Dendritic Polynitrato Energetic Motifs: Development and Exploration of Physicochemical Behavior through Theoretical and Experimental Approach

Pankaj Gaur,† Sagarika Dev,‡ Sunil Kumar,† Mahesh Kumar,§ Anuj A. Vargeese,∥ Pramod Soni,§ Prem Felix Siril,*† and Subrata Ghosh*†

†School of Basic Sciences, Indian Institute of Technology Mandi, Mandi 175001, Himachal Pradesh, India
‡Department of Chemistry, MCM DAV College for Women, Sector-36, Chandigarh 160036, India
§Terminal Ballistics Research Laboratory, Chandigarh 160003, India
∥Advanced Centre of Research in High Energy Materials, University of Hyderabad, Hyderabad 500046, India

Supporting Information

ABSTRACT: Considering the fundamental and most desirable characteristics of energetic materials, a series of 1,2,3-triazole-based heterocyclic energetic motifs nicely tuned with nitrato (−ONO₂) functionality were synthesized by a microwave-assisted environmentally friendly synthetic approach with good yields. Thermal stability and the nature of evolved gases on decomposition of structurally characterized energetic motifs were analyzed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) analysis and Fourier transform infrared coupled with TGA–DSC. The explosiveness of these motifs was explored by calculation of enthalpy of formation and density employing density functional theory, and the detonation performances (detonation pressure and velocity) were explored using EXPLO5_V6.03. All of these compounds were calculated to have better oxygen balance (−36 to −52%) as compared to that of trinitrotoluene (−74%). Most of the nitrate ester derivatives were found to exhibit low impact sensitivities, high densities, good thermal stabilities, and promising detonation properties, and PN₃ was observed to be a superior candidate in terms of its energetic characteristics. Hence, the experimental and theoretical outcomes strongly reflect that the present approach of developing dendritic high energetic materials bearing green explosive characteristics might be a potential pathway for designing and synthesizing green explosives with desired characteristics.

1. INTRODUCTION

Energetic materials (explosives, propellants, and pyrotechnics) are used for a variety of military purposes and industrial applications such as cutting labor costs, speeding up strenuous processes in mining, tunneling, construction, and agriculture, and thus making a tangible input to the world economy.¹ Recently, high energetic materials have gained a lead position in the framework of material science. Therefore, applied and fundamental aspects of current research have been focused on the development of high energetic materials with desirable characteristics such as high thermal stability, impact insensitivity, high energy and density, high enthalpy of formation, and most importantly, minimal environmental impact, which should be considered intensely.²−⁷ To fulfill such characteristic demands of energetic materials, complete combustion of the carbon backbone and the generation of N₂ as an end product on explosion are highly desirable. Hence, high nitrogen content and recommended oxygen balance are the key concerns in designing high energetic materials. As the nitrogen rich motifs fulfill standards like ecofriendliness and high heat of formation with exothermic combustion,⁸,⁹ heterocycle-based energetic materials have gained immense attention from the advanced material and chemical research community.¹⁰ In this context, triazole, tetrazole, and triazine have been synthesized and studied in recent years as a fascinating class of heterocyclic cores.¹¹,¹² Further, the introduction of functionalities like nitro (−NO₂), nitrate (−ONO₂) ester, nitramine (NH−NO₂), and nitromine (≡NNO₂) has enhanced the energetic properties of these compounds.¹³,¹⁴ Although, the presence of nitro functionality decreases the heat of formation, it leads to an enhancement in oxygen balance, which enables oxidation of all nonoxidizing components of motifs to their respective oxides and hence increases their energetic performance (detonation pressure and velocity).¹⁵ Moreover, the salts of above

Received: June 27, 2017
Accepted: October 20, 2017
Published: November 20, 2017

DOI: 10.1021/acsomega.7b00880
ACS Omega 2017, 2, 8227−8233
This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.
mentioned heterocyclic cores with ammonia, hydrazine, guanidine, nitrate, perchlorate, and picrate have the advantage of low vapor pressure over nonionic motifs, which eliminates the risk of exposure on inhalation, provides a high heat of formation, and high thermal stability, and interestingly, these desirable traits can be tuned via the choice of counter ions.\textsuperscript{16,17}

Although a lot of azole-based salts and polynitro compounds have been developed that are comparable to the well-known energetic materials such as research department explosive (RDX), trinitrotoluene (TNT), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane, and hexanitrohexaazaisowurtzitane, unfortunately, these are highly environmental hazardous as the release of these explosives to the environment leads to the contamination of surface and ground water, soils, and sediments.\textsuperscript{18,19} Therefore, more efforts are still needed to design and synthesize green explosives with tremendous energetic parameters such as high enthalpy of formation, stability, low impact sensitivity, and high detonation performance.\textsuperscript{20–23}

Herein, we describe the synthesis and characterization of triazole-based heterocyclic energetic motifs functionalized with nitrate ester as a new class of green energetic materials. As shown in Scheme 1, the molecular complexity was incorporated from a small molecular framework leading to dendritic structures by increasing the number of peripheral nitrate groups as well as triazole moieties to ensure the fundamental requisites of an energetic motif. The triazole ring was inserted as the core moiety as it not only provides the thermal stability but also couples with low impact and shock sensitivity,\textsuperscript{24} whereas nitrate functionality was incorporated to enhance the oxygen balance as well as the density of the motifs. A microwave-assisted approach was developed to synthesize the precursors of polynitrate esters with excellent yields and purity. Next, the molecular integrity and structural analysis of the newly synthesized compounds were examined using various spectroscopic techniques such as Fourier transform infrared (FT-IR) spectroscopy, NMR spectroscopy, mass spectrometry, and single crystal X-ray diffraction (SC-XRD) analysis. Furthermore, thermal properties were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and computational studies were done using the program package Gaussian 09.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. In general, the copper catalyzed (3 + 2) cycloaddition reaction between electron rich azides (dipoles) and electron deficient alkynes (dipolarophiles) in the presence of a protic solvent is the most common synthesis strategy for preparing 1,2,3-triazoles with high regioselectivity. But, the development of green and industrially companionable synthetic methodologies for the production of the triazole skeleton in small molecular entities has been an emerging area of curiosity for synthetic chemists in recent decades. In this context, herein, we describe the microwave-assisted safe synthesis of precursor azides and polyhydroxy 1,2,3-triazoles with excellent yield (>95%) and purity (Scheme 1). The azides were synthesized from the

\textsuperscript{a}(a) NaN_3, H_2O, 105 °C, 35 min, microwave (MW); (a') acetonitrile/H_2O (2:1), 30 min, 100 °C, MW; (a") dimethylformamide (DMF), NaN_3, 45 °C, 40 min, MW; (b) butyne-1,4-diol, 25–30 min, 85 °C, MW; (b') propargyl alcohol, CuSO_4·5H_2O/Na-ascorbate (10, 30 mol %), dichloromethane (DCM)/H_2O (1:2), 12 h, room temperature (RT); (c) LiNO_3, (CF_3CO)_2O, Na_2CO_3, acetonitrile, RT, 6–7 h.

**Scheme 1. Routes for the Chemical Synthesis of Triazole-Based Nitrate Esters**
H2O, DMF, and acetonitrile/water mixtures as solvents under using 10% MeOH/DCM as dense yellow oils, whereas corresponding nitrate ester derivatives using a mixture of polyhydroxy triazoles were easily converted into their 4a and 1a Triazoles synthesized by heating butyne-1,4-diol and the azides in a (HSQC) spectra as well as13C attached proton test (APT). supported by heteronuclear single quantum coherence. The NMR spectra were recorded in CDCl3 for compounds obtained as pure white solids on recrystallization with ethanol. Nitrate groups vary from 1.10 to 1.54 Å; O1\text{1a}, O2, O7 distances between C3\text{1a}, C5\text{1a}, C5\text{1a} = 1.19, 1.19, 1.10, 1.54, and 1.12 Å, respectively. Also, the bond in dry acetonitrile at room temperature for 6 was found to be 3.4 Å. Also, no H-bonding interactions with bond length 2.5–2.9 Å were observed. All selected crystallographic data and parameters of the compound are detailed in Table S1.

Table 1. Physical Properties of Polynitrate Esters

| compd | \(T_{\text{deg}}\) (°C) | \(\rho\) (g cm\(^{-3}\)) | OB\(^{\text{a}}\) (%) | \(\Delta H_{\text{f}}^{\text{d}}\) (kJ mol\(^{-1}\)) | \(\Delta E^{\text{e}}\) (kJ mol\(^{-1}\)) | \(V_{\text{d}}\) (km s\(^{-1}\)) | \(P_{\text{f}}\) (GPa) | \(H_{50}\) (cm) |
|-------|-----------------|-----------------|-----------------|------------------|------------------|-----------------|-----------------|-----------------|
| PN\(_1\) | 120 | 1.44 | -51.49 | -70.94 | 503.65 | 7.17 | 19.86 | 29 |
| PN\(_2\) | 155 | 1.73 | -36.35 | 36.04 | 510.41 | 7.95 | 26.27 | 46 |
| PN\(_3\) | 141 | 1.71 | -48.00 | 73.70 | 520.06 | 7.80 | 25.16 | 34 |
| PN\(_4\) | 154 | 1.66 | -40.00 | -35.77 | 487.25 | 7.68 | 24.36 | 209 |
| PN\(_5\) | 150 | 1.39 | -47.00 | 96.58 | 485.32 | 6.89 | 17.30 | 52 |

\(^{\text{a}}\)Onset decomposition temperature. \(^{\text{b}}\)Density (g cm\(^{-3}\)). \(^{\text{c}}\)Oxygen balance (OB). \(^{\text{d}}\)Calculated enthalpy of formation in gaseous phase (kJ mol\(^{-1}\)). \(^{\text{e}}\)Highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap. \(^{\text{f}}\)Detonation velocity (km s\(^{-1}\)). \(^{\text{g}}\)Detonation pressure (GPa). \(^{\text{h}}\)Height at which the motif detonates 50% (impact sensitivity).

2.3. Physical and Energetic Properties. Heat of formation is one of the most important properties of energetic compounds, and it reflects their inherent energy as well as nitrogen content. As is evident from Table 1, most of the motifs were found to exhibit positive gaseous heats of formation (36–96 kJ mol\(^{-1}\)) except PN\(_3\) and PN\(_4\). The condensed heats of formation (\(\Delta H_{\text{f}}\)) for motifs PN\(_3\)–PN\(_6\) were 2.42, –110.25, and 23.23 kJ mol\(^{-1}\), respectively. The considerable enthalpy of formation clearly reflected their high nitrogen richness and the presence of more nitrate groups (see Table 1). The calculated densities of these energetic motifs range between 1.39 and 1.73 g cm\(^{-3}\), as shown in Table 1. The densities of the motifs PN\(_3\), PN\(_4\), and PN\(_5\) were 1.73, 1.71, and 1.66 g cm\(^{-3}\), whereas PN\(_2\) and PN\(_6\) were found to be less dense (1.44 and 1.39 g cm\(^{-3}\), as shown in Table 1). Because density is a function of the packing parameter of the molecular framework, the aforementioned values of density clearly reflect that PN\(_3\), PN\(_4\), and PN\(_5\) have a highly compact molecular framework as compared to that of PN\(_2\) and PN\(_6\).

The impact sensitivity plays an important role in scaling up promising energetic materials, generally expressed in the form of \(H_{50}\) i.e., the height from which a hammer of standard weight falling upon the explosive will lead to a 50% probability of detonation. The \(H_{50}\) values were calculated for the corresponding energetic compounds (see Table 1) employing eq 1, as suggested by Cao.\(^{25}\)

\[H_{50} = 0.1926 + 98.64Q_{\text{NO}_2}^2 - 0.03405OB_{100}\]
$Q_{NO_2}$ is the net Mulliken charge on the nitro group ($NO_2$) and $OB_{100}$ is the oxygen balance of an energetic motif. As tabulated in Table S1, the characteristic $Q_{NO_2}$ and $OB_{100}$ values of the present energetic motifs were calculated using the reported method. Because $H_{50}$ is the direct function of the square of the net Mulliken charge on the nitro group ($Q_{NO_2}$), the superior $H_{50}$ of $PN_5$ over the other motifs can be attributed to its high $Q_{NO_2}$. Moreover, as illustrated in Table 1, all of the motifs were found to have lower impact sensitivities as compared to those of RDX (28 cm) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (32 cm), which again supported their promising energetic candidature.

After evaluation of the heats of formation and densities, the detonation performance of the motifs in terms of detonation pressure ($P$, GPa) and detonation velocity ($V_d$, km s$^{-1}$) was calculated using gaseous heat of formation for EXPLO5_V6.03. Their detonation velocities and pressures lie in the range 6.89–7.95 km s$^{-1}$ and 17.30–26.27 GPa, respectively. Energetic motifs $PN_5$, $PN_6$, and $PN_7$ exhibited high detonation pressures (26.27, 25.16, and 24.36 GPa) as well as detonation velocities (7.95, 7.80, and 7.68 km s$^{-1}$). Hence, the detonation performance of the present compounds clearly established that owing the promising energetic nature, this class of materials could find wide applications in the defense sector.

Oxygen balance, the most requisite property of an ecocompatible energetic motif to ensure complete conversion of the energetic backbone leading to the evolution of carbon dioxide and nitrogen, i.e., smokeless explosion, was calculated using the chemical formula $C_aH_bN_cO_d$ as $OB(\%) = -1600 \times \frac{(2a+b/2-d)}{MW}$ (values are reported in Table 1). The oxygen balance of these energetic compounds was...
found to be in an acceptable range from −36 to −52%, which is much better than TNT (−74%). The incorporation of nitrate groups not only improved their oxygen balance but also made them capable and potent energetic motifs with high heats of formation and detonation performance.

2.4. TGA–DSC Coupled with FT-IR. Further, thermogravimetric analysis and differential scanning calorimetric experiments were conducted to examine the thermal stability of these compounds. Their corresponding onset decomposition temperatures (120–155 °C) are shown in Table 1 and Figure S1. From the TGA and DSC thermal curves, it appears that the liquid products follow a three-step decomposition pattern, whereas the solid compounds follow a two-step decomposition process. The rate of mass loss in the first step for the solid compounds and the second step for the liquid products was quite high, indicating their energetic nature. It is also notable that the motifs PN₃–PN₆ decomposed exothermically by releasing 1447, 912, 999, and 758 J g⁻¹ as heats of decomposition. To gain an in-depth understanding of the decomposition pathway and products of these energetic motifs, IR spectroscopic analysis was also carried out using a TGA–DSC coupled with FT-IR technique. The IR spectra peaks at 3730, 3593, and 2304 cm⁻¹ clearly indicated the evolution of water and carbon dioxide as major decomposition products, whereas the peaks at 1509 and 1590 cm⁻¹ indicated the formation of N₂O and NO as other decomposition products (see Figure 2). Although the evolution of N₂ cannot be detected by FT-IR because it does not have a net dipole moment, the possibility of its evolution cannot be neglected.²⁶ Hence, the aforementioned findings clearly reflect the oxygen richness and ecotrifriendliness of these newly developed energetic motifs.

2.5. HOMO–LUMO Calculation. HOMO–LUMO gaps (ΔE) were calculated to understand the stability of these energetic motifs. As evidenced from Figure 3, the HOMOs and LUMOs are localized over the triazole moieties and nitrate (ONO₂) groups, respectively. The ΔE values as tabulated in Table 1 correspond to satisfactory thermal stabilities of these compounds.

3. CONCLUSIONS

In summary, a user-friendly microwave-assisted synthetic approach was developed for laboratory-scale synthesis of precursor azides and polyhydroxy triazoles for the synthesis of polynitrate esters as a new class of green energetic motifs. The newly synthesized compounds were structurally characterized by employing various spectroscopic techniques. Thermal behavior was evaluated using TGA–DSC coupled with FT-IR to evaluate the nature of gas release on thermal decomposition. Most of the motifs decomposed in the range of 140–155 °C, which indicated the moderate thermal stability of these new energetic materials. However, all of the motifs exhibited a low impact sensitivity, high density, moderate thermal stability, and good oxygen balance (−36 to −52%) except PN₄ which displayed better thermal properties and detonation performance (P = 26.27 GPa and Vd = 7.95 km s⁻¹). Hence, on the basis of comparative studies of their predicted physicochemical properties and performances, it was concluded that the motifs presented in this study not only display satisfactory energetic parameters, but also address the mandatory concept of ecotrifriendliness.

4. EXPERIMENTAL SECTION

4.1. Safety Precautions. As sodium azide and its derivatives are highly sensitive to mechanical stimuli and impact, they should always be in dilute solution, and extreme caution should be taken during their utilization as reactants. Although no difficulties were faced during the handling of these compounds, one should make all manipulations inside a hood behind the safety shield. Any mechanical action involving scratching or scraping should be avoided; all safety cautions should be exercised during handling.

4.2. General Information. Chemicals were purchased from commercially available resources and used without further purification.¹H, ¹³C, DEPT-135, and HSQC spectra were recorded on JEOL-JNM ECX-500 MHz NMR spectrometers by using CDCl₃/DMSO-d₆ as solvent. Chemical shifts are reported relative to tetramethylsilane (¹H and ¹³C). FT-IR spectra were recorded on a PerkinElmer FT-IR spectrometer. High-resolution mass spectrometry spectra were recorded on a Bruker impact-HD spectrometer. Single crystal X-ray diffraction studies were performed on an Agilent Technologies X-ray diffractometer system. A CEM-Discover microwave synthesizer was used for synthesis. The energy release and decomposition temperature were studied on a thermogravimetric analyzer and differential scanning calorimeter TGA/DSC 1 (Mettler Toledo). The thermograms were recorded from 25 to 1000 °C at a heating rate of 10 °C min⁻¹ under an inert atmosphere of nitrogen gas in an open alumina crucible.

4.3. X-ray Crystallography. A single crystal of PN₄ suitable for X-ray diffraction was grown in DCM/methanol at room temperature by slow evaporation. Diffraction studies were performed on an Agilent Technologies X-ray diffractometer system by irradiating the crystals using Cu Kα radiation (λ = 1.5406 Å) at 293(2) K, which revealed that it crystallizes in the monoclinic I2/a space group. Data were collected by standard “CrysAlisPro” software (online version) and reduction was undertaken with CrysAlisPro software (offline version). The molecular structure was solved by direct methods OLEX² and was refined using full-matrix least-squares (F²) on SHELXL. The positions of all nonhydrogen atoms were located and were refined anisotropically. After that, hydrogen atoms were obtained from the residual density map and refined with isotropic thermal parameters. The CCDC number 1043488 was obtained for PN₄ from “The Cambridge Crystallographic Data Centre (CCDC)” by depositing the structure at http://www.ccdc.cam.ac.uk/. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.4. Theoretical Study. All structures were optimized using the B3LYP functional with the 6-31g* basis set using the Gaussian 09 suite of programs.²⁷ The input files of molecular conformation of all compounds except PN₄ were generated in GaussView 5.²⁸ The SC-XRD structure for PN₄ was used as the input file for the density functional theory studies. Frequency calculations at the same level were performed to ensure that the structures correspond to minima. Single point energy calculations were performed at 6-31+g*. These single point energy values were used for calculation of the gas phase heat of formation. Volumes of each species were calculated using the B3LYP functional with the 6-31+g* basis set. The output files from the Gaussian package were obtained, and they were visualized in MOLDEN.²⁹ Then, the Z-matrix was seen and converted into an input file for MOPAC.³⁰ The input files for
MOPAC were executed and the heats of formation for the given molecules were obtained. The detonation pressure and velocity of the compounds were calculated using EXPLO5 V6.03. The condensed heat of formation ($\Delta H_f$) for PN$_4$–PN$_6$ was calculated using eqs 2 and 3:

$$\Delta H_f = \Delta H_g - \Delta H_{sub}$$  
(2)

$$\Delta H_{sub} \{J \ mol^{-1}\} \approx 188T_m$$  
(3)

where $\Delta H_{sub}$ is the enthalpy of sublimation and $T_m$ is the melting point (kelvin).

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00880. Detailed experimental procedures, theoretical results, thermal and structural characterization data for all compounds (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: prem@iitmandi.ac.in (P.F.S.).
*E-mail: subrata@iitmandi.ac.in (S.G.).

**ORCID**

Anuj A. Vargese: 0000-0003-2438-2472
Prem Felix Siril: 0000-0002-8818-7310
Subrata Ghosh: 0000-0002-8030-4519

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Financial support was received from DRDO through CDSW panel under ARMREB, India (Grant No. ARMREB/CDSW/2012). P.G. and S.K. are grateful to DRDO and UGC for their fellowship. We thankfully acknowledge the Director, IIT Mandi, for research facilities. Sophisticated instrument facility of Advanced Materials Research Center (AMRC), IIT Mandi, is thankfully acknowledged.

**REFERENCES**

(1) Kirk, R. E.; Othmer, D. F. Encyclopedia of Chemical Technology; Wiley: New York, 2004; Vol. S, pp 719.
(2) Wang, R.; Xu, H.; Guo, Y.; Sa, R.; Shreeve, J. M. Bis[3-(5-nitroimino-1,2,4-triazolato)]-Based Energetic Salts: Synthesis and Promising Properties of a New Family of High-Density Insensitive Materials. J. Am. Chem. Soc. 2010, 132, 11904–11905.
(3) Zhang, M.; Eaton, P. E.; Gilardi, R.; Hepta- and Octanitrotricycledienes. Angew. Chem., Int. Ed. 2000, 39, 401–404.
(4) Tao, G.-H.; Twamley, B.; Shreeve, J. M. A Thermally Stable Nitrogen-Rich Energetic Material-3,4,5-triamino-1,2,4-triazole (TATT). J. Mater. Chem. 2009, 19, 5850–5854.
(5) Klapótké, T. M.; Stierstorfer, J. The CN$^{-}$- Anion. J. Am. Chem. Soc. 2009, 131, 1122–1134.
(6) Gao, H.; Shreeve, J. M. Azole-Based Energetic Salts. Chem. Rev. 2011, 111, 7377–7436.
(7) Badgujar, D. M.; Talawar, M. B.; Asthana, S. N.; Mahulikar, P. P. Advances in Science and Technology of Modern Energetic Materials: An Overview. J. Hazard. Mater. 2008, 151, 289–305.
(8) (a) Huynh, M. H. V.; Hiskey, M. A.; Chavez, D. E.; Naud, D. L.; Gilardi, R. D. Synthesis, Characterization, and Energetic Properties of Diazido Heteroaromatic High-Nitrogen C–N Compound. J. Am. Chem. Soc. 2005, 127, 12537. (b) Brand, H.; Mayer, P.; Schulz, A.; Weigand, J. J. Nitro(nitroso) cyanomethanides. Angew. Chem., Int. Ed. 2005, 44, 3929.
(9) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. Energetic Nitrogen-Rich Salts and Ionic Liquids. Angew. Chem., Int. Ed. 2006, 45, 3584–3601.
(10) Klapótké, T. M.; Stierstorfer, J. M. The CN7 Anion. J. Org. Chem. 2004, 69, 1720–1722.
(11) (a) Ou, Y.; Chen, B.; Li, J.; Dong, S.; Li, J.; Jia, H. Synthesis of Nitro Derivatives of Triazoles. Heterocycles 1994, 38, 1651–1664. (b) Jin, C.-M.; Ye, C.; Piekarski, C.; Twamley, B.; Shreeve, J. M. Mono and Bridged Azolium Picrates as Energetic Salts. Eur. J. Inorg. Chem. 2005, 3760–3767.
(12) Badgujar, D. M.; Talawar, M. B.; Harlapur, S. F.; Asthana, S. N.; Mahulikar, P. P. Synthesis, Characterization and Evaluation of 1,2-bis(2,4,6-trinitrophenyl) hydrazine: A Key Precursor for The Synthesis of High Performance Energetic Materials. J. Hazard. Mater. 2009, 172, 276–279.
(13) Talawar, M. B.; Savabalan, R.; Senthilkumar, N.; Prabhu, G.; Asthana, S. N. Synthesis, Characterization and Thermal Studies on Furazan- and Tetrazine-Based High Energetic Materials. J. Hazard. Mater. 2004, 113, 11–25.
(14) (a) Gao, H.; Shreeve, J. M. Azole-based energetic salts. Chem. Rev. 2011, 111, 7377–7436. (b) Holl, G.; Klapótké, T. M.; Polborn, K.; Rienacker, L.; Varis, S. A Review of Polycyclic Aromatic Energetic Materials. Angew. Chem., Int. Ed. 2005, 44, 3929.
(15) (a) Huynh, M. H. V.; Hiskey, M. A.; Chavez, D. E.; Naud, D. L.; Gilardi, R. D. Synthesis, Characterization, and Energetic Properties of Diazido Heteroaromatic High-Nitrogen C–N Compound. J. Am. Chem. Soc. 2005, 127, 12537. (b) Brand, H.; Mayer, P.; Schulz, A.; Weigand, J. J. Nitro(nitroso) cyanomethanides. Angew. Chem., Int. Ed. 2005, 44, 3929.
(24) Agrawal, J. P.; Hodgson, R. D. Organic Chemistry of Explosives; John Wiley & Sons Ltd.: Chichester, West Sussex, England, 2007; p 191.

(25) Cao, C.; Gao, S. Two Dominant Factors Influencing the Impact Sensitivities of Nitrobenzenes and Saturated Nitro Compounds. J. Phys. Chem. B 2007, 111, 12399–12402.

(26) Kamlet, M. J.; Adolph, H. G. The relationship of Impact Sensitivity with Structure of Organic High Explosives. II. Polynitroaromatic explosives. Propellants, Explos., Pyrotech. 1979, 4, 30.

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

(28) Dennington, R.; Keith, T.; Millam, J. GaussView, version 5; Semichem Inc.: Shawnee Mission, KS, 2009.

(29) Schaftenaar, G.; Noordik, J. H. Molden: A Pre- and Post-processing Program for Molecular and Electronic Structures. J. Comput.-Aided Mol. Des. 2000, 14, 123–134.

(30) Stewart, J. P. Stewart Computational Chemistry, version 7.263W. http://OpenMOPAC.net/.

(31) (a) Hobbs, M. L.; Baer, M. R. In Calibrating the BKW-EOS with a Large Product Species Database and Measured C-J Properties, Proceedings of 10th International Detonation Symposium, Boston, Massachusetts, July 12–16, 1993; p 409. (b) Dobratz, B. M.; Crawford, P. C.; LLNL Explosives Handbook: Properties of Chemical Explosives and Explosive Simulants; Report UCRL-52997 Change 2; University of California, Lawrence Livermore National Laboratory: Livermore, CA, 1985. (c) Kamlet, M. J.; Jacobs, S. J. Chemistry of Detonation. I. A Simple Method for Calculating Detonation Properties of C-H-N-O Explosives. J. Chem. Phys. 1968, 48, 23–35. (d) Sučeska, M. Calculation of Detonation Parameters by EXPLO5 Computer Program. Mater. Sci. Forum 2004, 465–466, 325–330.