CrystEngComm



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Cite this: CrystEngComm, 2021, 23, 5377

Imino-bridged N-rich energetic materials: $C_4H_3N_{17}$ and their derivatives assembled from the powerful combination of four tetrazoles[†]

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This study reports the synthesis of a series of novel imino-bridged N-rich energetic compounds, namely $C_4H_3N_{17}$ (N%: 82.4) and their derivatives, which were formed by four tetrazole (CN4) moieties. $C_4N_{17}^{3-}$ could be acidified by different concentrations of HCl and N-rich anions such as $C_4H_2N_{17}^{-}$ and the neutral compound 3 ($C_4H_3N_{17}$) could be obtained. The new compounds all exhibit good energetic performance (D: 8023–9668 m s⁻¹; Td: 169–277 °C; IS > 25 J; FS > 252 N). Remarkably, the ammonia oxide adduct compound 8 ($C_4H_{15}N_{21}O_4$) was exceedingly powerful (D: 9668 m s⁻¹) similar to CL-20 (9706 m s⁻¹) and showed good stability (Td: 168 °C; IS > 40 J; FS > 360 N). Moreover, compound 11 ($C_4H_8NaN_{19}$) exhibits not only the thermal stability and high density of metallic salts but also the mechanical stability of nonmetallic salts, which provides an important strategy for the design and synthesis of energetic materials. Among them, compounds 3, 4, and 6–11 were characterized *via* single-crystal diffraction to further confirm their exact molecular structure and arrangement.

Received 21st May 2021, Accepted 15th June 2021

DOI: 10.1039/d1ce00674f

rsc.li/crystengcomm

Introduction

Given the increasing demands for high performance and the growing safety and environmental concerns, traditional explosives such as RDX, HMX, and CL-20, which generate energy through redox reactions, are increasingly unable to meet the requirements for specific applications in the military and civil fields. Therefore, the combination of these issues has prompted numerous researchers to focus on the design and synthesis of novel energetic materials (EMs), which must fulfill several key requirements, such as tailored energetic performance, insensitivity toward destructive stimuli, and substantial thermal stability.¹

From the standpoint of realizing excellent EMs, effective synthesis strategies for energetic compounds mainly focus on reducing sensitivity and increasing energy.² At present, N-rich compounds are prospective alternative energetic ingredients because of their high heat of formation (HOF), high density, and good oxygen balance.³ Compared to the traditional EMs mentioned earlier (RDX, HMX and CL-20), N-rich energetic compounds are environmentally friendly, mainly releasing N₂ after decomposition.⁴ N-rich heterocyclic backbones such as tetrazoles, triazoles, azines and oxadiazoles are essential

building blocks for the synthesis of N-rich compounds.⁵ Among them, the tetrazole group, a typical N-rich aromatic ring with surprisingly higher thermal stability and featuring a high nitrogen content (N%: 80.0) and high positive HOF (4.77 kJ g⁻¹), is an important ingredient of energetic compounds.⁶ Tetrazole energetic derivatives have been studied widely because of their interesting energetic properties and unique chemical structures.^{16a}

In the research of energetic materials, many energetic compounds with good energy performance have been developed based on tetrazole. For example, 1-diazidocarbamoyl-5-azidotetrazole⁷ (C_2N_{14} , Fig. 1A) exhibits a density of 1.723 g cm⁻³, thermal decomposition temperature of 110 °C, HOF of 1459 kJ mol⁻¹, detonation



Fig. 1 Selected N-rich energetic compounds containing (A) azide, (B) azo, or (C) nitro groups.

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[†] Electronic supplementary information (ESI) available. CCDC 2034088, 2047779, 2050808, 2051823, 2051824, 2053784, 2072406 and 2079019. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ d1ce00674f

velocity of 8960 m s⁻¹ and detonation pressure of 33.9 GPa. Similarly, 1,1'-azobis(tetrazole)⁸ (C₂H₂N₁₀, Fig. 1B) and N-(1-((1*H*-tetrazol-5-yl)methyl)-1*H*-tetrazol-5(4*H*)-ylidene) nitramide⁹ $(C_3H_4O_2N_9, Fig. 1C)$ also have high detonation performance. Unfortunately, high energetics and good stability are usually mutually exclusive aspects.¹⁰ They show unacceptable mechanical stability toward external stimuli which may be related to the presence of [-N₃], [-NO₂], and [-N=N-] in the molecule.9,11,12 According to the previous reports, tetrazole rings linked by [-NH-], [-CH₂-], and [C=O] bridges can form a planar symmetric structure with better stability.^{13–15} From the theoretical calculations of HOF for generating bistetrazoles, C-N linked bistetrazoles compounds have higher energy densities than the C-C linked ones.¹⁶ Herein, based on the above theoretical basis as a guide, we designed and synthesized a series of novel N-rich energetic compounds, namely C4H3N17 and their derivatives, which were formed by four tetrazole moieties linked by the [-NH-] bridge and C-N bond. As expected, they all have good energetic properties and stability. Importantly, the facile procedure, high yield and low cost of these compounds enable them to possess great potential for practical applications.

Results and discussion

Synthesis

The detailed synthetic pathway is shown in Scheme 1. To introduce the tetrazole group, the sodium salt of compound 1 was reacted with cyanogen azide to yield trisodium di(1'*H*-[1,5'-bitetrazol]-5-yl)amine compound 2. Compounds 3 and 9 were obtained after acidification to different extents with hydrochloric acid. Compound 3 was deprotonated with a base such as KOH, NH₃·H₂O, C₂H₁₀N₆H₂CO₃, N₂H₄·H₂O, and NH₂OH to form a series of high-energy ionic salts (4–8). Besides, the ammonia oxide adduct compound 8 was synthesized *via* treating compound 3 with excess hydroxylamine. Compound 9 was deprotonated with a base



Scheme 1 Preparation of compounds 2-9.

such as KOH and $NH_3 \cdot H_2O$ to form a series of novel energetic metal–organic frameworks (10 and 11). The synthesis of compound 11 provides an important strategy for the development of novel energetic materials.

Structural analysis

To further study the exact molecular structure and arrangement of these new compounds, colorless single crystals of compounds **3**, **4**, and **6–11**, suitable for X-ray diffraction, were obtained by slowly evaporating the solvent from the applicable saturated solution at 25 °C. The crystal structures with 3D frameworks are shown in Fig. 2. Detailed crystallographic data are provided in the ESI.[†]

Compound 3·2DMSO crystallizes in the monoclinic space group *C*2 with two formula units in its asymmetric unit and exhibits a calculated density of 1.568 g cm⁻³ at 296 K. The presence of two DMSO molecules affects the tight arrangement of the molecules, resulting in a low density. The four tetrazole rings are almost coplanar which is evident



Fig. 2 Molecular structures of compounds (a) 3-2DMSO, (b) 4-2.25H₂O, (c) 6, (d) 7·H₂O, (e) 8-2H₂O, (f) 9-3CH₃OH, (g) 10-2.25H₂O and (h) 11·H₂O.

from the torsion angles C2–N5–C1–N1 (2.2), N3–N2–C1–N1 (179.7), and N8–N9–C2–N5 (180.0). The bond length of C2–N5 (1.398(4) Å) is slightly longer than that of C1–N1 (1.370(3) Å), which is due to a π - π conjugation between the C2–N5 bond and two aromatic tetrazole rings.⁶

Compound 4.2.25 H₂O crystallizes in the monoclinic space group *C*2/*c* with two formula units in its asymmetric unit and exhibits a high calculated density of 1.992 g cm⁻³. In the entire molecular structure, three K joins with N to form a chelate ring structure containing metal ions and each anion can coordinate with twelve potassium cations.

The other $C_4N_{17}^{3-}$ and $C_4N_{17}H_2^{-}$ salts (compounds 6, 7·H₂O and 8·2H₂O) crystallize in the triclinic space group $P\bar{1}$ with two formula units in the unit cell and exhibit crystal densities of 1.625, 1.648, and 1.709 g cm⁻³ at 296 K, respectively. Notably, the structure of compound 6 is non-planar, which may be related to the rotation of the C1-N3 bond caused by the asymmetric hydrogen-bonding networks formed by the $C_4N_{17}^{3-}$ anion and guanidine cation (Fig. 3).

Compound 9.3CH₃OH and compound 11.H₂O crystallize in the triclinic space group $P\bar{1}$ with two formula units in their asymmetric unit and exhibit a calculated density of 1.517, 1.603 g cm⁻³ at 296 K, respectively, and the cations are composed of a sodium ion and two ammonium ions in compound 11. Compound 10.2.25 H₂O crystallizes in the triclinic space group C2/c with four formula units in its asymmetric unit and exhibits a high calculated density of 1.946 g cm⁻³ at 296 K. In the entire molecular structure, two K and one Na joins with N to form a chelate ring structure containing metal ions. High energy MOFs (HE-MOFs) (4 and 9-11) are synthesized by the assembly of metal ions and high nitrogen bidentate and (or) multidentate ligands. These derivative ligands are a unique class of energetic compounds with a stable structure and high nitrogen content (Fig. 4).¹⁷

Symmetric structures and the layer-by-layer assembly of molecular arrangements are ubiquitous in nature and possibly possess excellent balance and stability.^{18,19} As expected, in all the structures discussed in this study except for compound **6**, their molecular structures are arranged in layers, and the structure of $C_4H_3N_{17}$ is clearly planar symmetric. Similarly, their anions, $C_4H_2N_{17}^-$ and $C_4N_{17}^{3-}$, with dihedral angles of 4.37° and 9.41°, also have nearly planar structures (Fig. 5).



Fig. 4 (a-d) Packing diagrams for compounds 4, 9, 10 and 11.

Physical and chemical properties

In view of these novel compounds consisting of only four tetrazoles linked to the [-NH-] bridge and having a high nitrogen content, it would be interesting to study their key physical and energetic properties such as thermal stability, density, HOF, detonation performance, and mechanical sensitivity to examine their potential for use as high-energy density materials (HEDMs) (Table 2).

The thermal stability was evaluated by using differential scanning calorimetry (DSC) (ESI[†]). The results show that neutral compound **3** decomposes at 198 °C, whereas compounds **2**, **4**, **9**, **10**, and **11** demonstrate a high decomposition temperature up to 251 °C, 241 °C, 249 °C, 247 °C, and 206 °C, respectively. In particular, compound **6** exhibits the highest decomposition temperature of 277 °C and has the potential to be used as a heat-resistant energetic material.²⁰ Compounds **5**, **7** and **8** possess slightly lower decomposition temperatures of 191 °C, 176 °C, and 168 °C, respectively. Among them, compound **8** exhibits a two-stage



Fig. 3 (a) Molecular structure of compound 6; (b) packing diagram for compound 6; hydrogen bonds are shown in sky-blue lines; (c) non-

covalent interactions (NCIs) surrounding $C_4 N_{17}^{3-}$ in compound 6.

Fig. 5 Comparison of the arrangement, symmetry and planarity of (a and d) $C_4H_4N_{17}$, (b and e) $C_4H_2N_{17}^{-}$ and (c and f) $C_4N_{17}^{-3^-}$.

Table 1 Bond angles, bond lengths, and densities of the selected compounds 3, 4, 7, 8, 10 and 11

Compd	Bond angles	Value/°	Bonds	Lengths/Å	Density/g cm ⁻³
3	C1-N1-C1'	122.90	C1-N1	1.273	1.72
4	C2-N9-C3	116.55	C2-N9	1.333	2.05
			C3-N9	1.328	
7	C1-N1-C3	117.35	C1-N1	1.344	1.70
			C3-N1	1.336	
8	C1-N1-C3	116.54	C1-N1	1.337	1.82
			C3-N1	1.342	
10	C1-N1-C3	116.80	C1-N1	1.340	2.02
			C3-N1	1.341	
11	C1-N1-C3	117.30	C1-N1	1.344	1.76
			C3-N1	1.341	

decomposition process which may be related to the presence of hydroxylamine molecules in the molecule.²⁶

The density of the samples was measured using a gas pycnometer. The metal salts **2**, **4**, **9**, **10** and **11** had higher measured densities of 1.76–2.05 g cm⁻³. Compounds **3** and **5–8** do not have a tightly bound metallic bond structure within the molecule as compared to the metal salts, and they exhibit slightly lower measured densities, which were in the range of 1.63–1.82 g cm⁻³. Density is inseparable from the molecular structure of a compound. As shown in Table 1, the bond angle of the [–NH–] group in compound 3 (C₄H₃N₁₇) is 122.90°, while its bond angle range in C₄N₁₇^{3–} is 116.55° to 117.35°. In addition, the bond length of the C–N bond directly connected with [–NH–] was also analyzed, and the bond length ranged from 1.273 Å to 1.344 Å. A short bond length and small angle can form a more compact molecular structure, which is conducive to the high molecular density.

The energy source of the N-rich energetic materials originates from the fracture of the nitrogen–nitrogen bonds. Compounds **3** and **5–7** have high nitrogen contents up to 78.03–83.60%. Therefore, introducing tetrazole into the energetic compounds can increase the HOF.²¹ Compared with the currently commonly used energetic materials such

as RDX (0.42 kJ g^{-1}) and HMX (0.25 kJ g^{-1}),²¹ all these compounds have a better positive HOF (1.67–5.32 kJ g^{-1}).

Detonation performance was determined by comprehensive analysis of the molecular formula, density and HOF of the compound using the EXPLO 5-6.05.02 program. Compounds 3 and 9 have a high detonation velocity (8650 m s⁻¹ and 8641 m s⁻¹) close to RDX (8795 m s^{-1}) and compound 7 also has a high detonation velocity (9063 m s^{-1}) close to HMX (9144 m s^{-1}) .²¹ Remarkably, the ammonia oxide adduct compound 8 exhibits the highest detonation performance (D: 9668 m s⁻¹; P: 35.10 GPa) similar to CL-20 (9706 m s⁻¹). To our knowledge, there are a few reports on ammonia oxide adducts (Fig. 6). The presence of ammonia oxide can produce more hydrogen bonds thus improving the density and detonation properties of the energetic compounds. They have the most promising prospect of replacing the energetic materials in common use.^{2a,22}

The mechanical sensitivities were evaluated using the standard BAM method. As shown in Table 2, all the newly synthesized compounds show low mechanical sensitivity. The impact sensitivity and friction sensitivity of the corresponding metal salts (IS > 25 J; FS > 252 N) show slightly higher sensitivity than those of neutral compound 3 with an IS of 35 J and FS of 360 N. In particular, the good mechanical stability (IS > 35 J; FS > 360 N) of compound 11 is related to the fact that the cation is composed of a sodium ion and two ammonium ions, in which the ammonium ion helps to form a complex hydrogen bond network and reduces the mechanical sensitivity of the compound. By contrast, the metal-free salt compounds (5, 7, and 8) exhibit significantly lower mechanical sensitivities (IS > 37.5 J; FS > 360 N). Additionally, the slightly lower FS (324 N) of compound 6 may be related to the fact that the molecular structure is not planar.

The $C_4N_{17}^{3-}$ anion presents a near-planar structure and the hydrogen bonds (HBs, such as N-H…N, N-H…O and O-H…N) can be formed between layers with cations such as

Compd	T_d^a	d^b	N^{c}	$\Delta { m H_{f}}^{d}$	D^{e}	\mathbf{P}^{f}	IS^g	FS^h			
2	251	1.88	67.05	256.48/0.72			25	252			
3	198	1.72	82.34	1509.08/5.22	8650	30.95	35	360			
4	238	2.05	59.02	87.33/0.22	_	_	27.5	288			
5	191	1.69	82.33	497.06/1.67	8165	21.75	37.5	360			
6	277	1.63	78.03	878.81/1.88	8023	21.23	40	324			
7	179	1.70	83.61	1017.37/2.64	9063	28.30	37.5	360			
8	168	1.82	69.82	877.669/2.08	9668	35.10	40	360			
9	249	1.84	76.52	1299.046/4.17	8641	27.51	32.5	324			
10	247	2.02	61.47	_	_	_	27.5	288			
11	206	1.76	77.08	_	_	_	35	360			
RDX ⁱ	230	1.80	37.84	92.60/0.42	8795	34.9	7.4	120			
HMX ^j	280	1.91	37.84	70.40/0.25	9144	39.2	7.4	120			
$CL-20^k$	221	2.04	38.36	397.8/0.91	9706	45.2	4	48			

Table 2 Physical properties and energetic performance of compounds 2-9 compared with those of RDX, HMX and CL-20

^{*a*} Thermal decomposition temperature [°C] (onset, 5 K min⁻¹). ^{*b*} Density [g cm⁻³] (measured using a gas pycnometer; 298 K). ^{*c*} Content of nitrogen [%]. ^{*d*} Heats of formation [kJ mol⁻¹/kJ g⁻¹]. ^{*e*} Detonation velocity [m s⁻¹]. ^{*f*} Detonation pressure [GPa]. ^{*g*} Impact sensitivity [J]. ^{*h*} Friction sensitivity [N]. ^{*i*} Ref. 21*a*. ^{*j*} Ref. 21*a*. ^{*k*} Ref. 21*a*.

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compound 8.

hydrazine or hydroxylamine. To further analyze the differences in their stability, the non-covalent interactions (NCIs) of compounds **3**, 7 and **8** were studied using the Gaussian,²³ Multiwfn²⁴ and VMD²⁵ software programs. In Fig. 7a–f, extensive hydrogen-bonding networks (sky-blue lines) were observed in the packing system of compounds **3**, 7 and **8**. Compared to the bonds in neutral compound **3**, more strong hydrogen bonds were particularly observed in the ammonia oxide adduct compound **8**. A dense hydrogen-bond-network is beneficial to the formation of compact spatial structure, improving the mechanical stability of materials.²⁶

To further analyze the differences in their stability, the associated Hirshfeld surfaces and the 2D fingerprint plots of compounds 3, 7 and 8 were compared. More deep red dots,



Fig. 7 (a-c) Packing diagrams for compounds 3, 7 and 8. HBs are shown in sky-blue lines; (d-f) NCIs surrounding $C_4N_{17}H_3$ and $C_4N_{17}^{3-}$ in compounds 3, 7 and 8.



Fig. 8 (a-c) Hirshfeld surfaces of 3, 7, and 8, respectively; (d-f) fingerprint plots for 3, 7, and 8, respectively; (g) individual atomic contact percentage contribution to the Hirshfeld surfaces of 3, 7, and 8, respectively.

which are associated with hydrogen bonds, were present in compounds 7 and 8 than in compound 3 (Fig. 8a–c). The quantified non-covalent bond results are shown in Fig. 8g; in the crystals of compounds 3, 7 and 8, the percentage of hydrogen bonds was 53.6%, 59.3%, and 68.3%, respectively. In contrast, the percentage of the N…N bond showed a decreasing trend (17.6%, 13.50% and 10.80%). The comprehensive analysis results are consistent with their trend of increasing stability.

Conclusions

In conclusion, highly ordered structures tend to exhibit fascinating material properties. A family of novel N-rich highenergetic compounds was synthesized based on four tetrazoles and displayed a good balance between stability and energy (D: 8023 m s⁻¹-9668 m s⁻¹; P: 23.95 GPa-35.10 GPa; IS > 25 J; FS > 252 N). Furthermore, this work provides an important strategy for the development of energetic materials. Interestingly, compound 3 could be deprotonated by excess hydroxylamine, and an ammonia oxide adduct compound 8 was synthesized. It exhibits excellent energetic preference (*D* = 9668 m s⁻¹; *P*: 35.1 GPa; T_d : 168 °C; IS > 40 J; FS > 360) which highlights their practical application potential as a captivating class of highly energetic materials. In addition, a new method for synthesizing energetic materials was reported in this paper. Thus, compound 11 was obtained and had excellent physical and chemical properties.

Experimental section

Experimental procedures

Cautions! There have been no explosions when dealing with these compounds, but we strongly encourage to take strict precautions because of their high energy and mechanical sensitivity.

General methods

All reagents of analytical grade were purchased from Energy Chemical and used strictly in accordance with regulations. ¹H and ¹³C NMR spectra were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer operating at 500 and 126 MHz, respectively. IR spectra were recorded using KBr pellets with a Thermo Nicolet iS10 spectrometer. Elemental analyses were carried out on a Vario EL III CHNOS elemental analyzer. The melting and decomposition (onset) points were measured on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 K min⁻¹. Densities were confirmed at room temperature by using a Micromeritics AccuPyc 1340 gas pycnometer. Impact and friction sensitivity were obtained using a standard BAM Fallhammer and a BAM friction tester.

Syntheses

Trisodium di(1'H-[1,5'-bitetrazol]-5-yl)amine (2). At 0 °C, cyanogen bromide (3.148 g, 30 mmol) was dissolved in 100 mL anhydrous acetonitrile to which sodium azide (6.825 g, 105 mmol) was added. The reaction mixture was stirred at 0 °C for 4 h. After the inorganic salt being filtered off, the cyanogen azide solution was added to a solution containing hydrated bis(1H-tetrazol-5-yl)amine (1.2825 g, 7.5 mmol) which had been neutralized with sodium hydroxide (0.900 g, 22.5 mmol) in 40 mL water at ambient temperature. After stirring over 6 h at ambient temperature, a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 1.344 g, yield: 62%. ¹³C NMR (126 MHz, DMSO-d6): δ = 158.69, 155.62. IR (KBr): $\tilde{\nu}$ = 3463.75, 3320.21, 2117.69, 1625.89, 1590.69, 1555.04, 1519.07, 1466.83, 1338.40, 1300.63, 1277.96, 1149.54, 1091.62, 1011.04, 970.74, 910.31, 796.99, 737.18 cm⁻¹. Elemental analysis calcd for C4Na3N17 (355.02): C 13.53, N 67.05%; found: C 13.56; N 67.01%.

Di(2'*H*-[1,5'-bitetrazol]-5-yl)amine (3). At 0 °C, compound 2 (0.710 g, 2 mmol) was dissolved in 30 mL H₂O. To this solution, aq. 12 M HCl (1.5 mL) was slowly added dropwise over 1 minute. The reaction mixture was stirred at 0 °C for 2 h, and a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.544 g, yield: 87%. ¹H NMR (500 MHz, DMSO-d6): δ = 6.66 (s, 3H). ¹³C NMR (126 MHz, DMSO-d6): δ = 152.77, 152.02. IR (KBr): $\tilde{\nu}$ = 2172.99, 1680.48, 1647.97, 1607.10, 1557.19, 1480.44, 1404.99, 1352.81, 1125.82, 1080.44, 1034.62, 999.66, 918.91, 844.49, 769.01, 727.54, 709.44, 668.21 cm⁻¹. Elemental analysis calcd for C₄H₃N₁₇ (289.19): C 16.61, H 1.05, N 82.34%; found: C 16.64, H 1.02, N 82.32%.

Tripotassium di(1'*H*-**[1,5'-bitetrazol]-5-yl)amine** (4). At 25 °C, compound 3 (0.289 g, 1 mmol) was suspended in 15 mL acetonitrile and aqueous KOH (KOH: 0.168 g, 3 mmol; CH₃-CH₂OH: 5 mL) was added drop-wise at room temperature and stirred for 2 h; a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.312 g, yield: 91.2%. ¹³C NMR (126 MHz,

DMSO-d6): δ = 158.70, 155.62. IR (KBr): $\tilde{\nu}$ = 3464.32, 3318.03, 2117.82, 1624.87, 1553.96, 1488.39, 1337.65, 1283.19, 1148.62, 1093.47, 1015.91, 973.54, 909.50, 795.05, 742.59, 668.30 cm⁻¹. Elemental analysis calcd for C₄K₃N₁₇ (402.94): C 11.91, N 59.02%; found: C 11.94; N 58.97%.

Triammonium di(1'*H*-[1,5'-bitetrazol]-5-yl)amine (5). At 25 °C, compound 3 (0.289 g, 1 mmol) was suspended in 15 mL acetonitrile and 27% aqueous ammonia (0.21 mL, 3 mmol) was added drop-wise at room temperature and stirred for 2 h; a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.307 g, yield: 89.5%. ¹H NMR (500 MHz, DMSO-d6): δ = 7.56 (s, 12H). ¹³C NMR (126 MHz, DMSO-d6): δ = 158.25, 155.43. IR (KBr): $\tilde{\nu}$ = 3462.62, 3320.44, 2117.84, 1625.34, 1601.11, 1557.53, 1507.19, 1470.15, 1440.68, 1410.02, 1338.15, 1159.25, 1105.70, 1080.30, 1023.77, 1012.89, 973.37, 905.90, 797.46, 743.68 cm⁻¹. Elemental analysis calcd for C₄H₁₂N₂₀ (340.28): C 14.12, H 3.55, N 82.33%; found: C 14.15, H 1.01, N 82.29%.

Triguanidine di(1'*H*-**[1,5'-bitetrazol]-5-yl)amine (6).** At 25 °C, compound 3 (0.289 g, 1 mmol) was suspended in 15 mL acetonitrile and guanidine carbonate (0.27 g, 1.5 mmol) was added drop-wise at room temperature and stirred for 2 h; a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.417 g, yield: 89.4%. ¹H NMR (500 MHz, DMSO-d6): δ = 7.12 (s, 18H). ¹³C NMR (126 MHz, DMSO-d6): δ = 159.30, 158.03, 155.01. IR (KBr): $\tilde{\nu}$ = 3457.26, 3439.28, 3364.76, 3150.61, 1656.85, 1566.84, 1530.19, 1505.43, 1429.81, 1310.91, 1164.85, 1102.87, 1021.82, 737.55 cm⁻¹. Elemental analysis calcd for C₇H₁₈N₂₆ (466.47): C 18.03, H 3.89, N 78.08%; found: C 18.05, H 3.90, N 78.04%.

Trihydrazinium di(1'*H*-[1,5'-bitetrazol]-5-yl)amine (7). At 25 °C, compound 3 (0.289 g, 1 mmol) was suspended in 15 mL acetonitrile and 85% hydrazine hydrate (0.15 g, 3 mmol) was added drop-wise at room temperature and stirred for 2 h; a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.355 g, yield: 92.1%. ¹H NMR (500 MHz, DMSO-d6): δ = 7.19 (s, 15H). ¹³C NMR (126 MHz, DMSO-d6): δ = 158.45, 154.97. IR (KBr): $\tilde{\nu}$ = 3462.62, 3320.44, 2968.75, 2117.47, 1622.94, 1602.29, 1551.84, 1503.63, 1469.73, 1338.40, 1286.41, 1157.66, 1148.29, 1120.83, 1089.05, 1025,77, 1012.16, 958.27, 944.82, 909.72, 733.80, 652.03 cm⁻¹. Elemental analysis calcd for C₄H₁₅N₂₃ (385.33): C 12.47, H 3.92, N 83.61%; found: C 12.51, H 1.01, N 83.27%.

Trihydroxylaminedi (1'*H*-[1,5'-bitetrazol]-5-yl)amine (hydroxylamine) (8). At 25 °C, compound 3 (0.289 g, 1 mmol) was suspended in 15 mL acetonitrile and 50% hydroxylamine hydrate (0.99 g, 15 mmol) was added drop-wise at room temperature and stirred for 2 h; a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.382 g, yield: 90.8%. ¹H NMR (500 MHz, DMSO-d6): δ = 5.64 (s, 15H). ¹³C NMR (126 MHz, DMSO-d6): δ = 157.93, 155.45. IR (KBr): \hat{v} = 3462.62, 3320.44, 2113.17, 1659.88, 1626.20, 1583,52, 1551,75, 1516.37, 1337.24, 1296.27, 1166.15, 1148.11, 1109.44, 1009.86, 998.97, 972,50,

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905.90, 795.05, 734.19 cm⁻¹. Elemental analysis calcd for $C_4H_{15}N_{21}O_4$ (421.16): C 11.40, H 3.29, N 69.82, O 15.19%; found: C 12.52, H 1.01, N 69.83, O 15.18%.

Sodium di(1'H-[1,5'-bitetrazol]-5-yl)amine (9). At 0 °C, compound 2 (0.710 g, 2 mmol) was dissolved in 30 mL H₂O. To this solution, aq. 12 M HCl (0.2 mL, 2 mmol) was slowly added dropwise over 1 minute. The reaction mixture was stirred at 0 °C for 1 h, and a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.616 g, yield: 86.6%. ¹H NMR (500 MHz, DMSO-d6): δ = 5.47 (s, 2H). ¹³C NMR (126 MHz, DMSO-d6): δ = 152.25, 151.79. IR (KBr): $\tilde{\nu}$ = 3466.27, 3320.21, 2119.04, 1625.54, 1594.94, 1551.09, 1340.92, 1149.54, 1100.20, 1013.55, 973.26, 909.35, 791.95, 793.37, 580.70, 546.76 cm⁻¹. Elemental analysis calcd for C₄H₂NaN₁₇ (311.17): C 15.44, H 0.65, N 76.52%; found: C 12.47, H 0.66, N 76.48%.

Bipotassium sodium di(1'*H*-[1,5'-bitetrazol]-5-yl)amine (10). At 25 °C, compound 9 (0.311 g, 1 mmol) was suspended in 15 mL acetonitrile and aqueous KOH (KOH: 0.112 g, 2 mmol; CH₃CH₂OH: 3 mL) was added drop-wise at room temperature and stirred for 2 h; a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.306 g, yield: 91.5%. ¹³C NMR (126 MHz, DMSO-d6): δ = 158.56, 155.78. IR (KBr): $\tilde{\nu}$ = 1552.53, 1496.61, 1320.13, 1155.15, 1129.89, 1093.60, 1019.67, 743.18, 590.45, 575.09, 558.75, 546.83, 540.67 cm⁻¹. Elemental analysis calcd for C₇H₁₈N₂₆ (387.35): C 12.40, N 61.47%; found: C 12.43, N 61.44%.

Biammonium sodium di(1'*H*-[1,5'-bitetrazol]-5-yl)amine (11). At 25 °C, compound 9 (0.311 g, 1 mmol) was suspended in 15 mL acetonitrile and 27% aqueous ammonia (0.14 mL, 2 mmol) was added drop-wise at room temperature and stirred for 2 h; a white precipitate was filtered and washed with acetonitrile to give an amorphous white solid. White solid, 0.306 g, yield: 88.6%. ¹H NMR (500 MHz, DMSO-d6): δ = 7.66 (s, 8H). ¹³C NMR (126 MHz, DMSO-d6): δ = 158.57, 155.03. IR (KBr): $\tilde{\nu}$ = 1632.95, 1584.70, 1553.32, 1520.45, 1424.11, 1163.56, 1078.19, 1030.06, 742.30, 563.12, 546.55 cm⁻¹. Elemental analysis calcd for C₄H₈NaN₁₉ (345.23): C 13.92, H 2.34, N 77.09%; found: C 13.95, H 2.36, N 77.08%.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are most grateful to Prof. Chong. Zhang (Nanjing University of Science and Technology) for his help on the detonation performance calculation and mechanical sensitivity test. Special thanks to M.S. Ling Chen for her help and professional advice on the NMR test and NMR spectral analysis and we also sincerely thank Dr. Qi Sun (Beijing Institute of Technology), M.S. Zhe. Xing and M.S. Siyuan. Chen for their professional advice on article writing.

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