Sensitive Energetics from the N-Amination of 4-Nitro-1,2,3-Triazole

Dominique R. Wozniak,[a] Benjamin Salfer,[b] Matthias Zeller,[c] Edward F. C. Byrd,[d] and Davin G. Piercey*[a]

Energetic N-amino-C-nitro compounds 1-amino-4-nitro-1,2,3-triazole and 2-amino-4-nitro-1,2,3-triazole are characterized for the first time as energetic materials. These compounds were characterized chemically by nuclear magnetic resonance (NMR), infrared spectroscopy and X-ray crystallography. Compounds were also characterized energetically by differential scanning calorimetry (DSC), impact, and friction and found to possess sensitivities and performances classifying them as primary explosives with PETN-like performance.

1. Introduction

Within the field of energetic materials, the development of new explosives possessing high performance and high stability is a major goal.[1–7] Unfortunately, many examples exist suggesting that high performance and high stability are often mutually exclusive. There are three main ways to impart explosive energy content to an energetic molecule; the incorporation of fuel and oxidizer in the same molecule (as seen in traditional energetics such as RDX and PETN), creating compounds possessing ring or cage strain, and incorporating large amounts of nitrogen to give rise to high heats of formation. High-nitrogen content species are interesting in that their heats of formation increase as the nitrogen content increases, allowing a relatively straightforward method of increasing the heat of formation by simply increasing nitrogen content, and as such increased explosive performance. Unfortunately, increasing nitrogen content often is accompanied by an increase in sensitivity to mechanical or thermal stimuli.[8]

The 4-nitro-1,2,3-triazole heterocyclic backbone possesses a high heat of formation as a result of being a 1,2,3-triazole (the more energetic triazole when compared to the corresponding 1,2,4 triazole) and possesses a sufficient oxygen balance to oxidize all carbon in the ring to carbon monoxide.[9] Additionally, it is prepared in an easily-scaled 4-step process from readily available and economical precursors.[10–12] These factors make it a good precursor to new potentially high-performing energetic derivatives. 4-nitro-1,2,3-triazole being readily available solves one of the issues increasingly seen in new energetics work; long and difficult syntheses translating to new energetic materials that are much more expensive than presently used materials.[13]

The introduction of an N-amine has been shown to increase heat of formation and energetic performances while also providing new functionality to a compound for further derivatization.[14,15] Compounds possessing both amines and nitro groups on carbon atoms often have increased stability due to hydrogen bonding between the two groups.[16] In the case of N-amines with C-nitro compounds, this relationship is much less frequently observed.[17]

In this work, 2-amino-4-nitro-1,2,3-triazole (2) and 1-amino-4-nitro-1,2,3-triazole (3) were synthesized by the amination of the 4-nitro-1,2,3-triazolate anion using O-tosylhydroxylamine (THA) (Scheme 1). While these materials have been prepared by amination using hydroxylamine-O-sulfonic acid they have never been characterized as energetic materials.[17,18] These materials possess sensitivities comparable to primary explosives and possess performances similar to that of PETN. The 1-amino isomer, melting at 100 °C, is a potential melt-castable primary-like material.
2. Results and Discussion

2.1. Synthesis

The precursor 4-nitro-1,2,3-triazole (1), ethyl O-p-tolysulphonylethyl acetohydrazimate, and O-tosylhydroxylamine were synthesized according to literature procedures (Scheme 2, 3). The sodium salt of (1) was prepared by the reaction of one equivalent of (1) with one equivalent of 1 M sodium hydroxide in aqueous solution followed by evaporation. Dissolution of the isolated sodium salt of 4-nitro-1,2,3-triazole in acetonitrile was followed by the addition of three equivalents of O-tosylhydroxylamine in DCM solution. A small amount of water was added in order to ensure full dissolution of the 4-nitro-1,2,3-triazole salt. The resultant mixture was allowed to stir for two days at room temperature. After this reaction time, the solution was then evaporated to dryness and resuspended in ethyl acetate and filtered to remove the bulk of sodium tosylate impurities. The filtrate was then evaporated to dryness and purified by silica chromatography to yield pure (2) after evaporation of the eluent and a crude mixture of (2) contaminated with tosylate and 4-nitro-1,2,3-triazole.

It appears that some deamination of (2) occurs during the chromatography. The crude mixture of (2) was dissolved in ethyl acetate and washed several times with a saturated solution of sodium bicarbonate to yield pure (2) after evaporation of the ethyl acetate solution. Crystals suitable for x-ray crystallography were obtained for both compounds from the column fractions. It was discovered when trying to recrystallize (2) from hot water that it is susceptible to deamination forming the precursor 4-nitro-1,2,3-triazole, indicative of the same chemical instability of this compound seen during column chromatography. As a result, the yield of this isomer was lower.

The previous preparation of (2) and (3) used hydroxylamine O-sulfonic acid (HOSA) as the aminating agent while maintaining pH between 7–8, with the product crystallizing from solution. When this procedure was repeated, we were unable to reach the combined yield of 37% as stated. Interestingly, the authors of this previous work noted a ratio of 5:2 for products (2) and (3) respectively, while our synthesis yielded a near 1:1 ratio of products. The use of O-tosylhydroxylamine for the amination over HOSA gives improved overall yields (29.7%) and allows for easier access to product (3), which was previously only available as a minor product.

2.1.1. X-ray Structure

The crystallographic data and structure refinement details for (2) and (3) are summarized in Table 1. The structures for (2) and (3) are shown in Figure 1 and Figure 2, respectively. In (2) the

![Scheme 2. Production of O-tosylhydroxylamine (THA) aminating agent.](image)

![Scheme 3. Production of (1) from glyoxal and phenylhydrazine.](image)

![Figure 1. Molecular unit of (2). Ellipsoids are drawn at the 50% probability level.](image)
2.1.2. NMR Spectroscopy

2.1.2.1. ^1H NMR

In (2) the C–H proton appears at δ = 8.53 ppm and the N–NH$_2$ protons appear a δ = 8.24 ppm. In (3) the C–H proton appears at δ = 9.14 ppm and the N–NH$_2$ protons appears at δ = 7.53 ppm. These peaks match closely with those previously reported.\[14\]

2.1.2.2. ^13C NMR

In (2) the two carbon peaks appear at 129.83 ppm (C4) and δ = 149.91 (C5). In (3) the C4 and C5 carbon peaks shift to δ = 123.66 ppm and 151.65 respectively. These peaks match closely with those previously reported.\[16\] In (1) the C4 carbon peak appears at 123.66 ppm while the C5 peak is found at 153.94 ppm.

2.1.2.3. Infrared Spectroscopy

(2) and (3) were analysed by infrared spectroscopy. Bands characteristic of N–H stretching are found at 3347 and 3258 cm$^{-1}$ for (2) and 3356 and 3206 cm$^{-1}$ for (3). 18 N–O asymmetric stretches for (2) and (3) are found at 1536 and 1542 cm$^{-1}$ respectively. N–O symmetric stretches for (2) and (3) are located at 1368 and 1387 cm$^{-1}$ respectively.\[19\]

2.1.2.4. Mass Spectrometry

The [M–H$^+$] anion was observed in negative mode APCI at 128 m/z by a low-resolution mass spectrometer and confirmed by high-resolution mass spectrometry for both (2) and (3). [M–15] peaks were observed in both samples, corresponding to loss of the N-amine under mass spec fragmentation conditions.

2.1.2.5. Differential Scanning Calorimetry (DSC)

For determination of thermal stabilities of (2) and (3), differential scanning calorimetry (DSC) experiments were performed in sealed aluminum pans at a heating rate of 5 °C min$^{-1}$. The DSC of (2) shows a small preliminary exothermic peak starting at 100 °C and the main exotherm starting at 175 °C. The DSC of (3) shows melting at 100 °C and exothermic decomposition at 175 °C, making it a potential melt-castable energetic material.

2.1.3. Explosive Properties

2.1.3.1. Experimental Sensitivities

For initial safety testing, impact and friction sensitivities were determined for (2) and (3). Impact sensitivity was performed according to STANAG 4489 and modified according to instruction\[21\] on an O2M drophammer by the BAM method.\[22\] Friction sensitivity was carried out in accordance with STANAG 2287\[23\] and modified according to instruction\[24\] using a BAM friction tester. It was observed during testing that at frictional forces below 16–18 N, (2) partially decomposes without sound or light output forming an unidentified pinkish material but at friction of 16–18 N, detonates with a small crackling noise accompanied by formation of pink decomposition product. The same pink material was observed after (2) was detonated during impact testing. No such residue was observed during detonation of (3) during impact or friction testing and this material either explodes violently or shows no signs of decomposition. (2) and (3) both possess impact sensitivities of < 1 J. (2) displays friction sensitivity of 16–18 N while (3) possesses friction sensitivity of 14–16 N. Both (2) and (3) can be classified as “very sensitive”.\[25\] It is interesting to note that while many compounds containing C-amine and C-nitro lack this and remain highly sensitive. The same was seen previously for 2-amine-5-nitrotetrazole.\[14\]

2.1.3.2. Detonation Parameters

The detonation parameters calculated for compounds (2) and (3) are summarized in Table 2. Their sensitivities classify them as primary explosives. (3) has a detonation velocity of 8425 m s$^{-1}$, a PETN-like performance while (2) has a detonation velocity of 8601 m s$^{-1}$, which is in between RDX and PETN-like performance. It is interesting to note that (2) has a lower ΔH, than (3) but has a higher detonation velocity. This can be attributed to differences in their densities, 1.766 and 1.721 g cm$^{-3}$ respectively.
All reagents and solvents were used as received (Sigma-Aldrich, General Methods characterized for the first time as energetic compounds. While triazole (43) were synthesized by amination of 4-nitro-1,2,3-triazole and 1-amino-4-nitro-1,2,3-triazole (3) were synthesized by amination of 4-nitro-1,2,3-triazole with O-tosyldihydroxylamine. These compounds were characterized for the first time as energetic compounds. While the compounds possess detonation velocities comparable to PETN, they also possess primary explosive-like sensitivities.

### 3. Conclusions

2-amino-4-nitro-1,2,3-triazole (2) and 1-amino-4-nitro-1,2,3-triazole (3) were synthesized by amination of 4-nitro-1,2,3-triazole with O-tosyldihydroxylamine. These compounds were characterized for the first time as energetic compounds. While the compounds possess detonation velocities comparable to PETN, they also possess primary explosive-like sensitivities.

### Experimental Section

#### General Methods

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics, Fisher Scientific Co LLC) if not stated otherwise. Melting and decomposition points were measured with a TA Instruments Q20 DSC using heating rates of 5°C·min⁻¹. ¹H and ¹³C NMR spectra were measured with a Bruker AV-III-800 (5 mm QCI Z-gradient cryoprobe). All chemical shifts are quoted in ppm relative to TMS (¹H, ¹³C). Infrared spectra were measured with a PerkinElmer Spectrum Two FT-IR spectrometer. Transmittance values are described as “strong” (s), “medium” (m) and “weak” (w). Low resolution mass spectra were measured with an Agilent 1260 Infinity II Quaternary LC instrument. High resolution mass spectra were measured with a Thermo Fisher Scientific LTQ Orbitrap with APCI probe. Sensitivity data were determined using a BAM friction tester (Reichel & Partner Gmbh) and BAM Drophammer (OZM AP1 probe). Sensitivity data were determined using a BAM friction tester (Reichel & Partner Gmbh) and BAM Drophammer (OZM AP1 probe). Sensitivity data were determined using a BAM friction tester (Reichel & Partner Gmbh) and BAM Drophammer (OZM AP1 probe).

#### Caution!

The described compounds 1–3 are energetic materials with sensitivity to various stimuli. While we encountered no issues in the handling of these materials, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthened equipment) should be used at all times.

### Computational Methods

Enthalpy of formation and density were calculated using the Byrd and Rice method. The calculated densities were within 5.2% of densities calculated by x-ray crystallography. The molecular geometries were optimized using the B3LYP spin-restricted Kohn-Sham density functional theory (KS-DFT) with the 6–31G** Pople Gaussian basis set. Computational densities were obtained by dividing the mass of the molecule by the volume calculated from the volume contained within the B3LYP/6-31G** 0.001 electron/bohr³ isosurface of the electron density, and subsequently modified by electrostatic parameters generated from charge distributions of said isosurface. Crystal densities obtained from x-ray crystallography were used when computing detonation performances. For the prediction of the heat of formation, the B3LYP/6-311+ + G(2df,2p) energy is computed from the B3LYP/6-31G* optimized geometry to obtain the gas phase heat of formation. Finally, the heat of sublimation was calculated from the molecular surface area (determined from the volume contained within the 0.001 electron/bohr³ isosurface of the electron density) and pertinent electrostatic parameters.

The calculations of the detonation parameters for compounds (2) and (3) were performed using the EXPLO6.05 software package.

The software utilizes the Becker-Kistiakowsky-Wilson’s equation of state (CFEOS) for solid carbon. In order to calculate the equilibrium composition of the detonation products the program utilizes the modified White, Johnson, and Dantzig’s free energy minimization technique. EXPLO6.05 allows for calculation of detonation parameters at the CJ point. BKWN parameters (α, β, γ, θ) were used in the following BKW equation, with ξ representing the mol fraction of the i-th gaseous product and k being the molar co-volume of said i-th gaseous product:

\[
pV^n = 1 + xe^\alpha x \left(\frac{\kappa \sum X_k}{\sqrt{V + \theta}}\right)^\beta
\]

\[
\alpha = 0.5, \beta = 0.38, \gamma = 9.41, \theta = 4250
\]
X-Ray Crystallography Data

Data for (3) was collected using a Bruker D8 Quest diffractometer with kappa geometry, a copper target 1 μm mirror, a 1.54178 Å, a synchrotron radiation source (Mo Kα radiation, λ = 0.71073 Å), and a single crystal with dimensions of 0.95 mm × 0.70 mm × 0.50 mm. The data were processed using APEX3. The space groups were assigned and the structures were solved by direct methods using the SHELXLEXTL suite of programs and then refined by full matrix least squares against F2 with all reflections using SHELXL2018. The amino H atoms positions were freely refined. H atoms attached to carbon and hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å and oxygen hydrogen distances of 0.85 Å. Hydroxyl H atoms were allowed to rotate but not to tip to best fit the electron density. The electron density was evaluated for 1.2 times Ueq(C/N) and 1.5 Ueq(O). Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1966784 and 1966770 respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Amination of 4-nitro-1,2,3-triazole (1)

4-nitro-1,2,3-triazole (1 g, 8.77 mmol) was dissolved in water and 8.85 mL 1 M sodium hydroxide (8.77 mmol) was added slowly while stirring. The solution was stirred for 10 minutes and evaporated to dryness yielding the sodium salt of (1). The sodium salt was slurried in 250 mL of acetone. Separately 6.83 g freshly pulverized ethyl-O-tolysulphonilic acid hydrate (680 mL vigorously stirred ice/water slurry. The mixture was filtered. The filtrate was evaporated to dryness and purified by silica chromatography using a 2:1:1 ethyl acetate toluene-hexane eluent and then evaporated to dryness, resuspended in ethyl acetate and added at once to the solution of sodium salt of (1). The solution was stirred at room temperature for two days, and then evaporated to dryness, resuspended in ethyl acetate and filtered. The filtrate was evaporated to dryness and purified by silica chromatography using a 2:1:1 ethyl acetate toluene-hexane eluent to yield 0.162 g of pure (3) (1.26 mmol, 15.4%) and 0.410 g (2) contaminated with tosylate and decomposition products. The crude mixture was purified by resuspension in ethyl acetate and washing with saturated sodium bicarbonate solution. After drying over MgSO4 and evaporation to dryness 0.174 g of pure (2) was recovered (1.35 mmol, 14.3%). Crystals suitable for x-ray crystallographic analysis were obtained by slow evaporation of the column fractions.

2-amino-4-nitro-1,2,3-triazole (2)

1H NMR (DMSO-d6): δ = 8.53 ppm (1H, C−H), 8.24 (s, 2H, NH2); 13C NMR (DMSO-d6): δ = 149.9 ppm (C4), 129.83 (C5); HR-MS (APCI) m/z: Expected: 128.0203, Found: 128.0198, IR: ν = 3347 (cm−1), 1540 (cm−1), 1482 (cm−1), 1364 (cm−1), 1251 (cm−1), 1007 (cm−1), 949 (cm−1), 870 (cm−1), 843 (cm−1), 754 (cm−1), 709 (cm−1), 612 (cm−1), 554 (cm−1); DSC (5°C·min<sup>−1</sup>): 100°C (Tdc); BAM fraction: 16–18 N; BAM impact: < 1 J.

1-amino-4-nitro-1,2,3-triazole (3)

1H NMR (DMSO-d6): δ = 9.14 ppm (1H, C−H), 7.53 (s, 2H, NH2); 13C NMR (DMSO-d6): δ = 151.65 ppm (C4), 123.02 (CS); HR-MS (APCI) m/z: Expected: 128.0203, Found: 128.0209; IR: ν = 3356 (cm−1), 3341 (cm−1), 3303 (cm−1), 3206 (cm−1), 3163 (cm−1), 3112 (cm−1), 1714 (cm−1), 1617 (cm−1), 1542 (cm−1), 1504 (cm−1), 1483 (cm−1), 1364 (cm−1), 1320 (cm−1), 1251 (cm−1), 1007 (cm−1), 949 (cm−1), 870 (cm−1), 843 (cm−1), 754 (cm−1), 709 (cm−1), 612 (cm−1), 554 (cm−1); DSC (5°C·min<sup>−1</sup>): 100°C (Tcm), 175°C (Tdc); BAM fraction: 14–16 N; BAM impact: < 1 J.

Acknowledgements

Financial support of this work by The Army Research Office (ARO) under grant number W911NF-18-1-0463 is acknowledged. Financial support of our laboratory by Purdue University and The Office of Naval Research (ONR) also is acknowledged. The National Science Foundation is acknowledged through the Major Research Instrumentation Program under Grant No. CHE 1625543 for the single crystal X-ray diffractometer. We are indebted to and thank Ms. Shannon Creggan, Mr. Matthew Gettings, and Mr. Timothy Manship for many helpful and inspired discussions in support of our work.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: amination reactions • energetic materials • heterocycles • N-amines • primary explosives

[1] M. S. Klenov, A. A. Guskov, O. V. Anikin, A. M. Churakov, Y. A. Strelenko, I. V. Fedyanin, K. A. Lyssenko, V. A. Tartakovskiy, Angew. Chem. Int. Ed. 2016, 55, 11472–11475.
[2] D. G. Piercey, D. E. Chavez, B. L. Scott, G. H. Imler, D. A. Parrish, Angew. Chem. 2016, 128, 15541–15544.
[3] Y. Tang, D. Kumar, J. M. Shreeve, J. Am. Chem. Soc. 2017, 139, 13684–13687.
[4] L. Hu, P. Yin, G. Zhao, C. He, G. H. Imler, D. A. Parrish, H. Gao, J. M. Shreeve, J. Am. Chem. Soc. 2018, 140, 15001–15007.
[5] L. M. Barton, J. T. Edwards, E. C. Johnson, E. J. Bukowski, R. C. Sausa, E. F. C. Byrd, J. A. Orlicki, J. J. Sabatini, P. S. Baran, J. Am. Chem. Soc. 2019, 141, 12531–12535.
[6] N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, J. Mater. Chem. 2012, 22, 20418–20422.
[7] M. L. Gettings, M. Zeller, E. Byrd, D. G. Piercey, Z. Anorg. Allg. Chem. 2019, 645, 1197–1204.
[8] Y. Xu, Q. Wang, C. Shen, Q. Lin, P. Wang, M. Lu, Nature 2017, 549, 78–81.
[9] M. A. M. Rashid, S. G. Cho, C. H. Choi, Comp. Theo. Chem. 2018, 1730, 148–159.
[10] R. R. Gallucci, J. Chem. Eng. Data, 1982, 27, 217–219.
[11] T. B. Aleksandrovich, S. G. Viktorovich, M. G. Firsova, E. T. Georgievna, K. N. Petrunova, V. L. Ivanovna, S. R. Galeevich, S. G. Timofeevich, S. S. Viktorovich, Russian patent 2344130 C2, Russia.
[12] T. E. Eagles, M. A. Khan, B. M. Lynch, Org. Prep. Proced. 1970, 2, 117–119.
[13] P. E. Eaton, M. X. Zhang, R. Gilardi, N. Gelber, S. Iyer, R. Surapaneni, Propellant Explos. Pyrotech. 2002, 27, 1–6.
