3,6-Bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazene (BNDD): A Powerful Sensitive Explosive

Philip W. Leonard,*[a] Colin J. Pollard,[a] David E. Chavez,[a] Betsy M. Rice,[b] Damon A. Parrish[c]

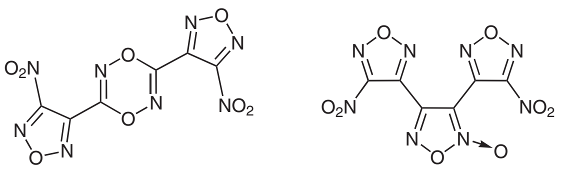
[a] Los Alamos National Laboratory, Weapons Experiments Division, Los Alamos, NM 87545, USA
[b] Army Research Laboratory, Aberdeen Proving Grounds, Aberdeen, MD 20783, USA
[c] Naval Research Laboratory, Laboratory for the Structure of Matter, Washington, DC 20375, USA
Fax +1(505)6670500; E-mail: philipl@lanl.gov

Received 23 May 2011

Abstract: The explosive 3,6-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazene (BNDD) was synthesized by oxidation of the corresponding diamine using hydrogen peroxide in sulfuric acid with sodium tungstate. The product exhibited detonations during sensitivity testing at low insult; the material is shock and friction sensitive. The synthesis of BNDD should only be pursued by knowledgeable researchers exercising extreme caution.

Key words: explosives, furazan, heterocycles, nitrogen, oxidation

Considerable interest has been given to the explosive material 3,4-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole 2-oxide [BNFF (**2**)] as a new potential main charge explosive.[1–3] BNFF, in older papers referred to as DNTF, has a high density (1.94 g/cc) and a high enthalpy of formation, implying strong performance. Sensitivity testing at Los Alamos National Laboratory (LANL) revealed that BNFF has an undesirable response to impact being considerably more sensitive than RDX as shown in Table 1. Consequently we endeavored to synthesize the constitutional isomer of BNFF, 3,6-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazene [BNDD (**1**), Figure 1] in the hopes of discovering a less sensitive but equally energetic material. BNDD has been mentioned in one patent and one unpublished report.[4] Energetic derivatives of the corresponding diamine [BADD (**5**), Scheme 1] have been published[5] however no detailed report of the sensitivity or thermodynamic properties of **1** was previously available in the open literature.

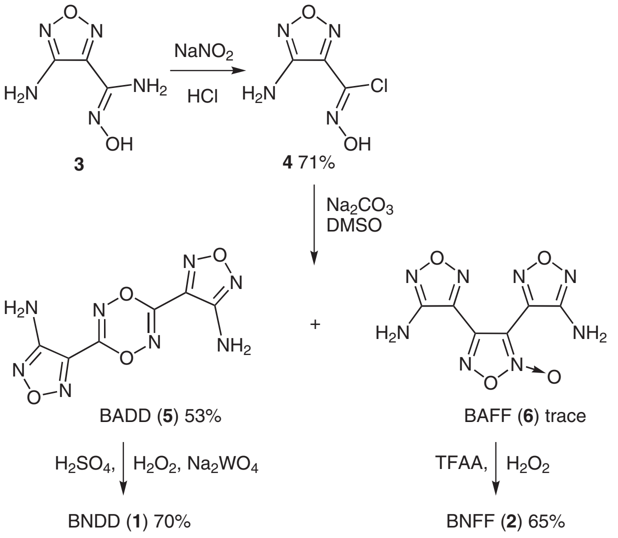


BNDD (**1**) BNFF (**2**)

Figure 1 The isomeric explosives BNDD (**1**) and BNFF (**2**)

Synthesis

As shown in Scheme 1, from 4-amino-*N′*-hydroxy-1,2,5-oxadiazole-3-carboximidamide (**3**), the corresponding imidoyl chloride, **4**, was formed by diazotization in aqueous HCl. The product was recovered in good yield and purity; however, it is a strong irritant to the skin and an inhalation hazard. Deprotonation of **4** in DMSO using aqueous sodium carbonate accomplishes selective dimerization to the dioxadiazene, **5**, through the intermediacy of the nitrile oxide.[6] This outcome is in contrast to the same reaction performed in a biphasic mixture of diethyl ether and water which provided primarily **6** (BAFF), with **5** as a significant contaminant.[7] More polar organic solvents, including DMSO, encourage formation of **5** as discussed by Lim et al.[2] Amine oxidation of the dioxadiazene isomer to the corresponding dinitro derivative **1** is notably more difficult than the equivalent transformation to make BNFF. Application of hydrogen peroxide in trifluoroacetic acid to **5** resulted only in the recovery of starting material whereas these conditions are sufficient to make BNFF in good yield. From Sheremetev's methods we ultimately ascended to the vigorous oxidant mixture of 90% hydrogen peroxide and sodium tungstate in sulfuric acid.[8] A considerable excess of sodium tungstate, added in stages, was required to drive the oxidation reaction to completion. Temperature control was critical as the reaction



Scheme 1 Synthesis of nitrofurazans **1** and **2**

SYNLETT 2011, No. 14, pp 2097–2099
Advanced online publication: 10.08.2011
DOI: 10.1055/s-0030-1261169; Art ID: S04611ST

would either fail to go to complete conversion or overheat and destructively outgas if improperly managed. Once proper conditions were discovered, isolation of the product was accomplished by quenching into water followed by filtration.

Physical Properties

BNDD is a white odorless crystalline powder. ^{13}C NMR gives the expected three signals; $\delta = 139.7$ and 152.4 ppm and a broad resonance at 159.9 ppm. After initial sensitivity testing we elected not to scaleup BNDD beyond gram quantities. BNDD was more sensitive to impact and spark than PETN run on the same instrument under the same conditions (see Table 1). Striking more than 10 mg of BNDD on a metal anvil with a hammer resulted in an incredibly loud report (hearing protection is strongly recommended). Preliminary D_H 50 measurements on a type 12 drop weight impact apparatus using the Neyer D-optimal method for statistical sampling gave a drop height of 8.8 cm, corresponding to an impact energy of 2.2 joules. Scraping the material never accomplished audible or visual evidence of initiation, however BNDD evinced a friction sensitivity of 116 N on the BAM friction test. Electrostatic discharge testing at LANL is expressed as the 3.4% threshold initiation level (TIL) for detonation. For BNDD the TIL was below 0.0625 J, a highly spark-sensitive compound. It should be noted that although the sensitivity of BNDD is significantly less than that of most primary explosives (e.g., lead azide) every event in spark, friction, and impact testing at the lowest insult was a 'high-order' detonation. As many materials show a graded response based on severity of insult, BNDD is especially hazardous because it is in exception to the normal insult-response relationship.

Table 1 Comparative Sensitivity of BNDD to PETN and RDX

Material	Impact D_H 50 [J]	Friction BAM [N]	Spark ABL 3.4% TIL[a] [J]	Exo.[b] onset/ peak DSC [°C]
BNDD	2.2	116	<0.0625	148/198
BNFF	3.1	213	0.0625	241/275
PETN	2.7	110	0.0625	168/205
RDX	14.7	180	0.125	200/217

[a] Threshold initiation level.
[b] Exo = exothermal.

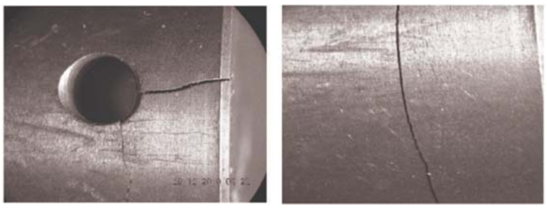


Figure 2 Damage to the impact testing striker

After six impacts during drop hammer testing it was discovered that both the anvil and striker of the impact testing apparatus had been fractured. Photographs of the damage to the striker are shown in Figure 2. Although not unheard of, this type of damage to the impact testing equipment is unusual and is generally indicative of material with a high detonation velocity.

X-ray Crystallography

X-ray quality crystals were grown from acetone by slow evaporation of the mother liquor. The structure of BNDD is shown in Figure 3; a quantitative description of the structure is complicated by the fact that the unit cell contains two non-identical conformers. Notable in this structure is the bending of the central six-membered, formally antiaromatic, ring into a twist-boat conformation, the average C–N–O–C torsion angle is 24.37° (averaged across both conformers). It is also noteworthy that the nitrofurazanyl moieties are skewed with respect to the central ring implying that π-conjugation among the three electron-deficient rings is unfavorable. In both conformers one nitrofurazanyl substituent is nearly perpendicular to the central ring (e.g. O1A–C6A–C7A–C11A = 82.7° in the conformer shown) while the other torsion angle is more acute, O4A–C3A–C15A–C19A = 60.8°. The inter-ring torsion angles and the bent central ring suggest a high degree of electronic localization in BNDD.

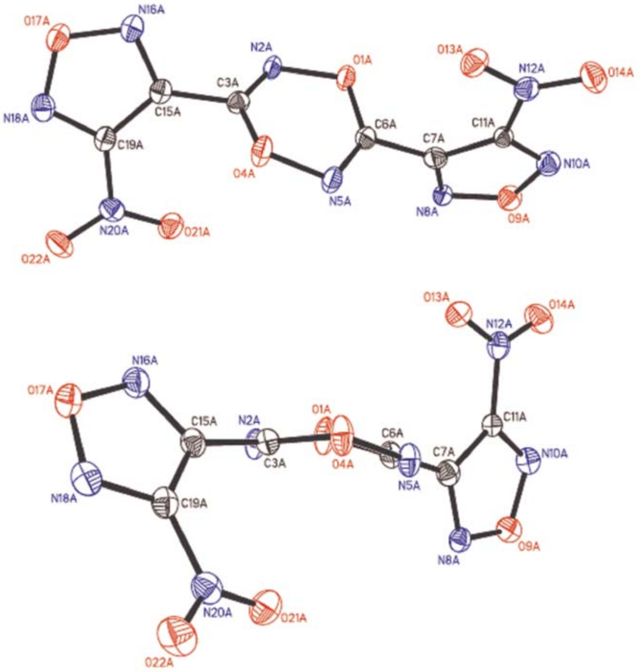


Figure 3 ORTEP plot of BNDD, ellipsoids at 50% probability level

The density of BNDD changed from 1.93 g cm^{-1} at –173 °C to 1.87 g cm^{-1} at 295 °C; performance calculations used the lower room temperature value as the theoretical maximum density (TMD). For details concerning the X-ray structure see the supplementary information and CCDC listing.[9]

Calorimetry and Heat of Formation

Performance predictions require an estimate of density and heat of formation (ΔH_f). For the purpose of performing calorimetry, pressed pellets are preferred in order to consolidate the material and to initiate a thorough burn. Pressing BNDD into calorimetry pellets was not performed for safety reasons. Consequently the heat of formation was calculated for **1** and **5** using a quantum mechanically based approach described previously.[10] The calculations predicted the diamine **5** to have a solid-state ΔH_f of 117 kcal/mol and 144.8 kcal/mol for BNDD. The heat of formation of BADD was measured at 110 kcal/mol.[12] It is not unusual for the calculated value to be higher than experiment as a quantitative burn is rarely achieved, quantification of residual matter is difficult, and the system is not perfectly adiabatic. Calorimetry on BNDD was attempted by consolidating the powder in the bottom of the crucible with solvent and then allowing the solvent to evaporate. The ΔH_f deduced from that single experiment was 142 kcal/mol, consistent with the calculated value.

Performance Calculations for BNDD

The performance of BNDD was calculated using the Cheetah thermodynamic code.[11] Calculations support the qualitative impression from sensitivity testing that BNDD is a very powerful explosive. At the room temperature crystal density of 1.87 g/cc BNDD is calculated to have a detonation velocity of 9040 m/s with a C-J pressure of 37.7 GPa. The high brisance predicted by Cheetah is consistent with the explosive's effect on metal parts and its strong sharp report upon detonation.

In conclusion, we have synthesized BNDD from the previously published BADD[13] and have demonstrated that it is sufficiently sensitive to be dangerous in contact operations with more than minimal quantities. In addition, BNDD is calculated to be a very powerful explosive, exceeding HMX in C-J pressure and nearly equal in detonation velocity.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

The authors would like to thank the Los Alamos National Laboratory Analytical team, particularly Annie Giambra for Elemental Analysis, Mary Sandstrom for DSC, and Daniel Preston for impact, friction, and spark sensitivity testing. This work was funded by the Joint Munitions Program. Except where indicated, this information has been authored by employees of the Los Alamos National Security, LLC. (LANS), operator of the Los Alamos National Laboratory under Contract No. DE-AC52-06NA25396 with the U.S. Department of Energy. Released for unlimited audience: LA-UR 11-00570.

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(13) **Preparation of 3,6-Bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (1)**: Concentrated sulfuric acid (8 mL, 148 mmol) and anhyd sodium tungstate (1.22 g, 74 mmol) were combined in a 50-mL round-bottomed flask and stirred. The flask was suspended in an ice bath. To the acidic solution, 90% hydrogen peroxide solution (4 mL, 148 mmol) was added dropwise. The solution was allowed to equilibrate for 10 min before adding 3,6-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine, (**5**; 1.00 g, 4 mmol) portionwise and CH_2Cl_2 (2 mL) to minimize foaming. The bath temperature was raised to 15 °C and a Vigreux column with a drying tube was attached. The solution became green then faded to an off-white color at which time sodium tungstate (0.61 g, 37 mmol) and 90% hydrogen peroxide (2 mL, 74 mmol) were added. After stirring for 30 min, the reaction was poured into 250 mL of ice water, stirred for 1 h, and vacuum filtered. The crude product (1 g) was dissolved into MeCN (30 mL), stirred for 10 min, and filtered. H_2O (50 mL) was added to the filtrate with stirring and the resulting precipitate collected yielding BNDD (**1**; 0.9 g, 2.9 mmol) in 70% yield; mp 99 °C. ^{13}C NMR (DMSO-d_6): $\delta = 139.7$, 152.4, 159.9. IR: 1671, 1587, 1556, 1481, 1088, 1029, 1011, 861, 825, 764 cm^{-1}. Anal. Calcd for $C_6N_8O_8$: C, 23.09; N, 35.90. Found: C, 23.13; N, 36.00.