted δ [ppm]	Experimental δ [ppm]
$\mathrm{N}\mathit{H}_3$-BH_2-DN	4.6	4.69
NH_3-$\mathrm{B}\mathit{H}_2$-DN	3.0	2.77
$\mathrm{N}\mathit{H}_3$-BH_2-O-N(O)N-NO_2	4.5	–
NH_3-$\mathrm{B}\mathit{H}_2$-O-N(O)N-NO_2	2.9	–
NH_3-$\mathit{B}\mathrm{H}_2$-DN	−8.2	−9.3
NH_3-$\mathit{B}\mathrm{H}_2$-O-N(O)N-NO_2	−2.1	–
NH_3-BH_2-N($\mathit{N}\mathrm{O}_2$)$_2$	−33.7	−34.3
NH_3-BH_2-N(NO_2)$_2$	−88.4	−91 (Et_2O)
$\mathit{N}\mathrm{H}_3$-BH_2-N(NO_2)$_2$	−358.3	−361
NH_3-BH_2-O-N(O)N-$\mathit{N}\mathrm{O}_2$	−23.1	–
NH_3-BH_2-O-N(O)N-NO_2	−28.0	–
NH_3-BH_2-O-N(O)N-NO_2	−38.9	–
$\mathit{N}\mathrm{H}_3$-BH_2-O-N(O)N-NO_2	−356.0	–

[a] The predicted ^{1}H and ^{11}B NMR chemical shifts were referenced to the experimentally measured values for BH_3NH_3. ^{14}N NMR chemical shifts were referenced to $MeNO_2$ and the predicted values were empirically corrected using a fit described previously.[9]

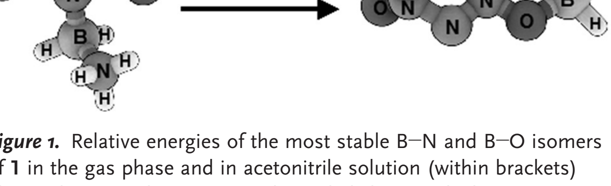

Figure 1. Relative energies of the most stable B–N and B–O isomers of **1** in the gas phase and in acetonitrile solution (within brackets) obtained using solvent-corrected coupled-cluster calculations (CBS-QB3 + SMD-M06-2X/cc-pVTZ).

Crystals of **1** were obtained from a solution in dichloromethane. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with eight molecules per unit cell ($Z = 8$, $Z' = 2$; Figure 2). To our knowledge, this is the first example of a structurally characterized Group 13 dinitramido compound

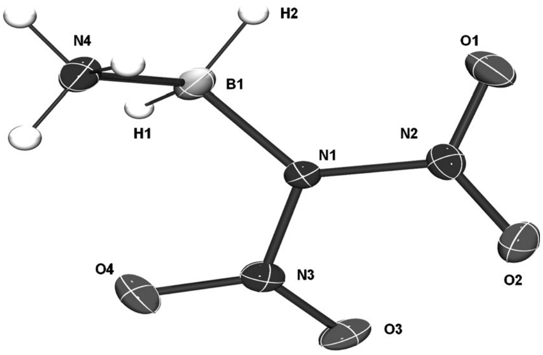

Figure 2. ORTEP[11] plot of one of the two molecules of the asymmetric unit of **1**. Thermal ellipsoids are set at 40% probability. Hydrogen atoms are depicted as spheres of arbitrary radius. N–H hydrogen atom positions were idealized. B–H hydrogen atoms were determined from the electron density map and the B–H distances were then restrained to 1.12 Å. Selected bond distances [Å]: N1–N2 1.3926(15), N1–N3 1.4046(15), O1–N2 1.2157(15), O2–N2 1.2214(16), O3–N3 1.2160(15), O4–N3 1.2197(15), N1–B1 1.5798(19), B1–N4 1.5895(18). Selected bond angles [°]: O1-N2-O2 125.20(12), O3-N3-O4 126.04(12), O4-N3-N1 113.26(11), O3-N3-N1 120.61(11), O1-N2-N1 115.57(11), O2-N2-N1 119.16(11), N2-N1-N3 115.64(11), N2-N1-B1 125.69(11), N3-N1-B1 118.47(11), N1-B1-N4 107.23(11), H1-B1-H2 115.7(13), H1-B1-N4 107.8(9), H1-B1-N1 107.7(9), H2-B1-N4 110.7(9), H2-B1-N1 107.4(9), O1-N2-N1-B1 −9.4(2), O4-N3-N1-B1 −33.4(2).

and a rare example of an N-bonded covalent dinitramido compound.[7] The asymmetric unit contains two B–N-bound conformers of **1** differing mainly by the O-N-N-B dihedral angles. As seen for the dinitramide anion,[8] the nitro groups are tilted (the two O-N-N angles for each nitro group in Figure 2 differ by 3 and 7°, respectively). This geometry is also evident in trinitromethyl-containing compounds, in which the two O-N-C angles differ for each nitro group.[5b] The angle between the two O-N-O planes are 42 and 41° for the two symmetry-independent molecules, respectively. Both B–N distances (1.5798(19) and 1.5895(18) Å in Figure 2) within each molecule of the asymmetric unit are statistically equal. It is worth noting that the central nitrogen atom of the dinitramido group in **1** is in a planar environment (the sum of the angles around the central nitrogen is 360°, within experimental error).

The vibrational spectra recorded for a sample of **1** containing significant amounts of ammonium dinitramide and circa 20 mol% of unidentified impurities show a relatively good match with the predicted ones (see the Supporting Information). The main features of the vibrational spectra are the two strongest bands at approximately 520 and 2460 cm^{-1}, which correspond to the antisymmetric and symmetric $B-H_2$ stretching modes, respectively. They are in the same range as detected for NH_3-BH_3 (2200–2500 cm^{-1})[10] and at similar frequencies as those found for the $[BH_2(azolate)_2]^-$ ions (2450–2550 cm^{-1}).[5a] Otherwise, the spectra are dominated by the NH_3 bands at circa 3500 cm^{-1} and the dinitramido modes in the 700–1600 cm^{-1} range.

Compound **1** is only marginally stable under ambient conditions. It underwent extensive decomposition upon isolation in the solid state, with an insoluble boron-containing colorless material and ammonium dinitramide as the major decomposition products. As solid **1** was not obtained in pure form, its friction and impact sensitivities could not be determined. Volatile materials collected from the evaporation of solutions of **1** contained only small amounts of N_2O, as detected by IR spectroscopy, implying a very slow and negligible decomposition of the dinitramido moiety. The compound is also air sensitive. From dichloromethane solutions of **1** in air, a tacky white solid started to precipitate and bubbles immediately originated from its surface. In one instance, the resulting decomposition products crystallized during their formation and were shown by single-crystal X-ray diffraction to be ammonium dinitramide. In another instance, a concentrated glyme solution containing HDN and **1**, when exposed to light, decomposed significantly whereas a similar sample kept in the dark did not, suggesting that **1** and/or HDN are photosensitive.

Besides being of academic value, ammonia–mono-(dinitramido)borane might be of interest as a HEDM. We have used the most recent enthalpy of formation (ΔH_f^0)–NIST data (NIST = National Institute of Standards and Technology) for the compounds in Equations (2) and (3), combined with reliable calculated CBS-QB3 reaction enthalpies, and estimated a value of $\Delta H_f^0 = -12.0 \pm 2$ kcal mol^{-1} for **1** in the gas phase. The ΔH_f^0 values (in kcal mol^{-1}) of the individual components that were used for our calculations are given in parentheses.

$$\begin{aligned}&NH_3 \cdot BH_2N(NO_2)_2\ (\mathbf{1}) \rightarrow \\ &N_2O\ (+19.6) + B(OH)_3\ (-237.2) + trans\text{-}N_2H_2\ (+50.9) \qquad (2)\\ &(\Delta H_r{}^0{}_{\text{CBS-QB3}} = -155.9\ \text{kcal mol}^{-1},\ \Delta H_f{}^0 = -10.8\ \text{kcal mol}^{-1})\end{aligned}$$

$$\begin{aligned}&NH_3 \cdot BH_2N(NO_2)_2\ (\mathbf{1}) \rightarrow \\ &N_2O\ (+19.6) + 2\,NO\ (+21.6) + H_2O\ (-57.8) + BH_3\ (+25.5) \qquad (3)\\ &(\Delta H_r{}^0{}_{\text{CBS-QB3}} = +43.6\ \text{kcal mol}^{-1},\ \Delta H_f{}^0 = -13.1\ \text{kcal mol}^{-1})\end{aligned}$$

The sublimation enthalpy ΔH_{sub} of solid **1** was calculated using the value for gaseous **1** and separate periodic DFT calculations on the unit cell determined experimentally from the X-ray data. We obtain a ΔH_{sub} of 26.7 kcal mol^{-1}, and arrive at an estimate for the heat of formation of **1** in the solid state of $\Delta H_{f(s)}{}^0 = \Delta H_f{}^0 - \Delta H_{sub} = (-12.0) - (26.7) = -38.7 \pm 5$ kcal mol^{-1}.

The specific impulse in vacuum, I_{sp} (vac.), of solid **1** as a rocket propellant was calculated as 333 s using the thermochemical code RPA v.1.2.8.0. The combustion process can be approximated by Equation (4).

$$NH_3 \cdot BH_2N(NO_2)_2\ (\mathbf{1}) \rightarrow 2\,N_2 + HBO_2 + 2\,H_2O \qquad (4)$$

Whether the preferred combustion product is HBO_2 or $B_2O_{3(liq)} + H_2O$ depends on the temperature of the products used in the computational code. The preferred product in the RPA code is HBO_2, whereas the Cheetah code predicts predominantly liquid B_2O_3 as the combustion product, with the differences in relative energies being small. The predicted performance of **1** would be on par with those of the N_2O_4/monomethylhydrazine bipropellant (342 s)[12] and the recently discovered liquid monopropellant nitryl cyanide ($NCNO_2$, $I_{sp} = 343$ s),[9] and would be significantly higher than that of the commonly used monopropellant hydrazine (I_{sp} = *ca* 233 s).[13] Although the limited thermal stability of **1** will prevent its use in a practical system, it is nevertheless of great interest to see how much room exists to improve on the performance of the presently used propellants, where a performance increase of about 10 s can double the payload of a rocket. Using the ΔH_f^0-NIST value for HBO_2 (−134.0 kcal mol^{-1}), the combustion enthalpy [Eq. (4)] of solid **1** is estimated to equal −210.9 kcal mol^{-1}. This corresponds to an energy density (combustion enthalpy per gram) of 1.55 kcal g^{-1}.

As an explosive, solid **1** is predicted to have a detonation pressure (P_{det}) of 29.9 GPa and a detonation velocity (V_{det}) of 8.5 km s^{-1}. Based on these values, **1** would have a performance comparable to pentaerythritol tetranitrate (PETN; P_{det} = 30.5 GPa, V_{det} = 8.5 km s^{-1}) and significantly greater than that of trinitrotoluene (TNT; P_{det} = 20.0 GPa, V_{det} = 7.1 km s^{-1}).

In conclusion, **1** is the first example of a structurally characterized Group 13 dinitramido compound. An analysis of the major NMR signals combined with quantum chemical calculations establishes that the obtained crystal structure is indeed that of the major compound formed in our reactions. Quantum chemical calculations confirm that in solution the detected B–N-connected isomer is thermodynamically favored over the B–O-connected isomer, whereas in the gas phase the two are predicted to be nearly degenerate in energy.

Evidence strongly suggesting the formation of the disubstituted $NH_3{\cdot}BH(DN)_2$ was also obtained by NMR spectroscopy. These compounds are very rare examples of powerful redox pairs, in this case hydrido and dinitramido ligands, in single small molecules.[4i,5b] Although $NH_3{\cdot}BH_2DN$ only has a limited stability under ambient conditions, its major decomposition pathway involves the elimination of ammonium dinitramide, indicating that the instability does not arise from intra- or intermolecular redox reactions. More likely, the compound might be undergoing oligomerization reactions similar to those known for ammonia–borane. Considering the high energy content of **1**, even its marginal stability is remarkable. The results from this study show that, contrary to previous reports on the instability of dinitramido compounds with Lewis acids,[6b] a careful choice of substrates can allow the isolation of dinitramido-substituted boranes.

Experimental Section

Caution! The materials used and synthesized in this study are highly energetic. They should be handled in quantities not exceeding the millimolar scale. Manipulations should be carried out behind blast shields and with adequate personal safety gear (face shield, heavy leather jacket and gloves, ear protection).

Synthesis of ammonia–mono(dinitramido)borane, $NH_3{\cdot}BH_2N(NO_2)_2$ (**1**): In a typical synthesis, glyme (5–10 mL) was condensed onto $NH_3{\cdot}BH_3$ (17 mg; 0.55 mmol). The mixture was frozen at −196 °C and a solution of known HDN concentration in glyme (1.25 g of solution, 0.53 mmol HDN; see the Supporting Information) was cannulated onto the frozen mixture. After evacuation of the vessel, the mixture was thawed and gas evolution was observed. The gases non-condensable at −196 °C were measured on a calibrated glass vacuum line and showed that the reaction had reached completion (circa 0.5 mmol of H_2 measured). An aliquot of the reaction mixture was cannulated into a J. Young NMR tube, and its NMR analysis established that **1** was the major species in solution, with only circa 20 mol % of NO_2-containing side products detected. The reaction mixture was then concentrated under vacuum until only a drop of viscous liquid remained. Dichloromethane was condensed onto the resulting liquid, yielding an oily deposit at the bottom of the reactor. The supernatant dichloromethane phase was filtered into a Teflon-FEP reactor and the extraction was repeated with an additional 5 mL of dichloromethane. The solid residue in the reaction vessel contained mostly ammonium dinitramide and some acetonitrile-insoluble solid (upon hydrolysis, the insoluble product displayed a ^{11}B NMR signal at circa $\delta = 15$ ppm and therefore was not boric acid). The dichloromethane extract was concentrated under vacuum to about one half of the initial volume. Some white material started precipitating, and the suspension was cooled to −80 °C and left standing overnight. The supernatant was transferred into a J. Young NMR tube and contained relatively clean **1** along with the unidentified impurities. On one occasion, colorless prismatic crystals suitable for single-crystal X-ray diffraction were obtained from the evaporation of such a dichloromethane extract. The white precipitate obtained from the concentration of the dichloromethane extract was dried under vacuum and contained **1** as the major species and the same impurities as observed in the supernatant, but was also severely contaminated with ammonium dinitramide.

1: ^1H NMR (500.000 MHz, 20 °C, CD_3CN): $\delta = 2.77$ (bqt, $^1J(^1H–^{11}B) = 111$ Hz), 4.69 ppm (bt, $^1J(^1H–^{14}N) = 50$ Hz); ^{11}B NMR (160.419 MHz, 20 °C, CD_3CN): $\delta = -9.3$ ppm (t, $^1J(^{11}B–^1H) = 113$ Hz); ^{14}N NMR (36.118 MHz, 20 °C, CD_3CN): $\delta = -34.3$ (s, $\tau_{1/2} = 6$ Hz, NO_2), −360.9 ppm (bm, NH_3-B). ^{11}B NMR (160.419 MHz, 20 °C, CH_2Cl_2, unlocked): $\delta = -9.6$ ppm (t); ^{14}N NMR (36.118 MHz, 20 °C, CH_2Cl_2, unlocked): $\delta = -36.8$ (s, NO_2), −358.7 ppm (bm, NH_3-B); ^{11}B NMR (160.419 MHz, 20 °C, diethyl ether, unlocked): $\delta = -8.9$ ppm (t); ^{14}N NMR (36.118 MHz, 20 °C, diethyl ether, unlocked): $\delta = -34.1$ (s, NO_2), −91 (broad, B-N-NO_2), −361.1 ppm (bs, NH_3-B).

Observation of ammonia–bis(dinitramido)borane, $NH_3{\cdot}BH[N(NO_2)_2]_2$ (**2**): A HDN solution generated in situ in CD_3CN (0.27 mmol) was added to ammonia–borane (2.1 mg; 0.068 mmol). After the resulting vigorous effervescence subsided, the solution was analyzed by NMR spectroscopy and monitored over circa one week. The solution initially contained **1** along with side products but, after approximately two days, contained significant amounts of some new species, including **2**.

2: ^1H NMR (500.000 MHz, 20 °C, CD_3CN): $\delta = 3.78$ (bqt, $^1J(^1H-^{11}B) = 143$ Hz), BH_2), 5.33 ppm (bt $^1J(^1H-^{14}N) = 45$ Hz); ^{11}B NMR (160.419 MHz, 20 °C, CD_3CN): $\delta = -0.7$ ppm (d, $^1J(^{11}B-^1H) = 149$ Hz); ^{14}N NMR (36.118 MHz, 20 °C, CD_3CN): $\delta = -32.7$ ppm (s, $\tau_{1/2} = 9$ Hz, NO_2).

Crystal structure determination: The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO diffractometer using Cu Kα radiation. The structure was solved by intrinsic phasing and refined using ShelX2014.[14] CCDC 1049933 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational details: The CBS-QB3[15] composite method was employed to screen the relative energies of the different isomers in the gas phase using Gaussian 09, rev A02.[16] CBS-QB3 is based on CCSD(T) energies extrapolated to the basis set limit using MP2 and MP4 calculations together with empirical corrections, and is expected to be highly accurate for thermochemistry. Its mean absolute deviation in the G2 test set is reported to be 0.87 kcal mol^{-1}.[15] Relative free energies in CH_3CN solution were estimated by correcting the CBS-QB3 energies using density functional theory (M06-2X[17]/cc-pVTZ) geometries and thermal corrections, which were evaluated in both the gas phase and in solution, the latter using SMD-PCM.[18] The effect of structural relaxation upon solvation is hence included in these energies. Nuclear magnetic shielding tensors were calculated in acetonitrile at the GIAO-PCM-B3LYP/6-311++(3df,3pd) level. Extended DFT calculations were performed using VASP, version 5.3.5.[19] The geometry was optimized using the PBE[20] GGA functional, in combination with the DFT-D3(BJ) dispersion correction.[21] The D3(BJ) correction was required to attain a good agreement with the experimental structure (the molecular volume is 130.3 Å^3 and 131.8 Å^3 from experiment and theory, respectively). Calculations of gaseous **1** were done using a 15 Å^3 periodic unit cell. Standard projected augmented wave (PAW) potentials[19b,22] were used together with a plane-wave kinetic energy cutoff of 800 eV. Brillouin zone sampling was performed on a Monkhorst-Pack mesh, which spanned $4 \times 2 \times 2$ k-points. Energies and forces were converged to < 1 meV per atom. $\Delta H_{\mathrm{sub}(\mathbf{1})}$ was approximated as $\Delta H_{\mathrm{sub}} \approx E_{\mathbf{1},\text{gas-phase}} - E_{(\mathbf{1},\text{solid})}$. The rocket propellant performance was predicted using the thermochemical code RPA v.1.2.8.0, assuming a combustion chamber pressure of 7 MPa, expansion to vacuum, and a nozzle expansion ratio of 70. Detonation parameters for **1**, PETN and TNT were calculated using the Cheetah v7.0 thermochemical code.[23] See the Supporting Information for further details.

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[1] O. A. Luk'yanov, V. P. Gorelik, V. A. Tartakovskii, *Russ. Chem. Bull.* **1994**, *43*, 89–92 and references therein.

[2] a) J. C. Bottaro, P. E. Penwell, R. J. Schmitt, *J. Am. Chem. Soc.* **1997**, *119*, 9405-9410 and references therein; b) J. C. Bottaro, R. J. Schmitt, P. E. Penwell, D. S. Ross, USA and Foreign 5,254,324, **1993**; International patent application number WO91/19669, **1991**.

[3] a) T. M. Klapötke, B. Krumm, M. Scherr, *Z. Anorg. Allg. Chem.* **2009**, *635*, 885–888; b) O. A. Luk'yanov, N. I. Shlykova, V. A. Tartakovsky, *Russ. Chem. Bull.* **1994**, *43*, 1680–1683; c) K. O. Christe, W. W. Wilson, G. Bélanger-Chabot, R. Haiges, J. A. Boatz, M. Rahm, G. K. S. Prakash, T. Saal, M. Hopfinger, *Angew. Chem. Int. Ed.* **2015**, *54*, 1316–1320; *Angew. Chem.* **2015**, *127*, 1332–1336; d) M. Rahm, S. V. Dvinskikh, I. Furó, T. Brinck, *Angew. Chem. Int. Ed.* **2011**, *50*, 1145–1148; *Angew. Chem.* **2011**, *123*, 1177–1180.

[4] a) C. R. Guibert, M. D. Marshall, *J. Am. Chem. Soc.* **1966**, *88*, 189–190; b) T. J. Groshens, *J. Coord. Chem.* **2010**, *63*, 1882–1892; c) D. Lu, C. H. Winter, *Inorg. Chem.* **2010**, *49*, 5795–5797; d) T. M. Klapötke, B. Krumm, R. Moll, *Chem. Eur. J.* **2013**, *19*, 12113–12123; e) T. M. Klapötke, M. Rusan, V. Sproll, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2433–2443; f) C. J. Snyder, P. D. Martin, M. J. Heeg, C. H. Winter, *Chem. Eur. J.* **2013**, *19*, 3306–3310; g) T. M. Klapötke, B. Krumm, M. Rusan, J. J. Sabatini, *Chem. Commun.* **2014**, *50*, 9581–9583; h) T. M. Klapötke, M. Rusan, V. Sproll, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1892–1899; i) O. P. Shitov, V. A. Tartakovskii, S. L. Ioffe, *Chem. Heterocycl. Compd.* **2015**, *50*, 1647–1657.

[5] a) R. Haiges, C. B. Jones, K. O. Christe, *Inorg. Chem.* **2013**, *52*, 5551–5558; b) G. Bélanger-Chabot, M. Rahm, R. Haiges, K. O. Christe, *Angew. Chem. Int. Ed.* **2013**, *52*, 11002–11006; *Angew. Chem.* **2013**, *125*, 11208–11212.

[6] a) G. Bélanger-Chabot, R. Haiges, K. Christe. High oxygen borates as potential green replacements for ammonium–perchlorate-based solid propellants. Symposium on Ionic Liquids—Science and Applications, 243rd National Spring Meeting of the American Chemical Society. San Diego, CA, March 25 **2012**; b) O. A. Luk'yanov, O. V. Anikin, V. P. Gorelik, V. A. Tartakovsky, *Russ. Chem. Bull.* **1994**, *43*, 1457–1461.

[7] a) S. Trammell, P. A. Goodson, B. P. Sullivan, *Inorg. Chem.* **1996**, *35*, 1421–1422; b) H.-G. Ang, W. Fraenk, K. Karaghiosoff, T. M. Klapötke, P. Mayer, H. Nöth, J. Sprott, M. Warchhold, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2894–2900.

[8] T. M. Klapötke, J. Stierstorfer, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4340–4346.

[9] M. Rahm, G. Bélanger-Chabot, R. Haiges, K. O. Christe, *Angew. Chem. Int. Ed.* **2014**, *53*, 6893–6897; *Angew. Chem.* **2014**, *126*, 7013–7017.

[10] C. Ziparo, D. Colognesi, A. Giannasi, M. Zoppi, *J. Phys. Chem. A* **2012**, *116*, 8827–8832.

[11] L. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849–854.

[12] a) "Modern Engineering for Design of Liquid-Propellant Rocket Engines": D. K. Huzel, D. H. Huang in *Progress in Astronautics and Aeronautics*, *Vol. 147*, American Institute of Aeronautics and Astronautics, Inc., Washington, **1992**; b) H. Stratton, "Theoretical Performance of Rocket Propellant Combinations", Advanced Programs, Rocketdyne Division, Rockwell International, 537A-2 rev. 2–88.

[13] a) T. M. Klapötke, *Chemistry of High-Energy Materials*, 2nd ed., De Gruyter, Berlin, **2012**; b) E. W. Schmidt, *Hydrazine and its Derivatives*, Wiley, New York **1984**; c) Airbus Defense and Space. Hydrazine Thrusters Brochure. http://cs.astrium.eads.net/sp/brochures/hydrazine-thrusters/hydrazine-thrusters.pdf (accessed: June 17 2015); d) P. Sjoberg in *Energetic Materials*, Part 1 (Eds.: P. Politzer, J. S. Murray), Elsevier, Amsterdam, **2003**, p. 401.

[14] a) G. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122; b) G. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8; c) G. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.

[15] J. J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **1999**, *110*, 2822–2827.

[16] Gaussian 09, Revision A.02; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. K. Staroverov, R., J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox Gaussian, Inc., Wallingford CT: **2009**.

[17] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[18] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[19] a) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186; b) G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758–1775.

[20] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[21] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[22] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.

[23] B. Sorin, E. F. Laurence, R. G. Kurt, W. M. Howard, W. K. I-Feng, P. C. Souers, P. A. Vitello. *Cheetah 7.0*, *rev2280*, Lawrence Livermore National Laboratory, **2012**.

[24] J. Towns, T. Cockerill, M. Dahan, I. Foster, K. Gaither, A. Grimshaw, V. Hazlewood, S. Lathrop, D. Lifka, G. D. Peterson, R. Roskies, J. R. Scott, N. Wilkins-Diehr, *Comput. Sci. Eng.* **2014**, *16*, 62–74.

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