

# The Synthesis and Characterization of Nitrooxy- and Nitrosooxyborazine Compounds

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 80<sup>th</sup> birthday*

*B*-Nitrosooxy-pentamethylborazine, *B*-nitrosooxy-pentamethylborazine and *B*-trinitrooxy-*N*-trimethylborazine have been synthesized and characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, and <sup>14</sup>N NMR spectroscopy, mass spectrometry, vibrational spectroscopy and elemental analysis. The <sup>11</sup>B NMR shifts were calculated and compared to the experimental results. The decomposition temperatures and the impact and friction sensitivities of these compounds have been determined as well.

**Key words:** Nitrosooxyborazines, Nitrooxyborazines, <sup>11</sup>B NMR Spectroscopy, Energetic Materials, Impact and Friction Sensitivities

## Introduction

The investigation of borazine, which was first isolated by Stock and Pohland in 1926, and its derivatives has been of interest for decades [1–5]. Borazine, the “inorganic benzene”, which shows a different reactivity compared to benzene due to the polarity of the BN bonds, is calculated to possess substantial aromatic character assuming that the resonance energy is a criterion for aromaticity [6]. Numerous fields of applications and a plenty of borazine compounds have been reported in literature [2–8]. The preparation of various symmetrically and unsymmetrically substituted borazine derivatives is well-known and has been extensively investigated. Derivatives of borazine with alkyl, alkoxy, halogen, pseudohalogen, and amino substituents on the nitrogen and boron atoms are described [9–14]. Metal  $\pi$ -complexes containing alkylborazine compounds as ligands are reported as well [15]. Borazine is described to be a convenient precursor compound for the synthesis of polyborazines and hence for boron nitride ceramics. *B,B,B*-Triaminoborazine was prepared as a molecular precursor for hexagonal boron ni-

tride showing excellent thermal and mechanical properties and structural similarities with graphite [7]. Among the various fields of applications of borazine derivatives, their use in propellants and related areas has also been considered and investigated [16]. Niedenzu and co-workers reported the synthesis of the energetic borazine compound *B*-trichloro-*N*-trihydroxyborazine, which could not be isolated due to its too sensitive character [17]. More stable and isolatable energetic borazine compounds are azido-borazines such as *B*-azidopentamethylborazine and *B*-triazidoborazine, which were obtained by Paine *et al.* [18]. Additionally, Meller and Wechsberg reported the preparation of *B*-triazido-*N*-trimethylborazine from *B*-trichloroborazine and sodium azide [19]. Besides energetic azido borazine molecules, borazine derivatives containing energetic nitro groups are also of high interest.

The investigation of *N*-nitroborazines was performed by Hirata [16]. Several syntheses of borazine using nitryl chloride and gaseous hydrogen chloride are described. The results of these examinations showed that borazine reacts violently with nitryl chloride in the absence of a diluent, and decomposition oc-

curred instead of the formation of the target compound. Synthesis attempts to introduce  $\text{ONO}_2$  or  $\text{ONO}$  groups into the borazine molecule were performed by Brennan *et al.* using *B*-trichloroborazine and silver nitrate and silver nitrite, respectively, but no stable products could be isolated [20].

Decades later, the synthesis and crystal structure of the first compound containing a nitrooxy group, 2,4-bis(dimethylamino)-1,3,5-trimethyl-6-(nitrooxy)borazine, was reported by Rodriguez and Borek [21]. The reaction of 2,4-bis(dimethylamino)-6-chloro-1,3,5-trimethylborazine with silver nitrate in acetonitrile resulted in the formation of 2,4-bis(dimethylamino)-1,3,5-trimethyl-6-(nitrooxy)borazine.

Although several syntheses of borazine derivatives using borazine as starting material are reported, borazine is not a suitable starting material for further syntheses due to its unfavorable properties like decomposition and polymerization tendencies at room temperature [16]. However, halogen-substituted borazines such as *B*-trichloroborazine, *B*-trichloro-*N*-trimethylborazine or *B*-bromopentamethylborazine do not polymerize or decompose at room temperature and are therefore suitable starting materials for further syntheses [22–24].

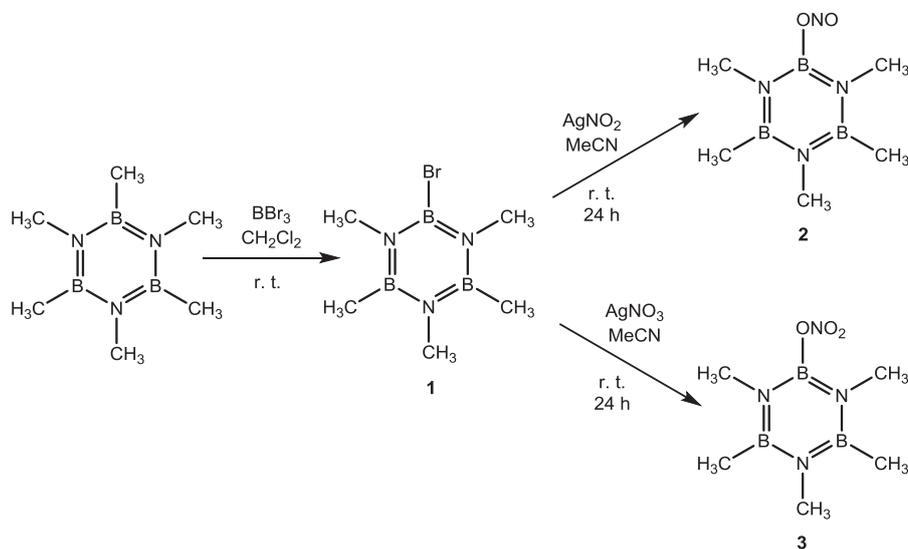
In this contribution the synthesis of *B*-nitrosooxy-pentamethylborazine (**2**), *B*-nitrooxy-pentamethylborazine (**3**) and *B*-trinitrooxy-*N*-trimethylborazine (**5**)

is described. Their characterization by NMR spectroscopy, elemental analysis, mass spectrometry and IR spectroscopy, as well as their thermal and energetic properties are reported. Additionally calculations of  $^{11}\text{B}$  NMR shifts of compounds **2**, **3** and **5** have been performed.

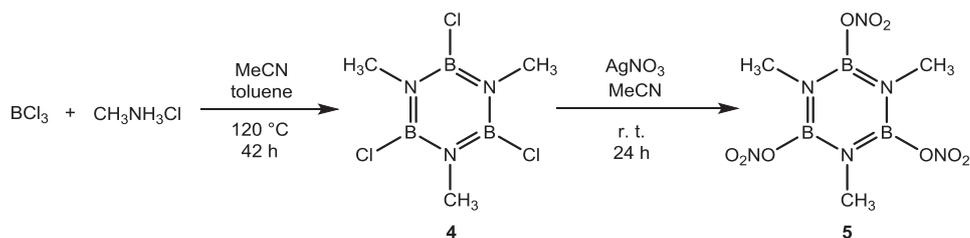
## Results and Discussion

### Synthesis

The starting material *B*-bromopentamethylborazine (**1**) was synthesized according to the literature procedure by the reaction of hexamethylborazine and  $\text{BBr}_3$  in dichloromethane at room temperature [24]. The products *B*-nitrosooxy-pentamethylborazine (**2**) and *B*-nitrooxy-pentamethylborazine (**3**) were synthesized using *B*-bromopentamethylborazine (**1**) and silver nitrite and silver nitrate, respectively, in stoichiometric ratios (Scheme 1). Both reactions were performed in dry acetonitrile at ambient temperature and under exclusion of light. The driving force of these reactions is the formation of silver bromide. The reaction was monitored *via*  $^{11}\text{B}$  NMR spectroscopy, and after 24 hours the  $^{11}\text{B}$  NMR shift indicated that a complete substitution of the bromo group by the nitrosooxy and nitrooxy moieties, respectively, had occurred. Af-



Scheme 1. Synthesis of compounds **1**–**3**.

Scheme 2. Synthesis of compounds **4** and **5**.

ter filtration the products were washed with dry diethyl ether and recrystallized from dry acetonitrile. Colorless solids were obtained in high purity and yield.

The synthesis of *B*-trichloro-*N*-trimethylborazine (**4**) was performed according to the literature procedure for *B*-trichloroborazine [22] by reacting methylammonium chloride with boron trichloride (1-molar solution in toluene) in acetonitrile (Scheme 2). *B*-Trinitrooxy-*N*-trimethylborazine (**5**) was obtained by the reaction of *B*-trichloro-*N*-trimethylborazine and silver nitrate in stoichiometric amounts in dry acetonitrile at room temperature and under exclusion of light. Here again, the driving force of the reaction is the formation of silver chloride. After filtration and recrystallization from dry acetonitrile, compound **5** was obtained as a colorless solid of high yield and purity.

#### Characterization

Compounds **2**, **3** and **5** were characterized by  $^{11}\text{B}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{14}\text{N}$  NMR spectroscopy, as well as elemental analysis, mass spectrometry and infrared spectroscopy.

The  $^{11}\text{B}$  NMR spectra of compounds **2** and **3** reveal chemical shifts near +36 ppm, which can be attributed to boron atoms containing methyl substituents. The substitution of the Br atom by the ONO group is indicated by the  $^{11}\text{B}$  signal shift from +31 ppm to +22 ppm, and the  $^{11}\text{B}$  chemical shift of compound **3** is found at +24 ppm suggesting the formation of the nitrate compound **3**. In the  $^1\text{H}$  NMR spectra both compounds show signals at around +2.9 ppm corresponding to the protons of the two *ortho* *N*-methyl groups. The protons of the *para* *N*-methyl groups exhibit chemical shifts at around +2.7 ppm. The protons of the boron-connected methyl groups of **2** and **3** show signals at +0.5 ppm. In the  $^{13}\text{C}$  NMR spectra

of compounds **2** and **3** the *N*-methyl groups in *ortho* position appear at +34 ppm, while the carbon atoms in *para* position exhibit a signal at +31 ppm. The boron-connected methyl groups of both compounds show a signal at +1 ppm. In the  $^{14}\text{N}$  NMR spectra of both compounds a signal at –286 ppm corresponds to nitrogen atoms of the borazine ring. The  $^{14}\text{N}$  signal of the ONO-group appears at –22 ppm. In the case of compound **3** a signal at –46 ppm corresponding to the ONO<sub>2</sub>-group is observed. The assignment of infrared absorptions was performed according to the literature [25]. In the IR spectra of both compounds strong bands of B–N stretching vibrations are visible in the region between 1455 and 1369 cm<sup>–1</sup>, and of B–N deformation vibrations in the 706–702 cm<sup>–1</sup> region. In the IR spectrum of compound **1** strong bands of B–Br stretching vibrations appear in the range between 1032 and 946 cm<sup>–1</sup>, which are not visible in the IR spectra of compounds **2** and **3**. However, these two compounds show B–O stretching vibrations in the range 1371 to 1335 cm<sup>–1</sup>.

In the  $^{11}\text{B}$  NMR spectrum of compound **5** one signal at +25.6 ppm is observed. Since the starting material **4** shows a  $^{11}\text{B}$  chemical shift at +30.3 ppm, the formation of **5** can be assumed. In the  $^1\text{H}$  NMR spectrum compound **5** shows a signal at +2.83 ppm corresponding to the three methyl protons, and in the  $^{13}\text{C}$  NMR spectrum a signal at +35.1 ppm for the carbon atoms of the three *N*-methyl groups. The  $^{14}\text{N}$  NMR spectrum of **5** reveals a shift of –46 ppm corresponding to the three ONO<sub>2</sub> substituents and a second signal at –139 ppm, which can be assigned to the ring nitrogen atoms. The assignments of IR vibrations were done according to ref. [25]. The B–O stretching vibrations are found in the 1387–1340 cm<sup>–1</sup> region, the B–N stretching vibrations appear between 1450 and 1359 cm<sup>–1</sup>, whereas the B–N deformation vibrations appear between 706 and 704 cm<sup>–1</sup>.

Compound	$-E$ (a. u.)	NIMAG	P. g.	$\delta^{11}\text{B}$ (ppm) calcd. isotr. shielding	$\delta^{11}\text{B}$ (ppm) calcd. (ref. to $\text{BF}_3\cdot\text{Et}_2\text{O}$ )	$\delta^{11}\text{B}$ (ppm) exptl. (ref. to $\text{BF}_3\cdot\text{Et}_2\text{O}$ )
<b>2</b>	643.690087	0	$C_s$	74.6 (2) 81.9	35.4 (2) 28.1 (1)	36 (2) 22 (1)
<b>3</b>	718.874416	0	$C_s$	74.8 (2) 86.3 (1)	35.4 (2) 23.7 (1)	36 (2) 24 (1)
<b>5</b>	1199.653977	0	$C_s$	84.4 (2) 86.8 (1)	25.6 (2) 23.2 (1)	25.6
$\text{BF}_3\cdot\text{Et}_2\text{O}$	558.164166	0	$C_1$	+110.0	0.0	0.0

Table 1. Calculated isotropic magnetic shielding (GIAO method [26–30], MPW1PW91/aug-cc-pVDZ) and relative  $^{11}\text{B}$  chemical shifts (ppm) referenced to  $\text{BF}_3\cdot\text{Et}_2\text{O}$ .

### Calculation of $^{11}\text{B}$ chemical shifts

As additional verification of the analytical data, the  $^{11}\text{B}$  NMR chemical shifts were calculated and compared to the experimental data.

In order to compute the  $^{11}\text{B}$  NMR chemical shifts for various high-nitrogen boron compounds, the isotropic magnetic shieldings were calculated using the GIAO (Gauge-Independent Atomic Orbital)

method implemented in G03 [26–30]. The structures were fully optimized and the frequencies calculated (NIMAG = 0) at MPW1PW91/aug-cc-pVDZ level of theory (Fig. 1). Subsequently, the NMR shielding tensors were calculated at the same level of theory using the GIAO method [27–30]. Table 1 summarizes the computed isotropic magnetic shieldings and relative  $^{11}\text{B}$  NMR chemical shifts (ppm) referenced to  $\text{BF}_3\cdot\text{Et}_2\text{O}$ .

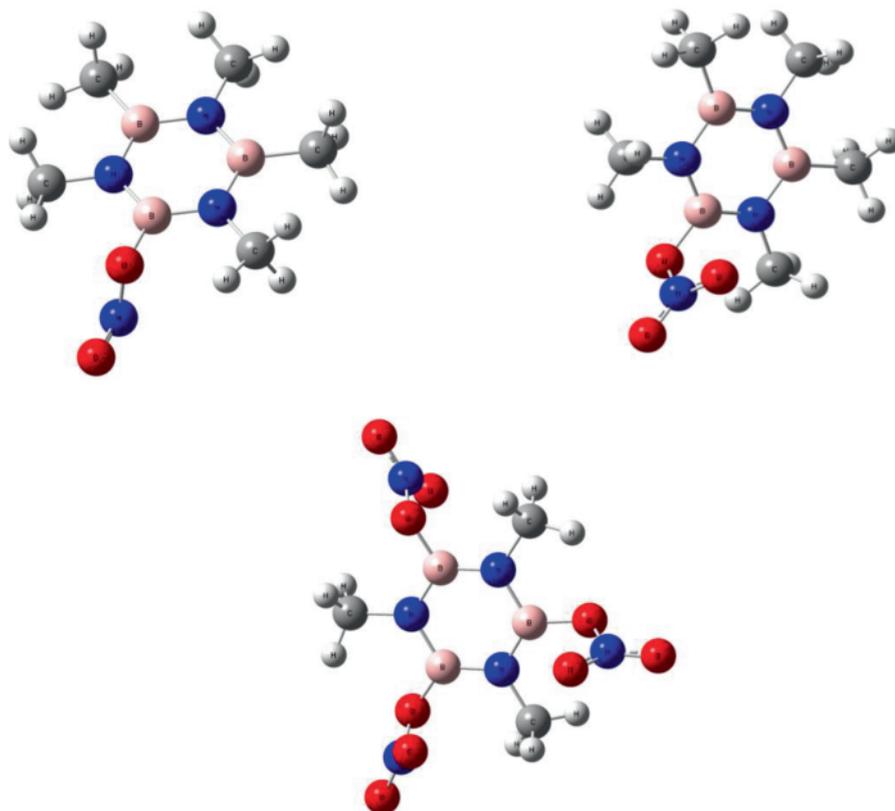


Fig. 1 (color online). MPW1PW91/aug-cc-pVDZ-optimized structures of compounds **2** (top left), **3** (top right) and **5** (bottom center) in idealized  $C_s$  symmetry.

	<b>2</b>	<b>3</b>	<b>5</b>
Chemical formula	C <sub>5</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub> B <sub>3</sub>	C <sub>5</sub> H <sub>15</sub> N <sub>4</sub> O <sub>3</sub> B <sub>3</sub>	C <sub>3</sub> H <sub>9</sub> N <sub>6</sub> O <sub>9</sub> B <sub>3</sub>
Formula weight, g mol <sup>-1</sup>	195.63	211.63	305.57
N, % <sup>a</sup>	28.64	26.48	27.50
Ω <sub>CO</sub> , % <sup>b</sup>	-122.68	-105.84	-15.71
Ω <sub>CO<sub>2</sub></sub> , % <sup>c</sup>	-163.57	-143.64	-31.42
Grain size, μm	< 100	< 100	< 100
IS, J	> 40	> 40	> 40
FS, N	120	80	80
T <sub>m</sub> , °C	-	76	83
T <sub>dec</sub> , °C	127	117	154

<sup>a</sup> Nitrogen content; <sup>b</sup> oxygen balance assuming the formation of CO; <sup>c</sup> oxygen balance assuming the formation of CO<sub>2</sub>.

The comparison of the calculated values with the experimentally determined shifts shows a good accordance. In the case of compound **5** experimentally only one <sup>11</sup>B NMR chemical shift at 25.6 ppm was detected, whereas the calculation requires two <sup>11</sup>B NMR signals at 25.6 ppm and 23.2 ppm for the assumed C<sub>s</sub> symmetry (Table 1). In solution, molecular dynamics seem to lead to a coalescence of these signals.

#### *Energetic and thermal properties*

The impact (IS) and friction (FS) sensitivities as well as the melting (T<sub>m</sub>) and decomposition (T<sub>dec</sub>) temperatures of compounds **2**, **3** and **5** are summarized in Table 2. Furthermore, the oxygen balance and the nitrogen content are given in Table 2. All three borazine derivatives are impact insensitive but show friction sensitivities of 120 N (**2**), and 80 N (**3** and **5**). The decomposition temperatures have been determined to be 127 °C (**2**), 117 °C (**3**) and 154 °C (**5**).

#### **Conclusion**

The borazine compounds *B*-nitrosooxypentamethylborazine (**2**), *B*-nitrooxypentamethylborazine (**3**) and *B*-trinitrooxy-*N*-trimethylborazine (**5**) have been synthesized and characterized *via* NMR and IR spectroscopy as well as elemental analysis and mass spectrometry. Calculations of <sup>11</sup>B NMR chemical shifts were performed showing a good accordance of calculated and experimentally determined values. The measurement of the impact and friction sensitivities revealed that all compounds are impact insensitive but friction sensitive. The decomposition temperatures have been determined to be moderate.

Table 2. Energetic and thermal properties of compounds **2**, **3** and **5**.

#### **Experimental Section**

All manipulations were carried out in an atmosphere of dry argon using standard vacuum line techniques. Solvents were dried by standard procedures. All other chemicals were commercially available and used as received. The NMR spectra were recorded using Jeol Eclipse 400, Jeol Eclipse 270 or Jeol EX400 instruments at an ambient temperature of 25 °C if not stated otherwise. Chemical shifts (δ) were calibrated using the residual undeuterated solvent as an internal reference and are reported according to the common convention in parts per million (ppm) downfield relative to tetramethylsilane (TMS, <sup>13</sup>C, <sup>1</sup>H), nitromethane (<sup>14</sup>N) or boron trifluoride etherate (<sup>11</sup>B) as external standards. Infrared (IR) spectra were measured with a Perkin-Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature, the samples were neat solids. Mass spectrometric data were obtained with a Jeol MStation JMS 700 spectrometer ((+)-DEI, (+)-DCI). The fragments are referred to the isotope with the highest natural abundance. Elemental analyses were performed with an Elementar Vario EL or an Elementar Vario EL micro cube, DSC measurements with a Perkin Elmer Pyris 6 DSC instrument at a heating rate of 5 °C min<sup>-1</sup> in closed aluminum containers with a hole (1 μm) on the top for gas release and a nitrogen flow of 5 mL min<sup>-1</sup>. The reference sample was an empty closed aluminum container. The impact and friction sensitivity was determined using a BAM drophammer and a BAM friction tester [31–35]. The sensitivities of the compounds are indicated according to the UN Recommendations on the Transport of Dangerous Goods [36]: impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive < 80 N, extreme sensitive < 10 N.

**CAUTION!** *The compounds described in this work are potential explosives, which are sensitive to environmental stimuli such as impact, friction and heat. While we encour-*

tered no problems in the handling of these materials, appropriate precautions and proper protective measures (safety glasses, face shields, leather coat, Kevlar gloves and ear protectors) should be taken when preparing and manipulating these materials.

#### Synthesis of *B*-nitrosooxypentamethylborazine (2)

*B*-Bromopentamethylborazine [24] (**1**) (0.5 g, 2.18 mmol) was dissolved in dry acetonitrile (12 mL) and cooled in an ice bath. To the cooled and stirred solution silver nitrite (0.34 g, 2.18 mmol) was added, and a yellow precipitate was immediately formed. Under exclusion of light the mixture was stirred at room temperature for 24 h and then filtered. After removing the solvent and recrystallization from dry acetonitrile a colorless solid (0.30 g, 71 %) was obtained. – IR (ATR):  $\tilde{\nu}$  = 3358 (m), 3074 (s), 3017 (s), 2943 (s), 2849 (s), 2779 (m), 2745 (m), 2530 (w), 2469 (w), 2379 (w), 2210 (w), 1580 (m), 1443 (s), 1415 (s), 1371 (s), 1360 (s), 1341 (s), 1330 (m), 1335 (s), 1316 (s), 1279 (s), 1251 (s), 1158 (m), 1109 (s), 915 (s), 896 (m), 882 (m), 846 (w), 807 (w), 785 (w), 754 (w), 713 (m), 675 (m), 528 (w), 481 (w)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.91 (s, 6H, 2-N-CH<sub>3</sub>), 2.73 (s, 3H, N-CH<sub>3</sub>), 0.59 (s, 6H, B-CH<sub>3</sub>) ppm. –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 34.9 (2C, N-CH<sub>3</sub>), 31.8 (1C, N-CH<sub>3</sub>), 1.9 (2C, B-CH<sub>3</sub>) ppm. –  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 36.4 (2B, B-CH<sub>3</sub>), 22.4 (1B, B-ONO) ppm. –  $^{14}\text{N}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = –22 (1N, ONO), –286 (3N, borazine ring) ppm. – MS ((+)-DEI):  $m/z$  = 149.5 [M-ONO]<sup>+</sup> (calcd. 195.63 for C<sub>5</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub>B<sub>3</sub>). – EA: C<sub>5</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub>B<sub>3</sub> (195.63): calcd. N 28.64, C 30.70, H 7.73; found N 26.56, C 30.35, H 7.54%. – IS: > 40 J (grain size < 100  $\mu\text{m}$ ). – FS: 120 N (grain size < 100  $\mu\text{m}$ ). – DSC: 127 °C (dec.).

#### Synthesis of *B*-nitrosooxypentamethylborazine (3)

To a cooled solution of *B*-bromopentamethylborazine [24] (**1**) (0.14 g, 0.62 mmol) in dry acetonitrile (4 mL) silver nitrate (0.32 g, 1.86 mmol) was added, and a slightly yellow precipitate was immediately formed. The reaction mixture was stirred at room temperature and under exclusion of light for 24 h and then filtered. The solvent was removed *in vacuo*, and the obtained solid was recrystallized from dry acetonitrile. As product a colorless solid was gained (0.10 g, 80%). – IR (ATR):  $\tilde{\nu}$  = 3360 (m), 3073 (s), 3022 (s), 2949 (s), 2855 (s), 2779 (m), 2745 (m), 2530 (w), 2469 (w), 2379 (w), 2210 (w), 1580 (m), 1440 (s), 1415 (s), 1371 (s), 1360 (s), 1344 (s), 1330 (m), 1335 (s), 1318 (s), 1277 (s), 1251 (s), 1152 (m), 1109 (s), 910 (s), 896 (m), 895 (m), 841 (w), 800 (w), 790 (w), 754 (w), 721 (m), 672 (m), 528 (w), 488 (w)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.98 (s, 6H, 2-N-CH<sub>3</sub>), 2.86 (s, 3H, N-CH<sub>3</sub>), 0.55 (s, 6H, B-CH<sub>3</sub>) ppm. –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 34.3 (2C, N-CH<sub>3</sub>), 31.4 (1C, N-CH<sub>3</sub>), 1.4 (2C, B-CH<sub>3</sub>)

ppm. –  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 36.4 (2B, B-CH<sub>3</sub>), 24.3 (1B, B-ONO<sub>2</sub>) ppm. –  $^{14}\text{N}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = –46 (1N, ONO<sub>2</sub>), –286 (3N, borazine ring) ppm. – MS ((+)-DEI):  $m/z$  = 196.1 [M-O]<sup>+</sup> (calcd. 211.63 for C<sub>5</sub>H<sub>15</sub>N<sub>4</sub>O<sub>3</sub>B<sub>3</sub>). – EA: C<sub>5</sub>H<sub>15</sub>N<sub>4</sub>O<sub>3</sub>B<sub>3</sub> (211.63): calcd. N 26.47, C 28.38, H 7.14; found N 24.78, C 18.29, H 6.99%. – IS: > 40 J (grain size < 100  $\mu\text{m}$ ). – FS: 80 N (grain size < 100  $\mu\text{m}$ ). – DSC: 117 °C (dec.).

#### Synthesis of *B*-trinitrooxy-*N*-trimethylborazine (5)

*B*-Trichloro-*N*-trimethylborazine (according to ref. [22]) (**4**) (0.5 g, 2.18 mmol) was dissolved in dry acetonitrile (20 mL) and cooled in an ice bath. To the cooled and stirred solution silver nitrate (1.11 g, 6.54 mmol) was added, and a yellow precipitate was immediately formed. Under exclusion of light the mixture was stirred at room temperature for 24 h and then filtered. Evaporation of the solvent and recrystallization of the residue from dry acetonitrile gave a colorless solid (0.54 g, 81%). – IR (ATR):  $\tilde{\nu}$  = 3440 (s), 3335 (s), 3210 (s), 2930 (s), 2851 (m), 2831 (m), 2521 (w), 2390 (w), 2259 (w), 2092 (w), 2038 (w), 1683 (m), 1640 (m), 1470 (s), 1415 (s), 1256 (m), 1231 (m), 1387 (s), 1361 (s), 1340 (s), 1197 (m), 882 (w), 795 (m), 709 (m), 656 (w), 520 (w)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.83 (s, 9H, 3-N-CH<sub>3</sub>) ppm. –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 35.1 (3C, 3-N-CH<sub>3</sub>) ppm. –  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 25.6 (3B, B-ONO<sub>2</sub>) ppm. –  $^{14}\text{N}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = –46 (1N, ONO<sub>2</sub>), –139 (3N, borazine ring) ppm. – MS ((+)-DEI):  $m/z$  = for 243.5 [M-ONO<sub>2</sub>]<sup>+</sup> (calcd. 305.57 for C<sub>3</sub>H<sub>9</sub>N<sub>6</sub>O<sub>9</sub>B<sub>3</sub>). – EA: C<sub>3</sub>H<sub>9</sub>N<sub>6</sub>O<sub>9</sub>B<sub>3</sub> (305.57): calcd. N 27.50, C 11.79, H 2.97; found N 25.88, C 11.59, H 2.48%. – IS: > 40 J (grain size < 100  $\mu\text{m}$ ). – FS: 80 N (grain size < 100  $\mu\text{m}$ ). – DSC: 154 °C (dec.).

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