北京理工大学

新体系教师聘期(中期)考核表

证明材料

姓　　名：尹平

现聘岗位：准聘教授

所在学科：材料科学与工程

研究方向：含能材料

所在单位：材料学院

填表时间：2022 年 02 月 18 日

目录

Chemical Engineering Journal 433 (2022) 134480

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

High performance and heat-resistant pyrazole-1,2,4-triazole energetic materials: Tuning the thermal stability by asymmetric framework and azo-bistriazole bridge

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ARTICLE INFO

Keywords:
Heat-resistant energetic materials
Pyrazole-1,2,4-triazole
Azo-bis(1,2,4-triazole) bridge
Promising candidates
Thermostability

ABSTRACT

Driven by ever-increasing application of thermal stable explosives in the deep mining and aerospace industries in recent years, the search for heat-resistant energetic materials with remarkable thermostability and high-energy level has attracted great attention. In this work, two advanced pyrazole-1,2,4-triazole-based heat-resistant explosives 5-(3,4-dinitro-1*H*-pyrazol-5-yl)-3-nitro-1*H*-1,2,4-triazole (**3**) and 1,2-bis(3-(3,4-dinitro-1*H*-pyrazol-5-yl)-1*H*-1,2,4-triazol-5-yl)diazene (**5**) were obtained using straightforward two-step synthetic routes. With a high crystal density of 1.873 g cm^{-3}, compound **3** features with an excellent thermal decomposition temperature of 336 °C, which ranges the highest among fully *C*-nitrated bicyclic azoles. In comparison to **3**, tetracyclic compound **5** exhibits enhanced thermostability (T_d = 354 °C), which is superior to that of **HNS** (T_d = 318 °C), and approaches that of **TATB** (T_d = 350 °C). Furthermore, the energetic properties (e.g., detonation velocity: 8568 and 8404 m s^{-1}, respectively) of **3** and **5** remarkably surpass those of **HNS** (7612 m s^{-1}) and **TATB** (8179 m s^{-1}), thereby highlighting **3** and **5** as promising candidates for advanced heat-resistant explosives. Our described molecular design, incorporating asymmetric structural motifs with azo-bis(1,2,4-triazole) bridge, will provide a synthetically simple approach for improving thermostability of energetic materials.

1. Introduction

Heat-resistant explosives with onset thermal decomposition temperature exceeding 300 °C are irreplaceable members among energetic materials (EMs), which have attracted widespread attention and have already achieved numerous developments in the military and civilian applications [1]. Especially in recent decades, to satisfy the growing demand in the special applied environments, e.g., space exploration and deep well blasting, the research on advanced thermal stable explosives is gradually becoming the focus of energetic materials community [2]. As compared to the traditional nitrobenzene-based thermostable explosives like trinitrotoluene (**TNT**), 1,3,5-triamino-2,4,6-trinitrobenzene (**TATB**), and 2,2′,4,4′,6,6′-hexanitrostilbene (**HNS**), nitrogen-rich heterocyclic compounds are emerged attractive candidates for preparing novel heat-resistant explosives. In addition to remarkable thermal stability, some representative compounds show unique benefits including good detonation performance, low mechanical sensitivity and high content of nitrogen gas as an environmentally friendly decomposition product, since the presence of a large number of inherently energetic N − N and C − N bonds [3]. However, how to fine-tune the thermostability in limited nitrogen heterocyclic skeletons by facile and efficient molecular design strategies remains a huge challenge and needs to be further explored [4].

Obviously, symmetric framework is a distinctive feature of traditional explosives such as cyclotrimethylenetrinitramine (**RDX**), cyclotetramethylenetetranitramine (**HMX**), and hexanitrohexaazaisowurtzitane (**CL-20**) [5]. In general, the popularity of symmetrical energetic molecules is mainly due to their ready availability and favorable crystal packing leading to high density [6]. Nevertheless, in the design and preparation of novel high-performance energetic compounds, owing to the limited structural units (e.g., benzene ring, nitrogen heterocycle, cage skeleton, etc.), the quantity and diversity of symmetric molecular scaffolds are greatly restricted, which is not conducive to molecular design of new energetic materials. Recently, through diversified screening and rational combination of various energetic rings, it is possible to access asymmetric energetic compounds displaying

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https://doi.org/10.1016/j.cej.2021.134480
Received 31 October 2021; Received in revised form 19 December 2021; Accepted 31 December 2021
Available online 6 January 2022

ARTICLE IN PRESS

Chemical Engineering Journal xxx (xxxx) xxx

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A strategy for stabilizing of N8 type energetic materials by introducing 4-Nitro-1,2,3-Triazole scaffolds

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A B S T R A C T

A series of multi-functionalized 4-nitro-1,2,3-triazole based C–N linked biheterocyclic energetic compounds were synthesized using CDI (1,1′-carbonyldiimidazole) induced dehydrative cyclization. Among these energetic analogues, the representative compounds **2** and **6** exhibit great potential as melt-castable explosive (**2**: T_m = 72 °C , T_d = 231 °C) and high-performance insensitive energetic material (**6**: d = 1.82 g cm^{-3}, D = 8688 m s^{-1}, IS > 40 J), respectively. More importantly, employing THA (*O*-tosylhydroxylamine) and SDIC(sodium dichloroisocyanurate), functionalized N8-branched compound (**F-N8B,** (*E*)-1,2-bis(4,5′-dinitro-2′H-[2,4′-bi(1,2,3-triazol)]-2′-yl)diazene) was synthesized via *N*-amination and oxidative azo coupling. In comparison to previously reported N8 type of energetic compounds, **F-N8B** exhibits improved impact sensitivity and friction sensitivity (IS = 7 J, FS = 72 N).

1. Introduction

In the field of energetic materials science, nitrogen-rich compounds containing long catenated nitrogen atom chains have attracted intense research from energetic community. Because of a large number of inherent N—N or N═N bonds within the structures, the long catenated nitrogen atom chains often result in high positive heats of formation, as well as high-energy.(1) Pioneering investigations have been made to achieve diversified challenging nitrogen atom chains, e.g., N7,(2,3,4) N8,(5,6,7) N10 (8,9,10) and even N11 (11) structures. Most of these compounds have high heats of formation, high nitrogen content (>60%) and good detonation velocity (up to 9426 m s^{-1}). However, the contradiction between high energy and stability is yet an unsolved task. Most long nitrogen-chains are extremely sensitive towards external mechanic stimuli.

No doubt designing and synthesizing these long nitrogen chains compounds are huge challenges.(12,13) Since we first achieved a stable compound (*E*)-1,2-di(1H-1,2,3-triazol-1-yl)diazene (**N8**, T_d = 193.8 °C) using oxidative azo coupling of N-NH$_2$ scaffolds, our continuing investigation on N8 structures was focused on regioisomeric compounds, named **N8L** and **N8B** (**N8L**, (*E*)-1,2-bis(4-nitro-1H-1,2,3-triazol-1-yl) diazene; **N8B**, (*E*)-1,2-bis(4-nitro-2H-1,2,3-triazol-2-yl)diazene), both of which have good detonation velocities (**N8L**, *D*, 8916 m s^{-1}; **N8B**, *D*, 8917 m s^{-1}). (5,6) Remarkably, the thermal stability and mechanic sensitivity of **N8B** are superior to those of **N8L** (**N8B**, T_d = 264 °C, IS = 2 J; **N8L**, T_d = 177 °C, IS = 1.5 J), and that is to say, **N8B** type is more conform to the rational design of energetic materials. (Fig. 1a) However, the N-amino precursors of **N8L** and **N8B** were synthesized via a poor regioselective N-amination (1.25:1), which led to a low total yield of **N8B**. Therefore, there are two difficulties to achieve highly regioselective synthesis of branched long nitrogen chains: (1) How to control the regioselectivity of N-amination reaction? (2) How to stabilize the metastable long catenated nitrogen atom chains?

Introducing a hindrance and stable functionalized group at 5-position into 4-nitro-1,2,3-triazole can be an alternative solution to current two problems. Aromatic nitrogen-rich azoles play an important role in High energy density materials (HEDMs) for their high heats of formation and good thermal stability from conjugated systems and planar structures.(14) 1,2,3-Triazole is an unexpectedly stable and energetic backbone compared to other compounds with three catenated nitrogen atoms. It has a high heat of formation (267.6 kJ mol^{-1}) comparable to furoxan (240.0 kJ mol^{-1}) and its isomer, i.e., 1,2,4-triazole (192.7 kJ mol^{-1}).(15) Featured with high performance and steric effect, 1,2,3-triazole is a favorable functionality to balance energetic property and reaction selectivity. However, owing to the difficulties of synthesis and functionalization, there is still a great demand to explore a strategy to introduce high-energy exlosophores into 1,2,3-triazole based backbone. (16–19) Given this background, we report a new strategy for stabilization of N8 type energetic materials (**F-N8B**, IS = 7 J, FS = 72 N) by incorporating a 4-nitro-1,2,3-triazole scaffold into the molecular structure. (Fig. 1b).

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https://doi.org/10.1016/j.cej.2021.133181
Received 4 August 2021; Received in revised form 20 October 2021; Accepted 21 October 2021
Available online 25 October 2021
1385-8947/

Chemical Engineering Journal 410 (2021) 128148

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

1,2,3-Triazole with linear and branched catenated nitrogen chains – The role of regiochemistry in energetic materials

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ARTICLE INFO

Keywords:
1,2,3-Triazole
Catenated nitrogen chains
Regiochemistry
Energetic materials

ABSTRACT

Two energetic molecules possessing a linear and branched N8 structure were synthesized based on the oxidative coupling of *N*-aminotriazoles. Despite the same chemical formula and azo functionality, the decomposition temperatures (T_d) of these two regioisomers reflect a gap of more than 80 °C. Based on the data of single crystal X-ray diffraction, comparative investigation associated with the bond length and stacking pattern rationalize the different properties of density and molecular stability. Theoretical analyses, *e.g.*, charge distribution and Hirshfeld surface, were carried out subsequently to gain more insight into the regiochemistry of catenated nitrogen-atom chains. The difference of charge distribution between two molecules caused by regional heterogeneity is the main reason for their different stabilities.

1. Introduction

Energetic materials for different purposes need to meet the corresponding technical targets, such as a primary explosive is sensitive to external stimuli and needs to quickly complete the transition from deflagration to detonation, and a propellant needs to display stable combustion and high specific impulse [1]. Although there is discrepancy in key targets, energetic materials have a common goal in their applications, including high energy output, good safety and environmental protection [2].

To achieve the above goals, many pioneering studies have been focused on high nitrogen content materials, the effective integration of structural units (nitrogen-rich heterocyclic ring, azo, nitro) through synthetic methods is the key field of energetic materials research [3]. The main reason is that molecules with high nitrogen content typically have high heats of formation, arising from large energy release which originates from the formation of N═N bonds [4]. With the above nitrogen-rich structure as the guarantee of high energy, more studies of energetic materials are focused on the discovery of an effective design and synthesis strategy that can meet the requirements of safety and environmental protection [5].

The importance of regional isomerization is reflected in many fields, such as organic synthesis, medicinal chemistry, and biology [6,7]. Furthermore, the impact of stereo- and regio-chemistry on energetic materials has attracted increasing attention with the prominent work of Baran [8] on a series of regioisomers of cyclobutane-based nitric esters as shown in Scheme 1a. The onset melting temperature of the two energetic molecules which are regional isomers of each other, are 85.9 and 146.9 °C respectively, contrary to the results predicted by theoretical calculations. NAPTO, a regioisomer of ICM-103, was reported recently, and displays a similar density and heat of formation with its isomer but shows significantly improved thermal stability (Scheme 1a, T_d = 203.2 °C) [9]. These studies show the effect of regional isomerization on the properties of energetic materials which is crucial to the design of new molecules.

The azo group has been reported not only as a highly energetic conjunctive linkage but also as one which dramatically increases the heats of formation of energetic molecules [10]. N-azo functionalization of nitrogen-rich azoles is a very effective design strategy to build energetic materials with long catenated nitrogen-atom chains [11]. The role of regional isomerization in energetic molecules with catenated nitrogen-atom chains is much less studied.

Now we report two regioisomeric energetic molecules, 1,2-bis(4-nitro-1*H*-1,2,3-triazol-1-yl)diazene (**N8L**) and 1,2-bis(4-nitro-1*H*-1,2,3-triazol-2-yl)diazene (**N8B**), which contain a linear nitrogen-atom chain and a branched nitrogen-atom chain, respectively. Two N1/N2-amino

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https://doi.org/10.1016/j.cej.2020.128148
Received 21 October 2020; Received in revised form 19 November 2020; Accepted 11 December 2020
Available online 16 December 2020

Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *J. Mater. Chem. A*, 2021, **9**, 12291

Tunable Dimroth rearrangement of versatile 1,2,3-triazoles towards high-performance energetic materials†

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Received 5th January 2021
Accepted 27th April 2021

DOI: 10.1039/d1ta00109d

rsc.li/materials-a

A highly efficient strategy of two different types of nitrogen-rich heterocyclic energetic compounds, featuring a single NH-bridge (–NH–) and a fused ring, was demonstrated by virtue of Dimroth rearrangement reactions using 4-amino-5-nitro-1,2,3-triazole as the precursor. Various nitrogen-rich compounds and their salts were prepared *via* this transformation and fully characterized using multinuclear NMR spectroscopy, IR, elemental analysis, and single crystal X-ray structuring. Their key properties, such as decomposition temperatures, densities, detonation velocities and pressures, and impact sensitivities, were obtained from theoretical calculations or experimental measurements. With different task-specific explosophores, the representative energetic compounds **6b** and **18** exhibit great potential as high performance insensitive energetic materials and organic primary explosives, respectively. This work gives the classic Dimroth rearrangement new vitality to access diversified task-specific energetic materials.

Introduction

The field of high energy density materials (HEDMs) has witnessed rapid development in military and civilian research systems.[1] Traditional HEDMs, such as RDX and TNT play irreplaceable roles in most currently used munitions. With a goal of balancing energy and stability, smart assembly of novel energetic backbones and functionalized groups is the first priority in structural innovation on a molecular level. However, unlike for most chemical materials, new synthetic methodologies for highly energetic moieties are still ongoing issues in the community of HEDMs.

Compared to the widely investigated building block azo-bridge (–N=N–), the NH-bridge (–NH–) in energetic compounds benefit from inter- or intramolecular hydrogen bonding interactions, which contributes greatly to the efficient crystal packing, and makes the compounds less sensitive toward external stimuli. However, traditional construction of such a structural motif *via* transition metal catalyzed cross coupling strategy is not suitable for nitrogen-rich heterocycles due to deactivation resulting from catalyst poisoning.[2] Other than from cross coupling reactions, *in situ* construction of NH-bridged energtics employ an acid-catalyzed cycloaddition of sodium azide and sodium dicyanamide to give 5,5′-bis(1*H*-tetrazolyl)amine (**H_2bta·H_2O**) as the monohydrate. A dehydration process at elevated temperature and reduced pressure gives the anhydrous product which exhibits good performance (*d*, 1.861 g cm^{-3}, D_v, 9120 m s^{-1}, IS > 30 J) (Fig. 1a).[3] In addition, the ionic derivatives of H_2bta exhibit excellent overall detonation properties superior to HMX.[4]

Fused nitrogen-rich heterocycles are attractive targets in preparation of HEDMs for their conjugated systems and coplanar structures that enhance heats of formation and thermal stabilities.[5] In 2016, Chavez's group developed a cyclization reaction of 3-amino-5-nitro-1,2,4-triazole and nitroacetonitrile with sodium nitrite and hydrochloric acid to obtain a fused triazolo-triazine bicycle (**DPX-26**) which displays favorable energetic performance comparable to RDX but with excellent insensitivity (Fig. 1b).[6] A fused ring that is functionalized by an azido group always produces primary explosive with good performance, like ICM-103.[7] Recently, we reported a metal-free explosive **1-1**, which shows a superior detonation performance (*d*, 1.82 g cm^{-3}, D_v = 8746 m s^{-1}) compared to commercial primary explosives (Fig. 1c).[8]

With three catenated nitrogen atoms, the 1,2,3-triazole ring has a high heat of formation comparable to furoxan and higher than the isomeric 1,2,4-triazole. However, limited to the characteristics of synthesis, functionalization and selectivity

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† Electronic supplementary information (ESI) available: DFT calculations; X-ray crystallography; NMR spectra. CCDC 1997519, 1997520, 2033555–2033557, 2033570, 2033571, 2013573. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ta00109d

OL Organic Letters

pubs.acs.org/OrgLett Letter

Construction of Bicyclic 1,2,3-Triazine *N*-Oxides from Aminocyanides

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Cite This: *Org. Lett.* 2021, 23, 734−738 Read Online

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ABSTRACT: Using a facile and cost-effective method, nine bicyclic 1,2,3-triazine 2-oxides were synthesized from *o*-aminocyanide substrates through an unusual nitration cyclization. The reaction mechanism was studied experimentally and theoretically. Moreover, nine 1,2,3-triazine 3-oxides were also obtained in good yields.

Triazines are a special class of heterocyclic compounds which are extensively studied for potential applications in agrochemicals,[1,2] pharmaceuticals,[3−5] energetic materials,[6,7] and synthetic intermediates.[8,9] Among the three possible isomers of triazine, 1,2,3-triazine is more favored than the 1,2,4- and 1,3,5-triazine isomers, largely due to their potent efficacy and less side effects as pharmaceuticals,[10] as well as higher energy content as energetic materials (Figure 1a).[11]

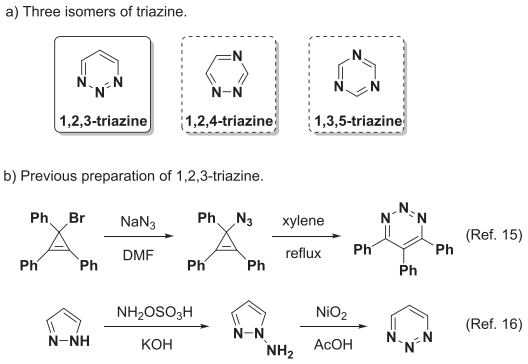


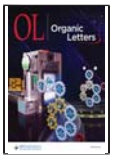
Figure 1. Structures and synthetic methods of 1,2,3-triazine.

However, 1,2,3-triazine is also the least studied due to synthetic difficulties in constructing such a catenated nitrogen chain in an aromatic ring. It was first prepared by Pinnow et al. in 1896 via reaction of 2-amino-*N*′-hydroxybenzimidamide with nitrous acid.[12] In 1910, Chandross et al. reported another approach via a pyrolytic rearrangement of 1,2,3-triphenylcyclopropyl azide.[13] Over the next 60 years, there were no significant advances in its synthesis until Igeta et al. reported the preparation of neat 1,2,3-triazine with an oxidative rearrangement from 1-aminopyrazole (Figure 1b).[14−16] Even now, it is still a great challenge to develop new facile and universal methods to prepare 1,2,3-triazine derivatives.

Although several monocyclic 1,2,3-triazine compounds have been reported over the past decades, 1,2,3-triazine *N*-oxides have attracted little attention. It was reported that the *N*-oxide functionality on aromatic heterocycles can enhance their pharmacological and energetic properties.[17−19] Few reports on preparation of 1,2,3-triazine *N*-oxides include a direct oxidation to 1,2,3-triazine 1-, 2-, and 3-oxides with *m*-chloroperoxybenzoic acid (*m*-CPBA)[20−23] and amino diazotization to a diazonium salt followed by reactions with a neighboring oxime to afford 1,2,3-triazine 1- or 3-oxide.[24,25] However, the majority of these reactions suffer from low tolerance of functional groups, multiple byproducts, and low selectivity of *N*-oxide positions. Thus, universal methods for the synthesis of 1,2,3-triazine *N*-oxide do not exist. Additionally, very little is known about the construction of bicyclic 1,2,3-triazine *N*-oxides. In recent efforts to develop new energetic compounds, two bicyclic compounds based on 1,2,3-triazine 2-oxide and 1,2,3-triazine 3-oxide skeletons were synthesized by us and Shreeve.[26,27] They showed promising detonation performances as primary explosives and fluorescent energetic materials. However, the reaction scope and mechanism of these methods for constructing other bicyclic 1,2,3-triazine *N*-oxides remain unclear.

In this work, we are interested in preparing a variety of bicyclic 1,2,3-triazine *N*-oxides from different *o*-aminocyanide substrates based on five- or six-membered aromatic rings. In method (I), *o*-aminocyanide is reacted with NaN_3 to give *o*-tetrazolylamine derivatives, followed by a one-step ring-closure reaction to yield the target products of bicyclic 1,2,3-triazine 2-oxides. In the first step reaction, 12 six- or five-membered

Received: November 29, 2020
Published: December 15, 2020



https://dx.doi.org/10.1021/acs.orglett.0c03952
Org. Lett. 2021, 23, 734−738

Energetic Materials Frontiers 2 (2021) 125–130

Contents lists available at ScienceDirect

Energetic Materials Frontiers

journal homepage: www.keaipublishing.com/en/journals/energetic-materials-frontiers

Comparative study on 1,2,3-triazole based azo- and triazene-bridged high-nitrogen energetic materials

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ARTICLE INFO

Keywords:
1,2,3-Triazole
Energetic compounds
Detonation performance
Comparative study

ABSTRACT

Two different 1,2,3-triazole based energetic compounds, featuring with azo (-N═N-) and triazene (-N═N–NH-) bridge were investigated. All newly synthesized compounds were fully characterized by multinuclear NMR spectroscopy, infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. Comparative study indicated that both of them are insensitive to the external mechanic stimuli, however, the other key energetic properties of azo compound (*E*)-1,2-bis(2-methyl-5-nitro-2H-1,2,3-triazol-4-yl)diazene(**2**), *e.g.*, density, detonation velocity and pressure are superior to those of triazene compound (*E*)-5,5'-(triaz-1-ene-1,3-diyl)bis(2-methyl-4-nitro-2H-1,2,3-triazole) (**1**). This work gives a revelation on the two different types nitrogen-bridged energetic materials, especially in rarely triazene-bridge type explosives.

1. Introduction

Recently, nitrogen-rich heterocyclic energetic compounds containing a bridge-linked structural motif have received considerable interest as explosives and propellants.[1,2] In comparison with carbon-containing bridges, *e.g.*, ethylene- and ether-bridges, catenated nitrogen-atom bridges have a number of N–N or N═N bonds which can gain additional energetic performance from high positive heats of formation other than the regular inter- or intramolecular redox reactions.[3] Hence, great efforts have been devoted to obtain catenated nitrogen-atom bridges energetic compounds.[4,5] For example, the heats of formation of N,N′-azo bridged tetrazole energetic compound (*E*)-1,2-bis(5-nitro-2H-tetrazol-2-yl)diazene(**A**)is as high as 1092 kJ·mol^{-1},[6] which is much higher than its N,N′-ether bridged compound 2,2'-(oxybis(methylene))bis(5-nitro-2H-tetrazole) (**B**).[7] Due to this reason, the detonation velocity of **A** also exceeds that of **B** (9184 *vs* 8892 m·s^{-1}, Scheme 1a).

Azo-bridge (-N═N-) is one of the most useful energetic building blocks to link two nitrogen-rich azoles.[8] The azo-linked energetic compounds, such as 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (**C**, TAAT)[9] and 3, 3′-diamino-4,4′-azofurazan (**D**, DAAzF),[10] have high positive heats of formation and favorable detonation properties, especially for TATT which features with the highest heat of formation (2171 kJ·mol^{-1}) among the reported energetic materials (Scheme 1b). Compared to the widely investigated azo-bridge (-N═N-), triazene-bridge (-N═N–NH-) has a longer catenated nitrogen atom chain, which can help to promote nitrogen content and heat of formation. In addition, the –NH– moiety can increase inter- or intramolecular hydrogen-bonding interactions, which makes energetic compounds less sensitive toward external stimuli. However, only few related works have been reported because of great difficulties in synthesizing and handling such long nitrogen-bridge skeleton. The most famous compound containing triazene-bridged structure is (*E*)-1,1'-(triaz-1-ene-1,3-diyl)bis(1H-tetrazol-5-amine) N_{11}, which has 11 catenated nitrogen-atom chain in a cocrystal (the bimolecular 5-aminotetrazole and corresponding chloride salt). The pure neutral compound could not be isolated due to its instability.[11] Sheremetev group reported the synthesis of (*E*)-4,4'-(triaz-1-ene-1,3-diyl)bis(3-nitro-1,2,5-oxadiazole) (**E**) but the key properties were not further described (Scheme 1c).[12] In 2009, bis(2-methyltetrazolyl)triazene (**F**) by diazotation of 2-methyl-5-aminotetrazole was synthesized by Klapötke group synthesized and its energetic properties, *e.g.*, density (*d*), 1.532 g·cm^{-3}, detonation velocity (v_D), 7982 m·s^{-1}, impact sensitivity (*IS*), 2.5 J, were studied as well (Scheme 1c).[13] Given the limited cases of this research, introduction of azo-bridge (-N═N-) and triazene-bridge into more nitrogen-rich heterocycles are significant for exploring new energetic

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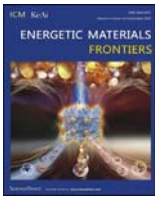
https://doi.org/10.1016/j.enmf.2021.03.006
Received 14 February 2021; Received in revised form 23 March 2021; Accepted 23 March 2021
Available online 28 April 2021

Energetic Materials Frontiers xxx (xxxx) xxx

Contents lists available at ScienceDirect

Energetic Materials Frontiers

journal homepage: www.keaipublishing.com/en/journals/energetic-materials-frontiers



N-amination of nitrogen-rich scaffolds: From single N–N bond formation to diverse energetic functionalization strategies

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ARTICLE INFO

Keywords:
Azoles
Nitrogen-rich
N-amination
Energetic materials

ABSTRACT

The bond-formation strategy associated with carbon and nitrogen atoms is one of the most vital fundamental techniques in the construction of organic molecules. In comparison to well-established methodologies of C–C and C–N bond formation in general synthetic chemistry, the development of N–N single bond formation for nitrogen-rich organic compounds is relatively rare. This paper summarizes the advances made in *N*-amination reagents and reaction conditions over the recent five years in terms of the N–N bond formation of high-energy frameworks, such as pyrazoles, 1,2,4-triazoles, 1,2,3-triazoles, and 1,3,4-oxadiazoles. Furthermore, this paper discusses the physiochemical properties of recent *N*-amino heterocyclic compounds and their energetic derivatives, thereby holding great promise as a guideline for rational structural modification of energetic materials. This work is aimed at providing an overall view of *N*-amination to access diversely functionalized energetic materials.

1. Introduction

The innovative strategy of bond formation has attracted intense attention from the synthetic community in both industrial and academic fields. The applications of coupling reactions have revolutionized the field of organic chemistry since it allows for the exploration of highly efficient and wide-scope catalytic systems. For example, given the tremendous utility of C–C bond formation, pioneering researches into name reactions (Suzuki, Heck, and Negishi reactions) have provided versatile palladium-catalyzed cross-coupling strategies by Nobel laureates and other organic chemists since the 1970s.[1–3] Regarding C–N bond formation, nucleophilic substitution, reductive amination, and newly emerging transition-metal-mediated C–N cross-coupling reactions (Buchwald−Hartwig, and Chan−Lam reactions)[4–6] have well been established over the past three decades, which contributes greatly to natural product synthesis, drug discovery, and organic functionalized materials (Fig. 1).

With the rapid development of energetic materials, the demand for new high-energy organic molecules has risen. The release of massive energy from energetic materials based on energy storage relies on numerous carbon-nitrogen and nitrogen-nitrogen bonds in the energetic nitrogen-rich scaffolds. Therefore, it is highly necessary to develop facile bond formation strategies for the construction of high-energy building blocks. However, the bond formation in nitrogen-rich architectures faces long-standing synthetic challenges caused by a series of synthetic problems: (1) the nitrogen site of N-heterocycles frequently leads to catalyst poisoning; (2) reductive amination is not compatible with strongly electronic-withdrawing groups, such as nitro and azo groups; (3) nucleophilic substitution is hampered by the steric effects of fully functionalized energetic backbones. Given this, exploring a suitable bond formation strategy is highly desirable for energetic materials.

Reflecting on the field of the bond formation in electron-deficient energetic heterocycles and nitro-substituted benzenes (Fig. 1), the C–N bond formation can be frequently performed using aromatic nucleophilic substitution (S_NAr), Chichibabin amination, and vicarious nucleophilic substitution (VNS).[7–9] Among them, S_NAr reactions have been widely utilized in some benchmark energetic materials, such as 1,3,5-triamino-2,4,6trinitrobenzene (TATB), 2,6-diamino-3,5-dinitropyrazine-1--oxide (LLM-105), and 2,4,6-triamino-5-nitropyrimidine-1,3-dioxide (ICM-102).[10,11] Similarly, the VNS amination of hydrogen is another useful methodology that allows an amino group to be introduced into nitrobenzenes and nitroazoles.[12] Nevertheless, in comparison to energetic C–N bond formation, the investigation of N–N single bond formation is relatively rare. Most research interests are devoted to the N═N

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https://doi.org/10.1016/j.enmf.2021.11.003
Received 31 August 2021; Received in revised form 18 October 2021; Accepted 9 November 2021
Available online xxxx

Please cite this article as: Pei L, Xie C-p, Yin P, , *N*-amination of nitrogen-rich scaffolds: From single N–N bond formation to diverse energetic functionalization strategies, Energetic Materials Frontiers , https://doi.org/10.1016/j.enmf.2021.11.003

Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *J. Mater. Chem. A*, 2021, **9**, 24903

Bridged and fused triazolic energetic frameworks with an azo building block towards thermally stable and applicable propellant ingredients†

Qiong Yu, ‡[a] Fengsheng Li,‡[b] Ping Yin, *[b] Siping Pang, *[b] Richard J. Staples [c] and Jean'ne M. Shreeve *[a]

The assembly of nitrogen-rich building blocks determines the energy storage capacity and affects the stability of energetic materials. Owing to the environmentally harmful properties of the propellant, ammonium perchlorate (AP), much research has explored halogen-free replacements which often suffer from poor thermal stability. In our goal of balancing performance and stability, we report access to an energetic molecule (**3**) by smart assembly of an azo bridge into trinitromethyl triazoles. Compound **3** exhibits a decomposition temperature of 175 °C, which approaches the highest among reported trinitromethyl derivatives. The density (1.91 g cm^{-3}) and oxygen balance (+29%) for **3** exceed other candidates, suggesting it as a high energy dense oxidizer (HEDO) replacement for AP in rocket propellants. One-step azo-involved cyclization of **3** give two fused nitro triazolones, (**FNTO**) **4** and its *N*-oxide **5**, having thermal stabilities and energies superior to the analogous derivatives of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazole-3-one (**NTO**). The comparison of properties of the fused triazolones **4** and **8** and their *N*-oxide derivatives **5** and **9** shows that formation of an *N*-oxide is an effective strategy which results in an increase of the decomposition temperature, oxygen balance, specific impulse, and detonation properties and in a decrease of the sensitivity of the corresponding energetic material. This work highlights bridged and fused triazolic energetic frameworks with an azo building block providing an alternative structural motif for seeking an applicable high-energy ingredient.

Received 2nd September 2021
Accepted 28th October 2021

DOI: 10.1039/d1ta07520a

rsc.li/materials-a

Introduction

Since Alfred Nobel successfully stabilized nitroglycerine by smart composite formulation a century and a half ago, sustained research efforts have been focused on high-energy density materials (HEDMs) by the scientific community. Although high energy and good stability are the continuing criteria for energetic materials, frontier research tends to stabilize these meta-stable ingredients from the molecular level. The rapid development of high-energy compounds provides a multi-disciplinary platform by merging not only composite materials, but also molecular design and synthetic innovation. Searching for new applicable HEDMs to replace the current benchmark materials is an effective way to improve the energy level.[1–3] However, the generation of new energetic molecules has faced a long-term scientific challenge since the pursuit of high-energy is at variance with safety requirements in production, storage, and transportation.

In general, synthetic innovation focused on rationalized energetic functionalization and new molecular scaffolds are the primary pathways to access new HEDMs. Therefore, most investigations have been devoted to the construction of nitrogen-rich heterocycles, as well as the smart late-stage functionalization of these high-energy backbones. Based on the structural features of high-energy molecules, rational incorporation of various nitrogen-rich building blocks is one of the most vital factors used to balance the energetic performance and stability. As one of the most important branches of HEDMs, the propellant is widely applied as the main power source in the design of rockets, missiles and launch vehicles. The major objective in the development of solid rocket propellants is to increase the energy. Currently, ammonium perchlorate (AP) which has been used as an excellent oxidizer in solid rocket propellants for many decades.[4] However, it releases perchlorate into groundwater systems and generates hydrogen chloride during burning likely resulting in environmental problems such as enhancing acid rain and depletion of the ozone layer.[5] Some promising AP replacements, *e.g.* ammonium dinitramide

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† Electronic supplementary information (ESI) available: Experimental details for the preparation, theoretical calculations, characterization of materials (PDF). CCDC 2008399, 2008400 and 2041417. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ta07520a

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Chemical Engineering Journal 412 (2021) 128697

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

One-step synthesis to an insensitive explosive: *N*,*N*′-bis((1*H*-tetrazol-5-yl) methyl)nitramide (BTMNA)

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ARTICLE INFO

Keywords:
One step synthesis
Energetic materials
Nitroamine
Tetrazole
Insensitive applicable explosive

ABSTRACT

RDX is used widely as a practical secondary explosive for civilian and military applications because of its high chemical stability and explosive power. However, a major shortcoming of RDX is its high sensitivity which leads to numerous accidents by accidental initiation. One of the major challenges in worldwide energetic materials research is the design and synthesis of insensitive high performing explosives. In this work, *N*,*N*′-bis((1*H*-tetrazol-5-yl)methyl)nitramide (BTMNA) (Mitchell et al., 2017) is obtained by a one-step reaction in >90 yield. The structure of BTMNA was confirmed by elemental analysis and X-ray single crystal diffraction. As a result of hydrogen bonding, the crystal density of BTMNA is 1.822 g/cm^3 at 100 K. The thermal decomposition temperature is 198 °C, and the impact and friction sensitivities are remarkable at 30 J, and 360 N. BTMNA, in its role as an insensitive RDX alternative, has a detonation velocity and pressure of 8732 m/s and 29.4 GPa, respectfully, thus making it a practical replacement for RDX.

During the last decade, new high-energy-density materials (HEDMs) have attracted considerable interest worldwide for civilian and military applications, and many compounds with high detonation performance have been synthesized [1]. However, it is extremely difficult to combine high detonation performance and low sensitivity into a single compound [2]. The cost of chemical syntheses of new HEDMs is a very important factor to be considered. Trinitrotoluene (TNT) was prepared in 1863 by German chemist Julius Wilbrand and was originally used as a yellow dye [3]. TNT is valued because of its insensitivity to shock and friction with a reduced risk of accidental detonation compared to more sensitive explosives such as nitroglycerin [4]. In industry, TNT is produced in a three-step process: 1) toluene is nitrated with a mixture of sulfuric and nitric acid to produce mononitrotoluene (MNT); 2) MNT is separated and then renitrated to dinitrotoluene (DNT); and finally 3) DNT is nitrated to trinitrotoluene (TNT) with an anhydrous mixture of nitric acid and oleum [5]. But the detonation performance of TNT is not good enough for modern explosive industry. So far, RDX is currently the most important explosive for military applications because its outstanding properties are based on its high chemical stability and high explosive power that considerably surpass that of TNT [6]. It is obtained by treating hexamethylenetetramine with white fuming nitric acid. But RDX has a high sensitivity value which results in accidental initiation. 1,1-Diamino-2,2-dinitroethene (FOX-7) was first synthesized 23 years ago [7]. Recently, this compound has emerged as a potential candidate for use as an insensitive HEDM, attracting substantial interest because of its high performance as an explosive is comparable to RDX with a markedly lower sensitivity to impact and friction which thus avoids accidental initiation [8]. The production of FOX-7 is based on a commercial starting material and the synthesis is straightforward. FOX-7 is attractive because of its straightforward synthesis at lower production costs and high detonation properties. The low sensitivity of this HEDM reduces dramatically the risk of serious and fatal accidents during its handling and application [9]. ATB (2,4,6-triamino-1,3,5-trinitrobenzene) is an insensitive high explosive (IHEs) and is useful where extreme safety is required. However, relative to RDX, TATB has a low detonation performance [10]. Although HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazoctane), TKX-50 (dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate) and Cl-20 (hexanitrohexaazaisowurtzitane) have higher detonation performances, due to their high sensitivity and complicated synthetic processes, their wide use in the explosive industry is modest [11]. As a result, one of the biggest challenges in worldwide energetic materials research is to synthesize a compound that balances sensitivity

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https://doi.org/10.1016/j.cej.2021.128697
Received 7 December 2020; Received in revised form 18 January 2021; Accepted 21 January 2021
Available online 27 January 2021

证书号第4932761号

发明专利证书

发明名称：5,5′-三氮烯桥连双(2-甲基-4-硝基-1,2,3-三唑)化合物的合成方法

发明人：冯尚彪;尹平;何春林;庞思平

专利号：ZL 2020 1 0448220.6

专利申请日：2020年05月25日

专利权人：北京理工大学重庆创新中心;北京理工大学

地址：401120 重庆市渝北区龙兴镇曙光路9号9幢

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2020年9月18日

附件：项目评审意见及修改意见表

项目批准号	22075023	项目负责人	尹平	申请代码1	B050601
项目名称	含能稠环分子设计中非芳香型杂环的合成策略				
资助类别	面上项目		亚类说明		
附注说明					
依托单位	北京理工大学				
直接费用	63.00 万元		起止年月	2021年01月 至 2024年12月	

通讯评审意见:

<1>具体评价意见:

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高能含能材料的研究一直具有重大的意义，也是国家战略发展中极其重要的一环。本项目结合申请人前期的研究基础创造性的提出了“芳香杂环+非芳香杂环”的策略，同时合理的设计骨架构建和官能团引入的方法。在含能化合物的性能上也综合考虑新型含能化合物的高能量和稳定性。该项目为未来含能材料的设计提供了新思路，具有一定的创新性。

二、请评述申请项目所关注问题的科学价值以及对相关前沿领域的潜在贡献。

项目为未来新型含能化合物的设计提供了新的思路，符合新型含能材料需要兼具高能和稳定两个特性的发展趋势，有较高的科学价值，可以对含能材料领域的发展做出贡献。

三、请评述申请人的研究基础与研究方案的可行性。

申请人研究基础深厚，发表了多篇高水平的学术论文。在化合物筛选上给出了充分的理论依据，在化合物合成路线设计细节上也有比较详细的阐述。研究方案总体可行。

四、其他建议

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能量与安全性的合理匹配是含能材料领域的热点，也是难点。申请者预通过构筑非芳香型富氮杂环含能骨架，经含能官能团的合理匹配，实现含能化合物的能量与安全性的平衡。思路新颖，方案合理，研究基础良好，建议资助。

二、请评述申请项目所关注问题的科学价值以及对相关前沿领域的潜在贡献。

三、请评述申请人的研究基础与研究方案的可行性。

四、其他建议

<3>具体评价意见:

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二、请评述申请项目所关注问题的科学价值以及对相关前沿领域的潜在贡献。

申请人开展了扎实的文献调研和资料查阅工作，对研究工作有较为深刻的理解和认识，通过对文献的综合分析，凝练了亟待解决的瓶颈问题，值得开展探索研究。

三、请评述申请人的研究基础与研究方案的可行性。

申请人研究基础较为扎实，研究能力较强，研究水平较高，发表了数篇高水平的代表性论文，研究方案细致可行，可行性分析理性客观，具有完成项目研究任务的实力。

四、其他建议
研究内容部分的撰写过于简单，申请人需结合研究工作具体细化。

修改意见：

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2020年9月18日

Invitation to Review for Current Topics in Medicinal Chemistry

发件人 **"吴昊星" <haoxingwu@hmrrc.org.cn>**
日 期 2018年10月07日 星期日 11:46
收件人 "pingyin" <pingyin@bit.edu.cn>
附 件 2个 (Evaluation Form - CTMC.doc ...)

Dear Prof. Yin at BIT

A manuscript entitled " Radionuclide-labeled peptides for imaging and treatment of CXCR4-overexpressing malignant tumors " has been submitted to Current Topics in Medicinal Chemistry.

I would be delighted if you could review for us. An abstract of the manuscript is at the end of this letter.

Current Topics in Medicinal Chemistry is a forum for the review of areas of keen and topical interest to medicinal chemists and others in the allied disciplines, aiming to contribute to the growth of scientific knowledge and insight, and facilitate the discovery and development of new therapeutic agents to treat debilitating human disorders.

We aim to provide a rapid service for our authors. Therefore, please respond to this invitation within 3 days of receiving this email, and provide your comments within 14 days of agreeing (***Evaluation Form***). If you need longer to provide your report please let me know. If you are unable to review at this time, I would be grateful if you could recommend another expert reviewer.

Many thanks in advance for your help. I look forward to hearing from you.

Yours sincerely,

Haoxing Wu
Guest Editor – Current Topics in Medicinal Chemistry
Bentham Science Publishers
Email：haoxingwu@scu.edu.cn/haoxingwu@hmrrc.org.cn

Title: Radionuclide-labeled peptides for imaging and treatment of CXCR4-overexpressing malignant tumors

Abstract: Malignant tumors are a major cause of death. The lack of methods that provide an early diagnosis and adequate treatment of cancers is the main obstacle to precision medicine. The C-X-C chemokine receptor 4 (CXCR4) is overexpressed in various tumors and plays a key role in tumor.

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Dear Dr. Yin,

ER-21-20662 "Theoretical design and selection of pyrazolo[3,4-d][1,2,3]triazole-based high-energy materials".

We recognise that the impact of the COVID-
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MANUSCRIPT DETAILS

TITLE: Theoretical design and selection of pyrazolo[3,4-d][1,2,3]triazole-based high-energy materials

AUTHORS: Jin, Xinghui; Liu, Luhao; Zhou, Jianhua; Hu, Bingcheng

ABSTRACT: In this study, we design a series of bridged energetic compounds based on pyrazolo[3,4-d]
[1,2,3]triazole to screen potential energetic materials with excellent detonation properties and acceptable sensitivities. The electronic structures, he

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日 期 2021年08月04日 星期三 19:56
收件人 "Ping Yin" <pingyin@bit.edu.cn>

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Title: Toward the defect engineering of energetic materials: a review of the effect of crystal defects on the sensitivity
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Kai Zhong; Rupeng Bu; Fangbao Jiao; Guangrui Liu

ABSTRACT:
Defects always exist in the applied energetic materials (EMs) and have a vital influence on the ignition mechanism and further the sensitivity. The d
induced enhancement of sensitivity, as that the molecules of defects possess thermodynamic and kinetic advantages in the external stimuli induce
decomposition over those in the perfect bulk. Besides, we present a perspective of the defect engineering of EMs, in which the structure-activity relationship and the efficient creation and use of defects are put forward.

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10-Aug-2021

Journal: Crystal Growth & Design
Manuscript ID : cg-2021-007399
Title : "Salt formation, to achieve a good balance between high energy and insensitivity of nitroform-based energetic compounds"
Author(s): Yang, Feng; Xu, Yuangang; Wang, Pengcheng; Lin, Qiuhan; Lu, Ming

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Manuscript Abstract for cg-2021-007399:

Energetic salts are one of the important research categories in the field of energetic materials. In this research, a series of energetic salts 5, 6, 7 and ray single crystal diffraction. As energetic compounds, their energy performance and sensitivity to mechanical stimuli have been explored. These cc 9.13 km s-1 and P = 30.5-37.4 GPa) and extremely high specific impulse (Isp = 262.63-
277.42 s), but also shows low sensitivity to mechanical stimuli. According to the crystallographic data, the relationship between molecular structure

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Thank you.

聘 书

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