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One step synthesis of nitrogen-rich green primary explosives from secondary explosives: synthesis, characterization, and performance study†

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Primary explosives are essential for initiating combustion or detonation in propellants and secondary explosives. Hence, there is a critical need to find a green and safe alternative primary explosive to replace the extremely toxic metal-based compounds. We have synthesized metal-free primary explosives and characterized them using various analytical techniques such as multi-nuclear magnetic resonance (NMR; ¹H, ¹³C, ¹⁵N), infrared spectroscopy (IR), elemental analysis (EA), high-resolution mass spectrometry (HRMS) and differential scanning calorimetry (DSC). The structure of 5,5'-diazido-4,4'-dinitro-1*H*,1'*H*-2,2'-biimidazole (**6**) was further supported by single crystal X-ray data. 5-Azido-4,4',5'-trinitro-1*H*,1'*H*-2,2'-biimidazole (**2**) and dihydroxylammonium-5-azido-4,4',5'-trinitro-[2,2'-biimidazole]-1,1'-diide (**3**) show excellent thermal stabilities (252 and 245 °C) and detonation velocities (8093 and 8494 m s⁻¹) compared to diazodinitrophenol (DDNP, 6900 m s⁻¹) and Pb(N₃)₂ (5877 m s⁻¹). Both compounds **2** and **3** are more insensitive to friction (>240 N) and impact sensitivity (5 to 10 J) than the benchmark materials DDNP (1 J, 24.7 N) and Pb(N₃)₂ (2.5 J, 0.1 N). Considering the overall fine-tuned performance, these newly synthesized compounds have significant potential to serve as primary explosives.

Introduction

Primary explosives are an essential class of energetic materials and refer to highly sensitive mixtures/compounds crucial in initiating explosive reactions.^{1,2} Primary explosives can be quickly initiated by small external stimuli or a simple initiating impulse (such as heat, a flame, friction, impact, or an electric spark).³ They are primarily applied in detonators to induce shock for initiating less-sensitive secondary explosives.⁴ Another vital application of them is as sensitizers in priming mixtures. Primary explosives play a crucial role in the reliable ignition of these priming compositions, making them sensitive to external stimuli enough to be easily ignited.^{5,6} Lead styph-nate, lead azide, mercury fulminate, silver azide, dinol, and tetrazene are classic examples of primary explosives, as shown in Fig. 1.^{7–9} Notably, concerns over environmental hazards, lead

and mercury toxicity, and health threats of the combustion products have led to a search for heavy metal-free compositions that would be less harmful yet have performance properties and other essential characteristics comparable to those of their lead-containing predecessors.^{10,11} In recently reported works, promising replacements for lead-free primary explosives were obtained using nitrogen-rich materials and their complexes with nontoxic sodium, ammonium, and iron cations.¹² Subsequent attempts to develop alternative primary explosives with potassium metal, such as potassium bis(dinitromethanide) furoxan (K2BDNMF),¹³ potassium dinitramino bistetrazole (K2DNABT),¹⁴ and other neutral nitrogen rich heterocyclic compounds like cyanuric acid triazide (CTA)¹⁵ and diazidobistriazole (DAZBT),¹⁶ have encountered challenges such as insufficient detonation properties and very high sensitivity, which could lead to casualties in the event of premature or accidental explosions. There is a continuous search for effective strategies for the design and synthesis of energetic materials by incorporating explosophores such as -NO₂, -NHNO₂, -NH₂, -N₃, driven by diverse objectives.¹⁷ One noteworthy approach involves the azidation of heterocyclic backbones, proving to be effective in creating primary explosives.¹⁸ Additionally, the incorporation of both azido and nitro groups has been investigated for the ability to create a balance of detonation properties.¹⁹ These materials, due to their susceptibility to impact initiation, have been extensively investigated as lead-free primary explosives.^{20–25} In light of

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† Electronic supplementary information (ESI) available: Synthesis, characterization data, computational details, crystal refinements, X-ray crystallographic file in CIF format for **6**. This material is available free of charge. CCDC 2312111. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4ma00430b>

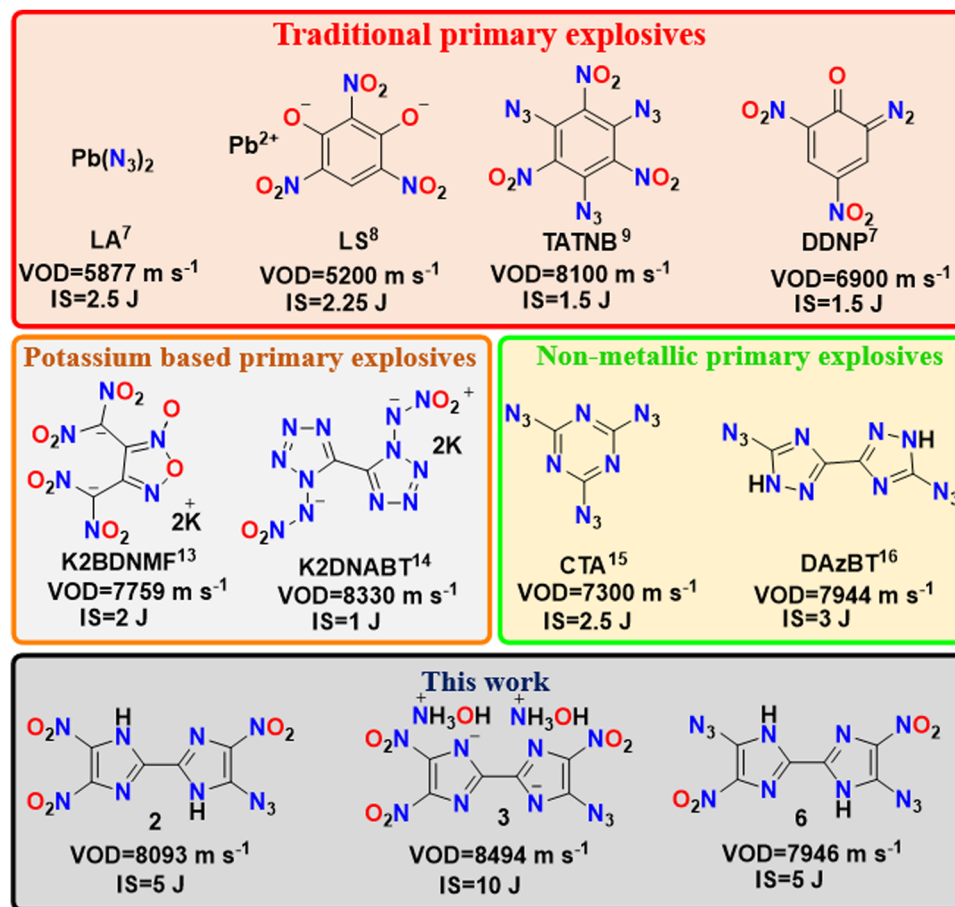


Fig. 1 Comparison of previous reports with this work.

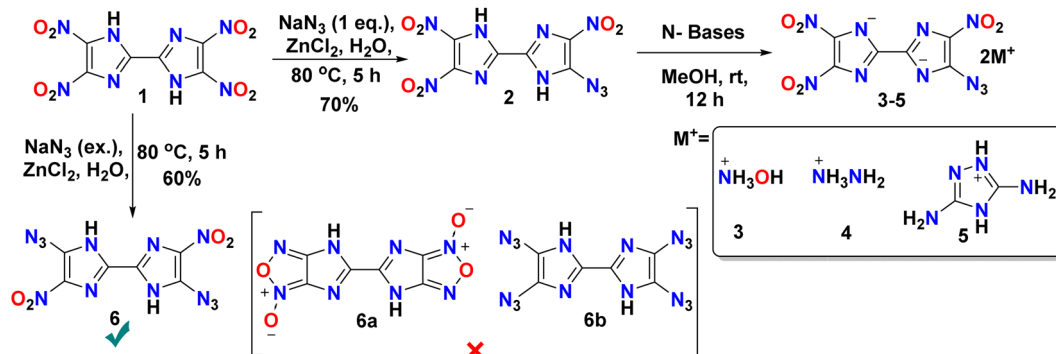
these advancements, imidazoles stand out as a distinctive class of compounds, offering a higher number of functional sites.²⁶ Backbones featuring two or more nitro groups, in conjunction with azido groups, are anticipated to serve as promising energetic ingredients for primary explosive formulations.^{27–29} The incorporation of a nitro-containing imidazole backbone presents numerous advantages, including a substantial nitrogen and oxygen content, good thermal stability, chemical robustness, and versatile structural functionality.^{30–32} Introduction of multiple nitro groups in these energetic compounds results in elevated density and favorable oxygen balance.³³ To obtain a better understanding of balanced properties, we report the synthesis of 5-azido-4,4',5'-trinitro-1*H*,1'*H*-2,2'-biimidazole (2), and 5,5'-diazido-4,4'-dinitro-1*H*,1'*H*-2,2'-biimidazole (6) using the Lewis acid, zinc chloride. Later, compound 2 was treated with various nitrogen-rich bases to obtain energetic salts. Recently, Tang *et al.* reported the synthesis of compound 6 from the reaction of the diazonium salt of 4,4'-diamino-5,5'-dinitro-1*H*,1'*H*-2,2'-biimidazole with a mixture of hydrazine monohydrate and sodium nitrite in acidic conditions or sodium azide.³⁴

Synthesis

4,4',5,5'-Tetranitro-1*H*,1'*H*-2,2'-biimidazole (1) was synthesized according to the procedure reported in the literature.^{35,36} It was

treated with different concentrations of sodium azide and zinc chloride in water at 80 °C for 12 hours, followed by acidification to pH = 2 using conc. HCl, which led to the formation of new precipitates, di and mono azido-substituted compounds 5-azido-4,4',5-trinitro-1*H*,1'*H*-2,2'-biimidazole (2) and 5,5'-diazido-4,4'-dinitro-1*H*,1'*H*-2,2'-biimidazole (6) in good yield rather than the expected furoxan and tetra azido substituted compounds 4*H*,4'*H*-[5,5'-biimidazo[4,5-*c*][1,2,5]oxadiazole] 1,1'-dioxide (6a) and 4,4',5,5'-tetraazido-1*H*,1'*H*-2,2'-biimidazole (6b). Even after using an excess amount of sodium azide, only compound 6 was produced and attempts to obtain the poly-substituted azide (6b) failed. The main reason behind the failure of this attempt is the addition-elimination mechanism which is not favored after the substitution of two azide. Moreover, to improve the yields of compounds 2 and 6, various solvent screenings were performed as shown in Table S1 (ESI[†]). The additive ZnCl₂ in water was found to be the most suitable combination. Compounds 2 and 6 were then treated with various nitrogen-rich bases such as hydroxyl amine monohydrate, hydrazine monohydrate and 3,5-diaminotriazole in methanol at room temperature to form their energetic salts. We failed to get the energetic salts from compound 6 but compound 2 afforded dihydroxylammonium-5-azido-4,4',5'-trinitro-[2,2'-biimidazole]-1,1'-diide (3), dihydrazinium-5-azido-4,4',5'-trinitro-[2,2'-biimidazole]-1,1'-diide (4),





Scheme 1 Synthesis of mono and di-azido substituted bis-imidazoles (2 and 6) and energetic salts of 2 (3–5).

and bis-3,5-diamino-4*H*-1,2,4-triazol-1-ium-5-azido-4,4',5',5'-trinitro-[2,2'-biimidazole]-1,1'-diide (5) in quantitative yields as shown in Scheme 1.

^{15}N NMR

Proton decoupled ^{15}N measurements were carried out for compound 3 and are shown in the ESI† (Fig. S9). The nitro group nitrogen signals appeared at δ (ppm) = -25.91 , and -35.40 ; imidazole moiety signals appeared at δ (ppm) -105.21 , -117.28 , -123.02 , and -129.06 ; azide group signals appeared at δ (ppm) = -157.03 , -187.09 , -231.50 ; while the hydroxylammonium peak appeared at -276.70 ppm.

Crystal structure

A suitable crystal of 5,5'-diazido-4,4'-dinitro-1*H*,1'*H*-2,2'-biimidazole (6) was obtained by slow evaporation of water having monoclinic space group *Pc* with two molecular units per unit cell and a crystal density of 1.69 g cm^{-3} at 100 K.

Compound 6 has low crystal density as it crystallized with six water molecules. The bond length of C2–N3 is $1.426(4)\text{ \AA}$, while that of C1–C1^a is $1.453(7)\text{ \AA}$ and of C2–C3 is $1.365(4)\text{ \AA}$, which indicates their partial single and double bond character, respectively. The nitrogen bond lengths in azide are N4–N5 = $1.253(7)\text{ \AA}$ and N5–N6 = $1.008(7)\text{ \AA}$. The two rings are coplanar with the torsional angle of N1–C1–C1^a–N1^a = -180.0° . The substituent on C2 (nitro) is in plane with the ring having the bond angle N1–C2–N3 = 120.3° , while the substituent on C3 (azido) is slightly tilted C2–C3–N4 = 139.1° . The interlayer distance between two planes is 2.96 \AA . The 3D crystal arrangement shows cross-linked crystal packing with intense non-covalent interactions (NCI) (Fig. 2a–d).

Physicochemical properties

Thermal stability is a crucial parameter to assess the resistance of energetic materials to detonation or decomposition when subjected to heat. A higher value of thermal decomposition (T_d)

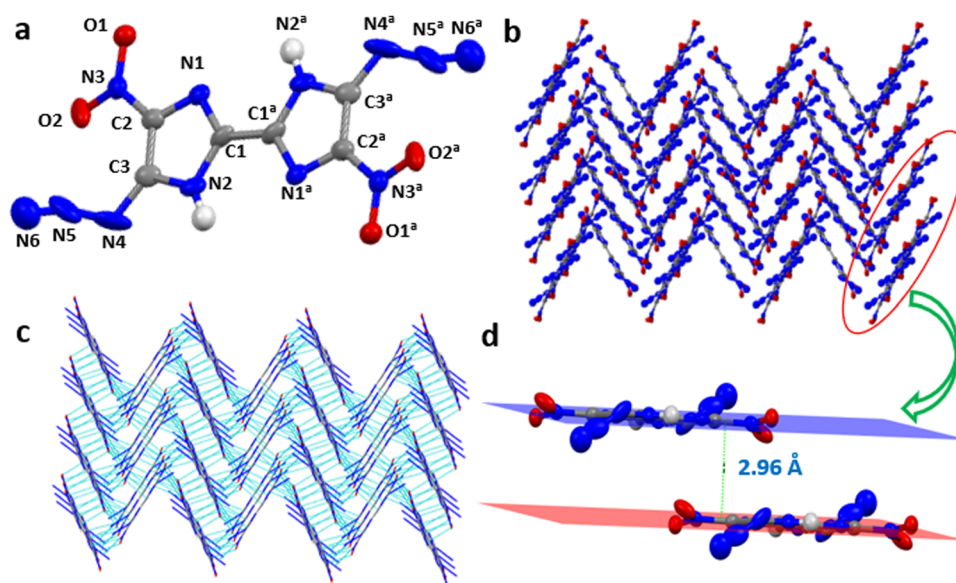


Fig. 2 (a) Crystal structure (water is omitted for clarity). (b) Cross-linked crystal packing along *b*-axis. (c) Non-covalent interactions along *b*-axis (wireframe model). (d) Interlayer distance between two layers for compound 6.



Table 1 Physicochemical and detonation properties of compounds (2–6) compared with DDNP and Pb(N₃)₂

Compd	T_d^a [°C]	ρ^b [g cm ⁻³]	HOF ^c [kJ mol ⁻¹]	VOD ^d [m s ⁻¹]	DP ^e [GPa]	N + O ^f [%]	IS ^g [J]	FS ^h [N]
2	252	1.77	458	8093	26.7	76.11	5	240
3	245	1.77	466	8494	30.0	78.70	10	360
4	131	1.65	684	8072	25.1	78.05	7.5	360
5	120	1.69	819	7593	21.3	73.99	10	360
6	112	1.76	755	7946	24.9	75.80	5	240
DDNP ⁱ	157	1.72	321	6900	24.2	64.74	1	24.7
Pb(N ₃) ₂ ⁱ	315	4.8	450.1	5877	33.4	28.86	2.5	0.1

^a Onset decomposition temperature under nitrogen gas (DSC, 5 °C min⁻¹). ^b Density measured by Anton parr Ultrapy 5000 micro gas pycnometer (25 °C). ^c Computed heat of formation. ^d Detonation velocity. ^e Detonation pressure. ^f Nitrogen and oxygen percentage. ^g Impact sensitivity. ^h Friction sensitivity. ⁱ Ref. 7.

indicates better thermal stability and the compound becomes less prone to accidental detonation. The thermal stabilities of newly synthesized poly nitro- and azido-containing imidazole compounds were determined using differential scanning calorimetry (DSC) measurements at a heating rate of 5 °C min⁻¹. As shown in Table 1, the thermal decomposition temperatures (T_d) of compounds 2–6 range between 112 and 252 °C. The diazido-substituted compound 6 has a decomposition temperature of 112 °C while its monoazido-substituted bis imidazole derivative 2 has a decomposition temperature of 252 °C. Di-cationic salts of compound 2, such as compounds 3, 4, and 5, possess decomposition temperatures of 245, 131, and 120 °C, respectively. Compounds 2 (252 °C) and 3 (245 °C) have the highest thermal decomposition temperatures, better than those of diazodinitrophenol (DDNP; 157 °C). The experimental densities of all the synthesized compounds (2–6) were measured using a gas pycnometer under helium environment at ambient temperature. The measured densities range between 1.65 and 1.77 g cm⁻³. The high densities of these molecules ensure better packing, which in turn results in high energy per unit volume. All these compounds possess high nitrogen and oxygen content (> 75%). The Gaussian 09 suite of programs was employed to compute the heats of formation (HOF) of synthesized imidazole derivatives.³⁷ Compounds incorporating polyazides exhibit elevated heats of formation, a trend attributed to increased energy content that correlates with the increased number of energetic azido groups within the molecule. The azido group is well known for its high energy content and is frequently employed to enhance HOF by approximately +300 kJ mol⁻¹, an outcome associated with an increase in nitrogen content. Both compounds 2 and 6 demonstrate highly positive HOF values, 458 and 755 kJ mol⁻¹, respectively. This high energy content is attributed to the presence of azido groups and a high number of C–N and N–N bonds within these compounds. The detonation velocity (VOD) and detonation pressure (DP) for all the synthesized compounds were evaluated using Explo-5 (version 7.01.01).³⁸ This assessment utilized measured densities and calculated heats of formation (HOFs). Neutral compounds 2 and 6 possess good VOD (8093, 7946 m s⁻¹) and DP (26.7, 24.9 GPa) properties. Energetic salts of compound 2 possess good detonation values such as compounds 3 (8494 m s⁻¹, 30 GPa), 4 (8072 m s⁻¹, 25.1 GPa), and 5 (7593 m s⁻¹, 21.3 GPa), which are better than those of classical primary explosives, DDNP (6900 m s⁻¹, 24.2 GPa) and lead azide

(5877 m s⁻¹, 33.4 GPa). To ensure safe handling, storage, and transportation of energetic materials, the sensitivities of compounds 2–6 to mechanical shock (impact) and friction were measured. The data for the impact and friction tests are summarized in Table 1. The impact and friction sensitivities of these compounds fall in the ranges 5–10 J and 240–360 N, respectively. Among them, neutral compounds 2 and 6 are comparatively more susceptible to impact (IS = 5 J) than its salts (IS = 7.5–10 J), but are better than DDNP (IS = 1 J) and lead azide (IS = 2.5 J). However, the friction-sensitivity tests show that all the compounds are insensitive towards friction (FS = 240–360 N).

Conclusion

In summary, we have synthesized 5-azido-4,4',5'-trinitro-1H,1'H-2,2'-biimidazole (2), its energetic salts (3–5), and 5,5'-diazido-4,4'-dinitro-1H,1'H-2,2'-biimidazole (6) in good yields. Compounds 2, 3, and 6 showed good densities (> 1.76 g cm⁻³). As a metal-free primary explosive, compound 3 revealed good detonation velocity and detonation pressure of 8494 m s⁻¹ and 30.00 GPa, respectively. Compounds 2 and 4 also have good detonation velocities of 8093 and 8072 m s⁻¹ and detonation pressures of 26.7 and 25.1 GPa, respectively. Compounds 2 and 3 show high thermal stabilities of 252 and 245 °C, respectively. All the synthesized compounds are sensitive to impact (5–10 J) and less sensitive to friction (240–360 N). The high nitrogen and oxygen percentages (> 75%) in their molecular backbones also ensure that fewer toxic gases are released after explosion. Considering all the aspects, these molecules can be used as a potential metal-free primary explosive in the defence field.

Author contributions

Parasar Kumar: conceptualization; methodology; investigation, validation; formal analysis; writing – original draft. Vikas D. Ghule: investigation, validation, software, formal analysis, review & editing. Srinivas Dharavath: conceptualization; methodology; validation, supervision; funding acquisition; software, project administration; writing – original draft; writing – review & editing. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.



Data availability

The data underlying this study are available in the published article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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