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Synthesis, Characterization, and Explosive Properties of the Nitrogen-Rich Borazine $[H_3N_3B_3(N_3)_3]$

Robert T. Paine,*,† Wolfgang Koestle,† Theodore T. Borek,† Gary L. Wood,†,‡ Eugene A. Pruss,† Eileen N. Duesler,† and Michael A. Hiskey§

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, and
Group DX-2, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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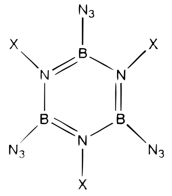
The azidoborazines $[Me_3N_3B_2(Me)_2B(N_3)]$ and $[H_3N_3B_3(N_3)_3]$ were prepared from the combination of Me_3SiN_3 and the chloroborazines $[Me_3N_3B_2(Me)_2BCl]$ and $(H_3N_3B_3Cl_3)$. The compounds have been characterized by analytical and spectroscopic methods. The molecular structure of $[H_3N_3B_3(N_3)_3]$ has been confirmed by single-crystal X-ray diffraction techniques: triclinic space group $P\bar{1}$ with $a = 8.579(1)$ Å, $b = 9.182(1)$ Å, $c = 12.043(1)$ Å, $\alpha = 104.62(1)°$, $\beta = 90.26(1)°$, $\gamma = 110.74(1)°$, and $Z = 4$. The thermal behavior of the azides have been examined by TGA/DTA. The explosion sensitivity of $[H_3N_3B_3(N_3)_3]$, which contains 82.58% nitrogen by weight, has been accessed by drop weight impact, spark, and friction tests. These measurements indicate that $[H_3N_3B_3(N_3)_3]$ is a relatively sensitive explosive. The Staudinger reactivity of the azides with Ph_3P was examined, and $[H_3N_3B_3(N_3)_3]$ was found to produce $[Ph_3P{=}NH_2](N_3)$. The molecular structure of this compound was determined by single-crystal X-ray diffraction techniques: orthorhombic space group $P2_12_12_1$ with $a = 10.649(2)$ Å, $b = 11.737(3)$ Å, $c = 13.364(4)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$.

Introduction

Azide compounds of group 13 elements are enjoying a renaissance in interest despite a reputation for fickle and nefarious behavior on the part of some derivatives.[1,2] With proper experimental care and attention, it appears that unpredictable explosive and poison hazards can be minimized and the chemistry of most compounds can be effectively studied. In fact, several derivatives are found to be useful starting materials for the formation of new ring compounds as well as for the synthesis of solid-state materials. Boron azides[3] appear to be particularly useful for these purposes. For example, Paetzold and coworkers[4] have described thermally promoted decompositions of simple azidoboranes, R_2BN_3 (R = alkyl, aryl, amino), that produce iminoboranes, $RB{\equiv}NR$. These compounds are stable where sufficient steric protection of the coordinatively unsaturated boron and nitrogen atoms is provided. Alternatively, the reactive iminoboranes form diazadiboretidine, $(RB{=}NR)_2$, or borazine, $(RB{=}NR)_3$, condensation products.[5]

A few borazines containing *B*-azido substituents, **1**, have been reported;[3] however, limited characterization or reactivity data are available for these compounds. In particular, Muszkat and co-workers,[6] in 1963, briefly noted the formation of tri-*B*-azidoborazines, $(HNBN_3)_3$ (**2**), $(CH_3NBN_3)_3$ (**3**), and $(C_6H_5NBN_3)_3$ (**4**) from metathesis reactions of NaN_3 with the respective tri-*B*-chloroborazines. Compound **2** was reported to be a white solid that did not melt below 300 °C. It contained about 10% chlorine impurity, and it exploded when attempts were made to purify it. This molecule was subsequently described in a patent,[7] and it was obtained chlorine free by extensive reflux of the reactants in chlorobenzene. The only additional characterization datum provided was the azide infrared stretching frequency. Meller and Wechsberg[8] also reported the synthesis of **3**, $(CD_3NBN_3)_3$, and $(EtNBN_3)_3$ (**5**) by similar reactions.



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We have a general interest in the chemistry of group 13 azides as solid-state materials precursors, and we report here investigations of two azidoborazines. The synthesis and characterization of the previously unknown 1-*B*-azidopentamethylborazine

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[†] University of New Mexico.

[‡] On sabbatical leave from Valdosta State College, Valdosta, GA.

[§] Los Alamos National Laboratory.

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$[Me_3N_3B_2(Me)_2B(N_3)]$ (**6**) are described along with an improved synthesis for triazidoborazine **2**. In addition, detailed characterization data are provided along with a description of the explosive sensitivity of **2**.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and products. Solvents were dried and degassed by standard methods, vacuum-distilled, and stored over an appropriate drying agent. All solvent transfers were accomplished by vacuum distillation. Azidotrimethylsilane was purchased from Aldrich and used as received. 2,4,6-Trichloroborazine and 6-chloro-1,2,3,4,5-pentamethylborazine were prepared as described in the literature.[9,10] Infrared spectra were obtained on a Nicolet 6000 FT-IR instrument. NMR spectra were recorded on Bruker 250 MHz and JEOL 400 MHz spectrometers. Spectral standards were Me_4Si (^1H, ^{13}C) and $F_3B{\cdot}OEt_2$ (^{11}B). Resonances downfield of the standards were assigned as $+\delta$. Mass spectra were measured on a Finnegan model 4500 GC/MS instrument with use of a solids probe. Elemental analyses were obtained from the UNM Microanalytical Services facility and Galbraith Laboratories. Thermogravimetric (TGA) and differential thermal analyses (DTA) were obtained from a Delta Series TGA7 analyzer (range 50−1400 °C, 10° min^{-1}, Ar atmosphere, 25 cm^3 min^{-1}). X-ray powder diffraction analyses were obtained with a Scintag model PAD-V diffractometer (Cu Kα radiation).

Caution! All of the azidoborazine materials described here should be handled with extreme caution. All may vigorously explode under various conditions.

Synthesis and Characterization of Compounds. 2,4,6-Triazidoborazine (2). A solution of Me_3SiN_3 (5.3 mL, 4.60 g, 40.0 mmol) in diethyl ether (40 mL) was added to a solution of $(HNBCl)_3$ (2.45 g, 13.3 mmol) in diethyl ether (40 mL) held at −78 °C. The mixture was allowed to warm slowly, and it was stirred at 23 °C (12 h). The solvent and volatile residues were removed by vacuum evaporation leaving a white solid. The solid was redissolved in fresh Et_2O (40 mL), the mixture was filtered, and the solvent was evaporated, leaving white solid **2**: yield 2.1 g (97%). The solid could be further purified by recrystallization or sublimation. Recrystallizations could be accomplished from a minimum volume of cold (−20 °C) Et_2O or tetrahydrofuran (THF). Sublimation was accomplished with an ice-cooled coldfinger in a standard vacuum sublimator with an oil bath temperature of ∼110 °C or with a simple evacuated glass tube placed in an oven (107 °C) with a small heat gradient. Sublimations were complete and thin platelet crystals formed. Purified samples displayed sharp melting points: 152−153 °C. Soluble: Et_2O, THF, CH_3CN, CH_2Cl_2. Sparingly soluble: benzene, toluene, hexane. Mass spectrum (30 eV) [m/e (%)]: 204, M^+ (100). Infrared spectrum (KBr; cm^{-1}): 3424 (s), 3409 (m), 3363 (s), 2144 (s), 1465 (s), 1382 (m), 1310 (m), 1069 (m). NMR spectra (C_6D_6): $^{11}B\{^1H\}$ δ 26.5; ^1H δ 3.43. Anal. Calcd for $H_3B_3N_{12}$ (M_r = 203.57): H, 1.48; N, 82.6; B, 15.93. Found: H, 1.56; N, 79.89; B, 15.21; C, 1.57.

6-Azido-1,2,3,4,5-pentamethylborazine (6). A solution of Me_3SiN_3 (2.6 mL, 2.26 g, 19.6 mmol) in Et_2O (50 mL) was added to a solution of $[Me_3N_3B_2(Me)_2B(Cl)]$ (3.63 g, 19.6 mmol) in Et_2O (50 mL) at −78 °C. The mixture was slowly warmed to 23 °C and stirred (12 h). The resulting solution was filtered and the solvent evaporated from the filtrate, leaving a colorless oil, which was vacuum-distilled (75−78 °C, 74 mTorr). A colorless oil, **6**, was collected: yield 3.48 g (93%). The oil slowly crystallized upon standing: mp 70−72 °C. Soluble: Et_2O, THF, CH_3CN, toluene. Mass spectrum (30 eV) [m/e (%)]: 193, M^+ (61). Infrared spectrum (KBr; cm^{-1}): 2952 (s), 2916 (s), 2835 (m), 2154 (vs), 2147 (vs), 1472 (vs), 1457 (vs), 1416 (vs), 1376 (vs), 1279 (s), 1257 (m), 1091 (s), 1019 (s), 880 (s), 656 (m), 625 (m), 574 (m). NMR spectra (C_6D_6): $^{11}B\{^1H\}$ δ 37.2 ($B_{3,5}$), 25.0 (B_1); ^1H δ 2.70 (6H, $N_{1,5}$-CH_3), 2.62 (3H, N_3-CH_3), 0.32 (6H, $B_{2,4}$-CH_3); $^{13}C\{^1H\}$ δ 34.46 (N_3CH_3), 32.48 ($N_{1,5}$-CH_3), −0.5 (BCH_3). Anal. Calcd for $C_5H_{15}N_6B_3$ (M_r = 191.65): C, 31.34; H, 7.89; N, 43.85. Found: C, 31.42; H, 7.93; N, 41.59.

Reaction of $(HNBN_3)_3$ with Ph_3P. A sample of **2** (0.72 g, 3.54 mmol) and Ph_3P (0.93 g, 3.54 m mol) were dissolved in THF (50 mL), and the mixture was refluxed (12 h). A colorless solid (1.3 g) formed that was insoluble in THF, toluene, Et_2O, and hexane. The solid was then refluxed with CH_3CN (20 mL) for 30 min, and the mixture was filtered while hot. The filtrate was slowly concentrated to 5 mL, and colorless crystals of **7** were deposited: yield 0.47 g (41.6%); mp 183 °C dec.

Pyrolysis of $(HNBN_3)_3$, 2. The bulk pyrolysis of **2** was examined by using a standard horizontal tube furnace. A sample of **2** (0.67 g, 3.3 mmol) was placed in a Pt crucible, and this was loaded, under dry nitrogen, into a quartz pyrolysis tube. The tube was purged with a slow stream of N_2 gas and heated to 1200 °C (8 h). The solid remaining in the crucible (0.1 g, 15%) was bone-colored. Infrared spectrum (KBr; cm^{-1}): 1390 (vs), 791 (m). XRD (d, Å): 3.47 (002), 2.12 (100). Anal. Calcd for BN (24.82): B, 43.56; N, 56.44. Found: B, 43.10; N, 55.75; C, 0.93.

Explosive Sensitivity Characterization of $(HNBN_3)_3$, 2. Three small-scale tests have been designed to evaluate the sensitivity of energetic materials to stimuli which may cause accidental initiation. The drop-weight machine or drop hammer evaluates impact sensitivity. In the test, a 2.5 kg weight is dropped from a set height onto a 40 mg sample of the explosive on 150 grit garnet sandpaper. A series of drops is made from different heights and explosion or nonexplosion is recorded. The criterion for explosion is a sound level of 120 dB recorded from a microphone set 33 in. from the point of initiation. The test results are summarized as H_{50}, the height in centimeters at which the probability of explosion is 50%. The H_{50} of **2** was determined to be 16.2 cm.

The second test evaluates the susceptibility to initiation by human electrostatic discharge. The test is performed by placing approximately 10 mg of energetic material in an insulating plastic cup with a conductive steel base. The sample is covered with Pb foil and the entire assembly held in place by an insulating plastic cover containing a hole to expose the Pb foil. This assembly is centered below a brass dressmaker's needle, and the steel base and needle are charged to a difference of 15.24 kV. The needle is then lowered, piercing the foil, and a spark is discharged through the energetic material when the needle is 0.085 in. above the steel base. The total energy of the spark is 0.36 J and is a conservative value for the amount of electrostatic energy discharged by the human body. The test is interpreted by examining the Pb foil for tears or other damage as evidence of reaction. Compound **2** was determined not to be sensitive to human electrostatic discharge.

The final test determines the initiation sensitivity of an energetic material to friction. This test is performed by placing approximately 1 mg of material on a porcelain plate underneath a rounded porcelain striker. The striker is pivotal to an arm of variable length to which weights are hung, allowing different loads to be achieved between the porcelain grinding surfaces. The plate is then mechanically driven underneath the striker at a given load. The criterion for reaction is an audible or visual reaction or both as detected by the operator. The test results are reported as a 50% load, the weight in kilogram where the probability of initiation is 50%. The 50% load for compound **2** was determined to be 10.6 kg.

Crystallographic Measurements and Structure Solutions. Suitable crystals of **2** and **7** were obtained by sublimation and slow solvent evaporation, respectively. Crystals were mounted in glass capillaries under nitrogen and centered on a Syntex P3/F automated diffractometer. Determinations of the crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner. Data were collected with use of Mo Kα radiation (λ = 0.710 73 Å), a highly oriented graphite crystal monochromator, a scintillation counter, and a pulse height analyzer. Selected data collection parameters are summarized in Table 1. The space group assignments[11] were made by inspection of small data sets, and absorption corrections were made on the basis

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(11) Space group notation: *International Tables for X-ray Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. I, pp 73−346.

Table 1. Crystallographic Data for **2**, $[HNB(N_3)]_3$, and **7**, $[Ph_3PNH_2](N_3)$

	2	**7**
chem formula	$H_3B_3N_{12}$	$C_{18}H_{17}N_4P$
fw	203.57	320.33
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	8.579(1)	10.649(2)
b, Å	9.182(1)	11.737(3)
c, Å	12.043(1)	13.364(4)
α, deg	104.62(1)	90
β, deg	90.26(1)	90
γ, deg	110.74(1)	90
V, Å^3	853.8(2)	1670.4(7)
Z	4	4
D_{calcd}, g cm^{-3}	1.584	1.274
T, °C	20	20
μ, cm^{-1}	0.120	0.169
λ(Mo Kα), Å	0.710 73	0.710 73
R_F/R_{wF},^{a} %	2.89/5.76	3.34/5.09

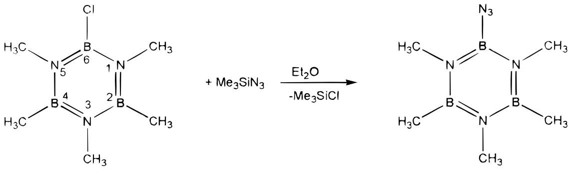
^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF} = \Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]$, $w^{-1} = \sigma^2(F) + gF^2$.

of ψ scans.[12] Redundant and equivalent data were averaged and converted to unscale $|F_o|$ values following corrections for Lorentz and polarization effects. There was a small (~2%) decrease in the intensities of the standard reflections of **2**, but no corrections were applied.

All calculations were performed on Siemens SHELXTL PLUS (Microvax II and PC versions)[13] structure determination systems. Solutions of the data sets were by direct methods, and full-matrix least-squares refinements were employed.[14] Neutral-atom scattering factors and anomalous dispersion terms were used for all non-hydrogen atom coordinates during the refinements. Listings of non-hydrogen atom coordinates, anisotropic thermal parameters, hydrogen atom coordinates, and bond distances and angles are provided in the Supporting Information.

Results and Discussion

The existence of 6-azido-1,2,3,4,5-pentamethylborazine, **6**, apparently has not been reported previously. The compound is obtained in high yield as a colorless crystalline solid from the 1:1 combination of Me_3SiN_3 and 6-chloro-1,2,3,4,5-pentamethylborazine in Et_2O (eq 1). The compound is indefinitely stable[15] in the absence of moisture; however, it slowly hydrolyzes in damp air. The compound is analytically pure, and it melts sharply without decomposition. Upon cooling, it recrystallizes.

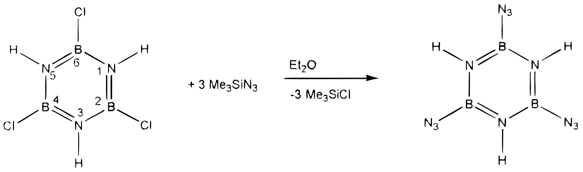


6

(1)

Compound **6** displays an intense parent ion in its EI mass spectrum along with several fragment ions: the most intense ion corresponds to $(M - N_2)^+$ at *m*/*e* 162. The infrared spectrum of **6** is very similar to the spectrum of $(CH_3NBN_3)_3$.[8] On the basis of assignments given by Meller,[8] intense bands at 2154 and 2147 cm^{-1} may be assigned to azide stretching frequencies. The ^{11}B NMR spectrum of **6** shows two resonances centered at δ 37.2 and 25.0 in a 2:1 ratio. The lower field resonance can be confidently assigned to the two equivalent $B_{2,4}-Me$ groups based upon chemical shift[16,17] and area ratio. The higher field resonance is assigned to the B_6-N_3 group. This shift is in the general region found for *B*-pseudohalogen-substituted borazines.[17] The ^1H NMR spectrum shows resonances at δ 2.70, 2.62, and 0.32 in a 2:1:2 ratio that are assigned to $N_{1,5}-CH_3$, N_3-CH_3, and $B_{2,4}-CH_3$, respectively. The $^{13}C\{^1H\}$ NMR spectrum contains resonances at δ 32.48, 34.46, and −0.5 that are assigned to $N_{1,5}-CH_3$, N_3-CH_3, and $B_{2,4}-CH_3$, respectively.

Triazidoborazine, **2**, as noted in the Introduction, has been previously reported to form from combination of $(HNBCl)_3$ and NaN_3.[6,7] On the basis of the descriptions in the literature, the product is not obtained in a pure state, and this may be responsible for the reported tendency for samples to easily detonate. Paetzold and co-workers[4] have noted that azidoboranes can be conveniently prepared by reactions of B−Cl groups with Me_3SiN_3. The obvious benefits of this reagent include the facts that Me_3SiN_3 is readily soluble in organic solvents and the elimination product, Me_3SiCl, is volatile and easily removed along with solvent by vacuum evaporation at 23 °C. No salt byproducts are formed that require separation from reaction mixtures. In practice, the 1:3 combination of $(HNBCl)_3$ with Me_3SiN_3 in Et_2O results in ready elimination of Me_3SiCl at 23 °C with formation of the target species **2** in high yield (eq 2).



2

(2)

Compound **2** is relatively pure when recovered by vacuum evaporation of the solvent and Me_3SiCl, although elemental analysis suggests a small retention of organic solvent in the crude product. Samples were further purified by recrystallization from cold Et_2O or THF or by vacuum sublimation at ~110 °C. Given the earlier reports,[6] it was surprising that no evidence for detonation of samples of **2** during workup were encountered. Nonetheless, as described below, this compound does detonate under some conditions and care should be exercised in working with the compound. Unlike previous reports, pure samples of **2** display a sharp melting point at 152−153 °C. Compound **2** is easily introduced into a mass spectrometer; it shows a parent ion envelope in the EI mass spectrum (*m*/*e* 204−202), and the ion at *m*/*e* 204 is the base peak in the spectrum. The fragment-atom pattern is rich in species, and it is noted that ions corresponding to $(M - N_2)^+$ and $(M - 3N_2)^+$ are observed. The infrared spectrum of **2** contains a strong band at 2144 cm^{-1} that is assigned to the azide stretching mode. The ^{11}B NMR

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(12) The empirical absorption corrections use an ellipsoidal model fitted to azimuthal scan data that are then applied to the intensity data: *SHELXTL Manual,* Revision 4; Nicolet XRD Corp.: Madison, WI, 1983.

(13) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses absorption, anomalous dispersion, and scattering data compiled in: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 55−60, 99−101, 149−150. Anomalous dispersion terms were included for all atoms with atomic numbers greater than 2.

(14) A general description of the least-squares algebra is found in: *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinement minimizes $\Sigma w(|F_o - F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$.

(15) Samples have been stored under dry nitrogen in our laboratory for more than 4 years with no visible decomposition.

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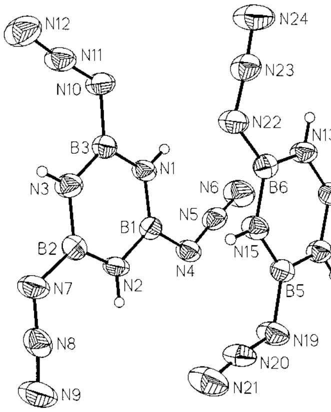


Figure 1. Molecular structure and atom-labeling scheme for $[HNB(N_3)]_3$, **2**. The view shows both unique molecules in the asymmetric unit.

Table 2. Bond Lengths (Å) and Angles (°) for 2 $[HNB(N_3)]_3$

(a) Bond Lengths

molecule 1

B(1)−N(1)	1.411(2)	B(3)−N(10)	1.455(2)
B(1)−N(2)	1.420(2)	N(4)−N(5)	1.242(2)
B(2)−N(2)	1.419(2)	N(5)−N(6)	1.125(2)
B(2)−N(3)	1.419(2)	N(7)−N(8)	1.229(2)
B(3)−N(3)	1.423(2)	N(8)−N(9)	1.127(2)
B(3)−N(1)	1.416(2)	N(10)−N(11)	1.230(2)
B(1)−N(4)	1.467(2)	N(11)−N(12)	1.129(2)
B(2)−N(7)	1.453(2)		

molecule 2

B(4)−N(13)	1.412(2)	B(6)−N(22)	1.458(2)
B(4)−N(14)	1.424(2)	N(16)−N(17)	1.225(2)
B(5)−N(14)	1.420(2)	N(17)−N(18)	1.129(2)
B(5)−N(15)	1.412(2)	N(19)−N(20)	1.234(2)
B(6)−N(15)	1.427(2)	N(20)−N(21)	1.128(2)
B(6)−N(13)	1.414(2)	N(22)−N(23)	1.245(2)
B(4)−N(16)	1.460(2)	N(23)−N(24)	1.124(2)
B(5)−N(19)	1.460(2)		

(b) Bond Angles

B−N−B(ring)$_{av}$	B−N−B(ring)$_{av}$
N−B−N(ring)$_{av}$	N−B−N(ring)$_{av}$
N−N−N$_{av}$	N−N−N$_{av}$

(c) Hydrogen-Bonding Parameters

N−H···N$_x$	sym *x*	H···N$_x$	N···N$_x$	N−H−N^x	H−N$_x$−N
Type **9** H-Bonds					
N(1)−H(1a)···N(9)	$x, 1 + y, z$	2.474	3.244	149.4	152.9
N(2)−H(2a)···N(18)	$-x, -y, 1 - z$	2.386	3.233	168.2	139.4
N(13)−H(13a)···N(21)	$x, 1 + y, z$	2.466	3.253	152.6	152.9
N(15)−H(15a)···N(12)	$1 - x, -y, -z$	2.3328	3.184	173.2	142.0
Type **9′** H−Bonds					
N(3)−H(3a)···N$_{22}$	$1 - x, -y, -z$	2.735	3.557	160.4	102.3
N(14)−H(14a)···N(4)	$-x, -y, 1 - z$	2.776	3.583	157.0	104.1

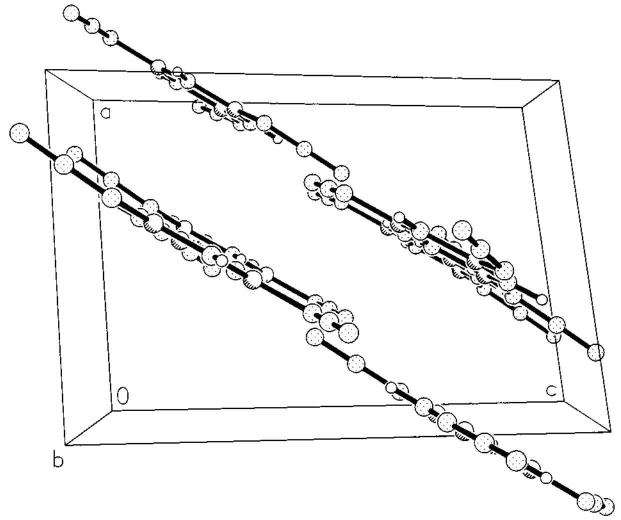
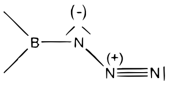


Figure 2. Unit cell projection along the *b* axis for $[HNB(N_3)]_3$, **2**.

spectrum displays a single resonance, *δ* 26.5, and this resonance position is comparable to that assigned to the B−N$_3$ group in **6**. The ^{1}H NMR spectrum contains a broad singlet at *δ* 3.43 that is assigned to the N−H group.

Sublimation of samples of **2** produced X-ray-quality single crystals, and the molecular structure of **2** was consequently determined by X-ray diffraction techniques. A view of the molecule is shown in Figure 1, and selected bond lengths and angles are summarized in Table 2. There are two unique molecules in the asymmetric unit and four molecules in the unit cell. Both molecule 1 and molecule 2 are completely planar. In molecule 1, the mean deviation, including all atoms, is 0.004 Å, with the largest deviations occurring for N(9), −0.156 Å, N(11), 0.150 Å, and N(12), 0.269 Å. In molecule 2, the mean deviation is 0.003 Å, with the largest deviations appearing for N(18), 0.111 Å, and N(24), 0.106 Å. The two rings lie in parallel planes with an interplanar angle of <2°. This arrangement is nicely illustrated in a unit cell view shown in Figure 2. The average B−N(ring) bond length, 1.418 Å, is comparable with the average B−N(ring) distance in $[(HN)_3(HB)_2BNH_2]$,[18] 1.418 Å, while these are shorter than the average B−N(ring) distances in $(HNBH)_3$[19], 1.436 Å, and $(HNBNMe_2)_3$,[20] 1.433 Å. As expected, the average B−N(ring) distance in **2** is shorter than the average exo B−N$_3$ distance, 1.459 Å. The average internal borazine ring angles are B−N−B = 121.8° and N−B−N = 118.2°. The exo azido groups are slightly bent, N−N−N(av) = 174.4°, and they form an average B−N−N angle of 118.5° with the borazine ring. The average BN−N distance in the exo azido groups, 1.234 (2) Å, is clearly shorter than the typical N−N single-bond distance (1.45 Å)[2e] and more comparable to an N═N double-bond distance (1.25 Å).[2e] This distance in **2** also is shorter than the comparable distance in cyanuric azide $(NCN_3)_3$, 1.266 (2) Å.[21] The average terminal N−N distance in the azido groups, 1.127 (2) Å, is longer than a typical N≡N distance, 1.098 Å,[2e] and it is also longer than the related distance in $(NCN_3)_3$, 1.116 (2) Å. These data suggest that the charge distribution in the B−N−N−N fragments of **2** may be somewhat less asymmetric than found in the C−N−N−N fragments of $(NCN_3)_3$. That is, the classical valence bond representation depicted by **8** is favored over that of **8′**.[21] One mechanism that might contribute to this structural feature is hydrogen bonding. There are two potential idealized H-bond interaction modes,



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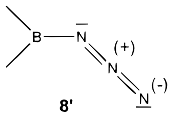

8'

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(19) Harshbarger, W.; Lee, G. H.; Porter, R. F.; Bauer, S. H. *Inorg. Chem.* **1969**, *8*, 1683.

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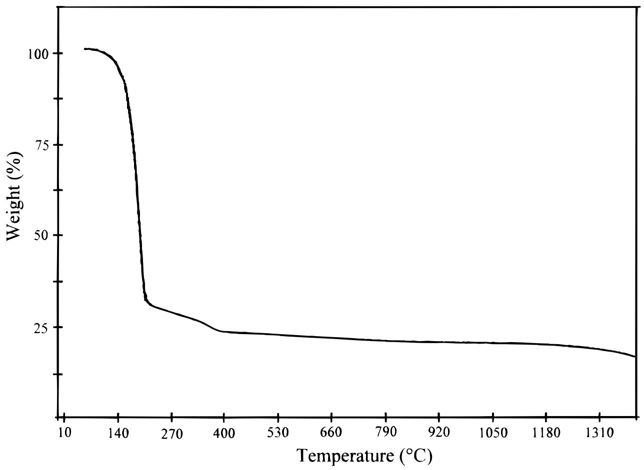
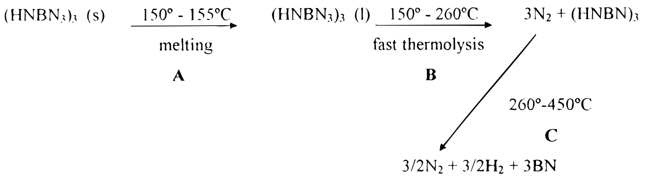
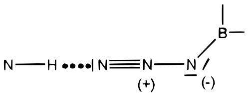


Figure 3. TGA trace for **2**.

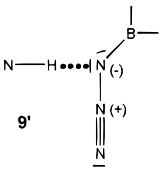
Scheme 1



and they are depicted by **9** and **9′**. H(1a), H(2a), H(3a), H(13a), H(14a), and H(15a) are capable of participating in H-bonding with neighboring azido groups in a second molecule, and calculated distances between molecules **1** and **2** are listed in Table 2. It is obvious that the range of observed distances of the type depicted by **9** (2.33−2.47 Å) is shorter than the range represented by **9′** (2.74−2.78 Å). Such interactions would be expected to weaken and lengthen the idealized terminal N≡N triple bond interaction.



9



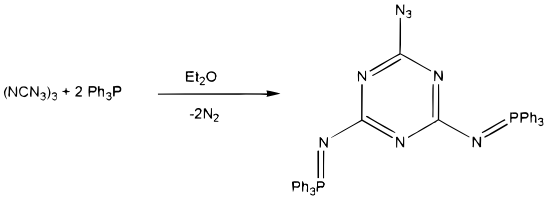
9′

A TGA trace for **2** is presented in Figure 3. It shows an abrupt weight loss (∼70%) in the temperature range 50−220 °C followed by a more gradual loss (∼7%) from 220 to 460 °C. The average (four runs) total weight loss was 77%. The DTA shows a major endotherm centered at 155 °C that corresponds to the melting process and two exotherms centered at ∼260 and ∼420 °C. These events appear to be consistent with the processes summarized in Scheme 1. The theoretical weight losses accompanying these three idealized steps are as follows: step A, 0%; step B, 41.3%; step C, 22.1% (total 63.4%). The observed TGA trace shows an ∼5−10% weight loss prior to melting, which may result from loss of recrystallization solvent. Taking this into account, the observed total weight loss is close to that calculated. The larger observed weight loss in step B is consistent with a fast thermolysis event.

The TGA analysis data and Scheme 1 suggest that **2** should be a precursor for BN, although with low ceramic yield. In fact, careful pyrolysis of samples (0.5−1.0 g) of **2** using a tube furnace (1200 °C) produces BN powder. The samples have a bone color, instead of the expected pure white color and elemental analyses show small, variable carbon contamination (1−2%). The carbon likely comes from small amounts of organic solvent left from recrystallization of **2**. Powder XRD of the ceramic powder shows two broad reflections: $2d$ (Å) = 3.47 and 2.12. The breadths and positions of the reflections are consistent with formation of turbostratic BN with small particle size.

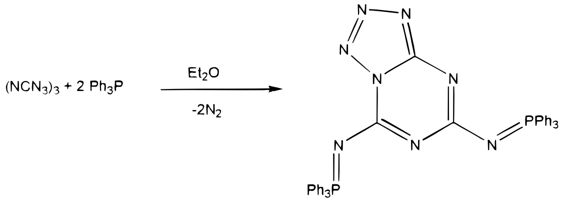
The explosive sensitivity properties of **2** reveal that this material is sensitive to both impact and friction. A drop-weight-impact test on a 40 mg sample of **2** gave an H_{50} value of 16.2 cm, which compares to a value of 22.9 cm for HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocine) or 14 cm for PETN (pentaerythritol tetranitrate). Usually any value of 14 cm or less is considered extremely hazardous. Furthermore, a friction sensitivity test on **2** showed extreme ease of initiation, which is not uncommon behavior for azides. A value of 10.6 kg compares with 13.0 kg for PETN. PETN is considered a primary explosive to both impact and friction. Electrostatically this compound is safe to handle, as a 0.36 J spark failed to elicit any reaction. These results confirm that **2** should be handled with considerable caution.

The reactivities of **2** and **6** are also of interest, and in this respect, we examined the Staudinger reactivities[22] of **2** and **6** toward Ph_3P. Parallel chemistry with $(NCN_3)_3$ was first reported by Kesting,[23] and the suggested outcome is summarized in eq 3. This chemistry was recently reexamined by Klapötke and co-workers,[21] and instead of **10**, the product isolated was the interesting tetrazole isomer **11**, shown in eq 4. In the case of **6**, we observe that the 1:1 reaction with Ph_3P leads to no discernible reaction, as **6** is quantitatively recovered. Reaction of **2** with Ph_3P in a 1:1 ratio in refluxing THF gives a colorless solid (**7**) with limited solubility and a melting point of 183 °C. The melting is accompanied by gas evolution.



(3)

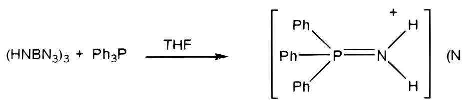
10



(4)

11

A single-crystal X-ray diffraction analysis led to the identification of the product as depicted in eq 5. The compound crystallizes in the chiral space group $P2_12_12_1$, and the asymmetric unit is composed of the $[Ph_3P{=}NH_2^+]$ cation and N_3^- anion. A view of the molecule is displayed in Figure 4, and selected bond lengths and angles are summarized in Table 3.



(5)

7

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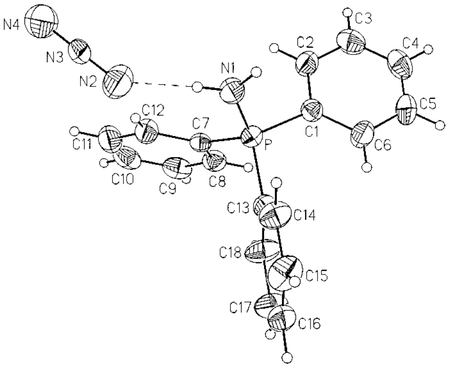


Figure 4. Molecular structure and atom-labeling scheme for $[Ph_3P{=}NH_2](N_3)$, **7**.

Table 3. Bond Lengths (Å) and Angles (deg) for **7**, $[Ph_3PNH_2](N_3)$

(a) Bond Lengths

P−N(1)	1.612(3)	P−C(13)	1.803(3)
P−C(1)	1.785 (3)	N(2)−N(3)	1.154(3)
P−C(7)	1.794(3)	N(3)−N(4)	1.148(4)

(b) Bond Angles

N(1)−P−C(1)	106.9(2)	C(1)−P−C(7)	109.8(1)
N(1)−P−C(7)	109.8(2)	C(7)−P−C(13)	107.3(1)
N(1)−P−C(13)	113.1(2)	N(2)−N(3)−N(4)	176.8(4)
C(1)−P−C(13)	109.9(2)		

(c) Hydrogen Bonding Parameters

N−H···N_x	sym *x*	N−H	H···N	N···N	N−H···N
N−H(1a)···N(2)	*x*, *y*, *z*	0.919	1.957	2.785	176.9
N−H(1b)···N(4)	0.5 + *x*, 0.5 − *y*, −*z*	0.918	1.964	2.865	166.6

There is no crystallographic symmetry on the unit. The arrangement of groups about the phosphorus atom is tetrahedral with average C−P−C and C−P−N angles of 108.7 and 109.9°, respectively. The P−N(1) distance, 1.162(3) Å, is close to the ideal double-bond distance, P=N, of 1.57 Å as compared to the normal P−N single-bond length, 1.76 Å.[24]

The azide group is linear, N(2)−N(3)-N(4) = 176.8(4)°, with N−N bond distances of N(2)−N(3) = 1.154(3) Å and N(3)−N(4) = 1.148(3) Å. These distances compare well against those in $(Me_4N)N_3$,[25] 1.155(5) and 1.176(5) Å, and other ionic azides.[26] There is hydrogen bonding between the azide and NH_2 group, and the network is shown in Figure 5. The bond lengths and angles in one unit are also listed in Table 3. It is interesting to note that **7** was probably first observed by Staudinger in 1921;[27] however, it has been assumed to have a cyclic nonionic tetrazole structure represented by **12**, because the compound reacts slowly with Ag(I). A related trityl azide−triphenylphosphine adduct has been postulated;[28] however, in view of the structure determination of **7**, this proposal should be revisited.

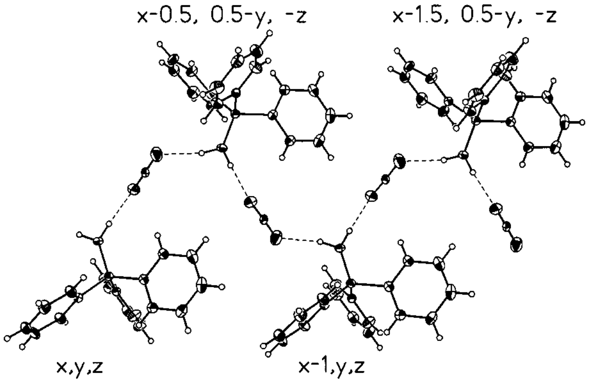
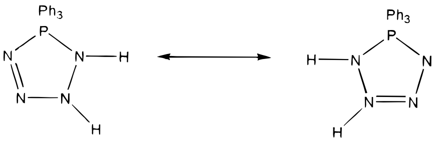


Figure 5. Hydrogen-bonding chains for $[Ph_3P{=}NH_2](N_3)$, **7**.



12

The synthesis, structure, reactivity, and explosive characteristics of **2** described here provide interesting new information on this known but poorly understood molecule. In addition, the data collected here suggest that **2** is a precursor to boron nitride and a confined-volume, high-energy synthesis may provide a method to obtain new powder morphologies of BN. Further studies of the explosive performance characteristics are underway, and they will be reported later along with results from electronic structure calculations.

Acknowledgment. R.T.P. thanks the UNM Center for Microengineered Materials (CMEM) and the National Science Foundation (Grant CHE-9508668) for support of this research.

Supporting Information Available: Additional information on the collection of X-ray data, final atomic coordinates, H atom coordinates, thermal parameters, and bond lengths and angles for **2** and **7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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