Journal of Fluorine Chemistry 283-284 (2025) 110427

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Synthesis and characterization of 5-(trifluoromethyl)tetrazol-based energetic salts

Jiawen Deng [a,1], Lukang Lin [d,1], Yahan Zhang [b,1], Xu Yao [a], Jun Zhang [c], Jin-Hong Lin [b,*], Wenbin Yi [a,d,*], Xing Zheng [a,c,*], Ji-Chang Xiao [b,*]

[a] Institute of Pharmacy and Pharmacology, Hengyang Medicinal School, University of South China, Hengyang, Hunan 421001, China
[b] State Key Laboratory of Fluorine and Nitrogen Chemistry and Advanced Materials, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China
[c] Department of Pharmacy, Hunan Vocational College of Science and Technology, Third Zhongyi Shan Road, Changsha, Hunan, 410004, China
[d] College of Chemical Engineering, Nanjing University of Science & Technology 200 Xiaolingwei, Nanjing 210094, China

ARTICLE INFO

Keywords:
Energetic salts
Insensitive
Trifluoromethyl

ABSTRACT

Two types of 5-trifluoromethyl tetrazole-based energetic salts were successfully synthesized from trifluoroacetamide and sodium azide. The synthetic approach is characterized by its simplicity and safety. The X-ray diffraction analysis reveals the presence of both intermolecular and intramolecular hydrogen bonding within the crystal lattice of energetic salts. The synthesized compound **4** demonstrated notable physical properties, including high densities (1.64 g cm^{-3}), great thermal stability (with decomposition temperatures of 167 °C), and excellent insensitivity (impact sensitivity exceeding 40 J). These attributes suggest that the compound **4** possess promising energetic performance and is potential candidates for use as insensitive high-energy materials.

1. Introduction

Energetic materials, which are compounds or mixtures capable of releasing substantial energy in a brief span when subjected to external stimuli, have found extensive application over the past centuries. In the pursuit of superior energetic materials, ensuring safety has become paramount, significantly influencing their development and practical implementation [1,2]. Therefore, key objectives in the creation of new energetic materials include reducing sensitivity, enhancing thermal stability, and maintaining safety throughout their lifecycle [3–7]. Traditional heat-resistant explosives, such as hexanitrostilbene (HNS [8]), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB [9]), and 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) [10], achieve their remarkable thermal endurance through hydrogen bonding and π−π stacking interactions facilitated by nitro-aromatic structures. The growing demands from space exploration and deep-sea missions necessitate the development of even more thermally stable and insensitive energetic materials. Nitrogen-rich compounds stand out as innovative examples of high-energy-density materials, celebrated for their capacity to absorb significant amounts of heat, exhibit high density, and demonstrate reduced sensitivity to various stimuli [11–18]. Among these, heterocyclic systems like pyrazoles [19–23], 1,2,3-triazoles [24,25], 1,2,4-triazoles [26,27], tetrazoles [28–33], 1,3,5-triazines [34,35], and 1,2,4-triazines [36]. have proven valuable in crafting insensitive high-energy-density materials that meet modern requirements for performance and safety. The ongoing research into these nitrogen-based frameworks aims to uncover novel compounds with optimized properties, pushing the boundaries of what is possible in the design of advanced energetic materials for a range of critical applications.

In comparison with conventional explosives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrohydro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and others, energetic materials containing tetrazolium as the fundamental structure offer numerous advantages [37–40]. (1) Upon decomposition, these materials produce environmentally benign nitrogen gas. (2) They can endure harsh corrosive conditions, including exposure to strong acids and bases, without degradation. (3) The preparation of tetrazolium-based energetic materials often involves a single-step reaction, such as the addition of sodium azide to a nitrile, making the process more straightforward and efficient [41]. Salt-based energetic materials are also generally advantageous in

---

[*] Corresponding authors.
E-mail addresses: jlin@sioc.ac.cn (J.-H. Lin), yiwb@njust.edu.cn (W. Yi), zhengxing9166@sohu.com (X. Zheng), jchxiao@sioc.ac.cn (J.-C. Xiao).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.jfluchem.2025.110427
Received 20 February 2025; Received in revised form 25 April 2025; Accepted 25 April 2025
Available online 7 May 2025
0022-1139/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

terms of lower vapour pressure, higher density, better thermal stability, a less complex and cost-effective synthesis compared to non-salt-based counterparts. In 2008, Shreeve's group [42] reported a series of 5-aminotetrazole energetic salts, characterized by their positive heat of formation ($\Delta H_f > 3.0$ kJ/g) and notable impact insensitivity (IS > 40 J). In 2023, the same group [43] reported the synthesis of a bis-tetrazole ring energetic salt, BTzNM-Na, which exhibited excellent thermal stability and favourable detonation properties ($T_d = 217$ °C, $D = 8746$ m s^{-1}, $P =$ 29.8 GPa).

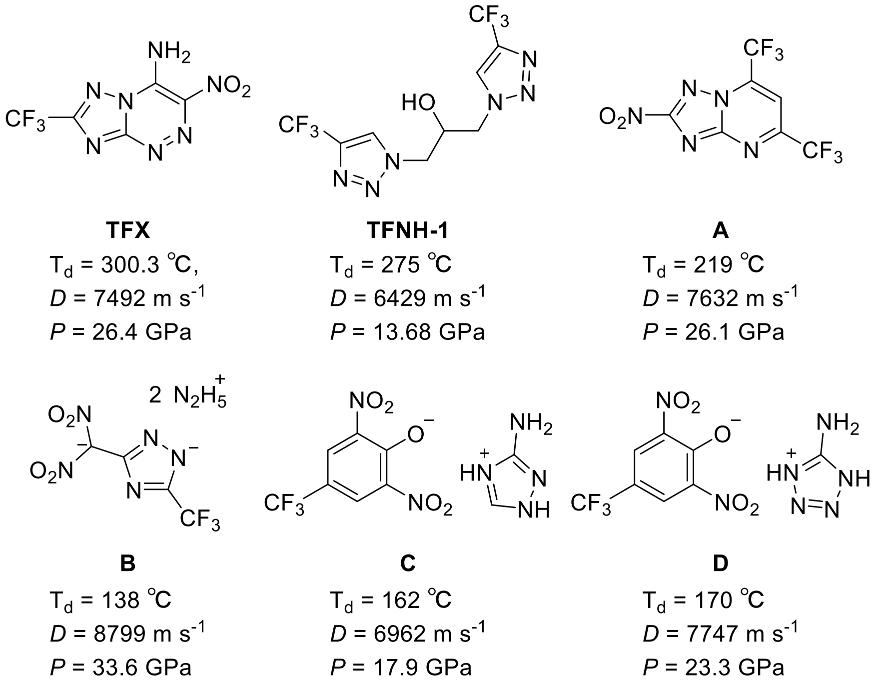
The trifluoromethyl group plays a crucial role in organic synthesis, medicinal chemistry, and the development of energetic materials [44]. Incorporating trifluoromethyl groups into triazoles and other nitrogen-containing heterocycles, as well as into larger ring systems, has been shown to increase the density of energy-rich compounds while also reducing their sensitivity [45–48]. Over recent years, there has been a notable rise in the synthesis of trifluoromethyl-containing energetic materials for use as explosives [44,45,49] (Scheme 1**: TFX; TANH-1; A**). These compounds generally exhibit favorable explosive properties and thermal stability. Despite many studies on energetic materials with trifluoromethyl, there is still little research on trifluoromethyl-containing energetic salts. Most documented cases of energetic salts are also characterized by suboptimal thermal stability. Shreeve's group [50] synthesized a class of insensitive trifluoromethyl triazole containing energetic salts through a four-step reaction, which exhibited excellent impact and friction sensitivity but poor thermal stability (Scheme 1**: B**). Balachandar's group [51] reported a class of trifluoromethyl azole containing energetic salts, which demonstrated favorable blast properties but poor thermal stability (Scheme 1**: C; D**). Inspired by the methodologies employed by the Norris [52] and Ellis [53] groups, we synthesized 5-trifluoromethyltetrazole sodium salt from trifluoroacetamide via the first generation of trifluoroacetonitrile gas, followed by its reaction with sodium azide. This approach led to the formation of two nitrogen-rich energetic salts of 5-trifluoromethyltetrazole through a simple and efficient decomposition reaction. To evaluate the impact of the trifluoromethyl group on the properties of energetic materials, we also prepared two structurally analogous methyltetrazole salts for comparative analysis. This comparison aims to underscore the benefits of incorporating the trifluoromethyl moiety, such as enhanced density, stability, and performance, while preserving the ease of synthesis and ensuring safe preparation.

2. Results and discussion

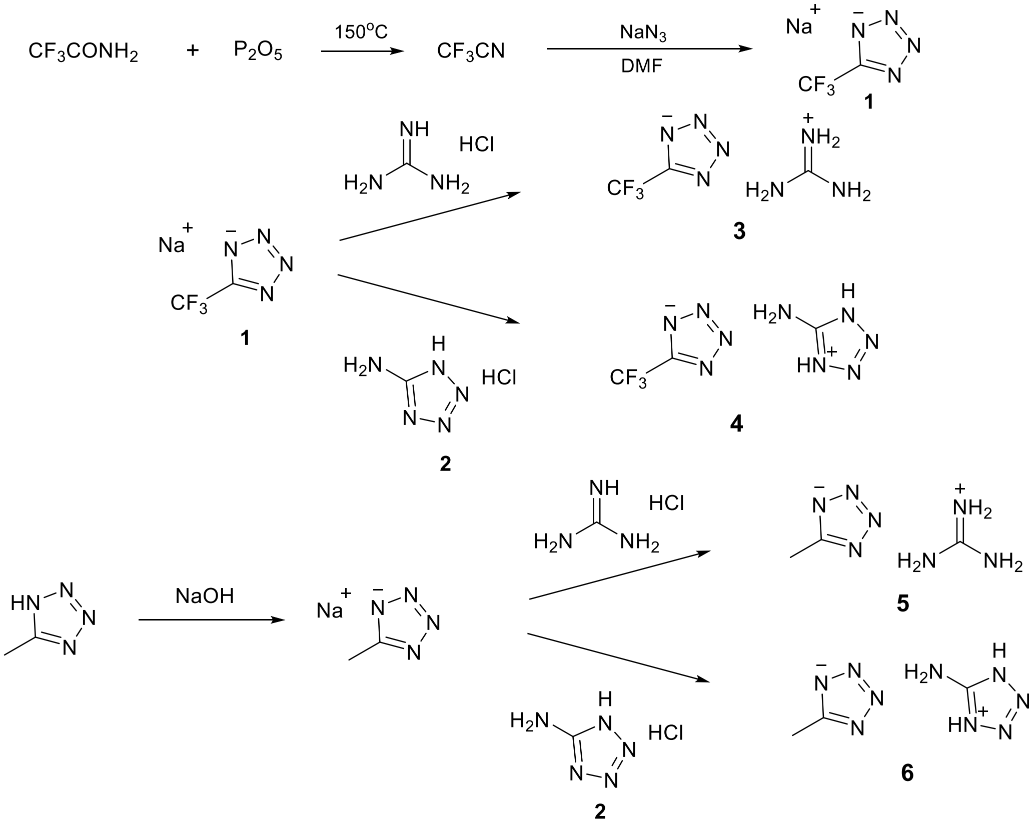
In this study, we synthesized trifluoroacetonitrile by dehydrating trifluoroacetamide with phosphorus pentoxide, and then reacting the resulting high-temperature stream of trifluoroacetonitrile with sodium azide, achieving a 98 % yield of compound **1**. Through subsequent metathesis reactions, we obtained compounds **3** and **4** from compound **1**. Ethyl acetate was strategically selected as the reaction solvent for the synthesis of compound **3** based on its immiscibility with aqueous phases and metathesis byproduct NaCl, combined with the compound's preferential solubility in this medium. This solvent system enabled efficient phase separation while maintaining optimal reaction homogeneity. Additionally, we synthesized structurally analogous methyltetrazole salts **5** and **6** (see Scheme 2) for comparative analysis. Notably, all reactions proceeded efficiently without inert gas protection. The reaction duration was strictly maintained at 2 h for the formation of salts **3~6** to minimize hydrolytic degradation, with subsequent products immediately stored in hermetically sealed containers as precautionary measures against moisture-induced decomposition. The structure of compound **3** was confirmed via single-crystal X-ray diffraction analysis [54].

Crystallization conditions were systematically screened using solvent matrices (ethanol, acetone, dichloromethane, tetrahydrofuran, etc.) at varying ratios. Optimized crystallization of compound **3** was achieved in a methanol/diethyl ether (1:5 v/v) system, providing single crystals suitable for X-ray diffraction analysis. The crystallographic data for **3**·Et_2O in CIF format is provided in the Supporting Information and the CCDC number is 2414,874. Compound **3** with Et_2O adduct crystallized as a monoclinic crystal (**3**·Et_2O) with space group C2/c. The crystal structure contained eight molecules per unit cell ($Z = 8$), and the crystal density was determined to be 1.342 $g\cdot cm^{-3}$ at 170 K.

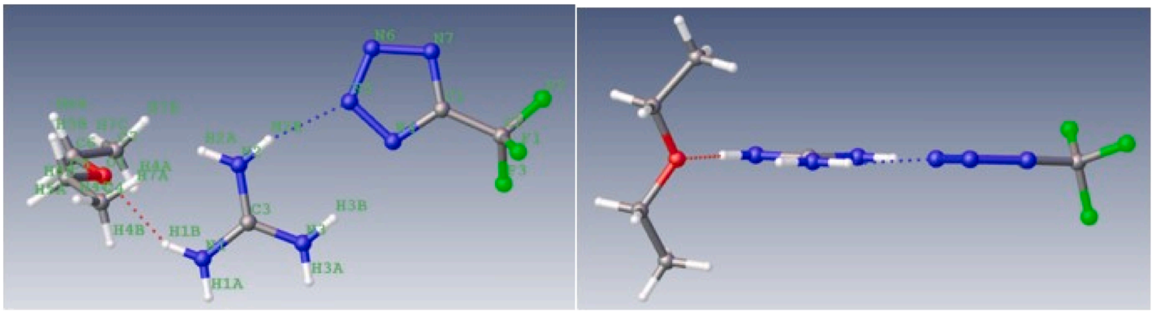
Utilising olex2 software for calculations revealed that the dihedral angle of the tetrazole ring with the guanidino group (∠N1-C3 -N2-N3) was 3.49 ° (Fig. 1), indicating that the two rings were almost co-planar, a configuration that may be more conducive to favourable molecule-to-molecule π-π stacking.



Scheme 1. Structure of trifluoromethyl group based energetic materials.



Scheme 2. Synthesis of compound 3 –6.



(a) (b)

Fig. 1. (a) Molecular structure and labeling for 3·Et_2O. (b)Edge view showing the planarity of the backbone of 3·Et_2O.

As illustrated in Fig. 2, a significant intramolecular *N* – *H*···O Ionic bond (N2—H5b··N5) is observed to form between the adjacent amino group and the tetrazole ring, with a distance of 2.03 Å between H5b and N5. Additionally, an intermolecular hydrogen bond has been identified between the amino group and Et_2O (N1 -H3b—O). The angle between the guanidino plane and the plane of the ether molecule is measured at 79.32°, indicating that the two planes are nearly perpendicular to each other. Furthermore, analysis of the stacking diagram reveals the presence of ether molecules between the molecules of compound **3**. This suggests that the observed stacking is not optimal, resulting in sub-optimal utilisation of space. This may, in turn, be the underlying cause of the low theoretical density.

Thermal stability is a critical consideration for energetic materials that must withstand elevated temperatures, such as military explosives. In this study, the thermal stability of compounds **3** and **4** were analyzed using DSC and TG-DTG. The DSC thermograms demonstrates that the thermal behavior of **3** can be categorized into two distinct stages (Fig. 3). The initial phase is characterized by a sharp endothermic peak, indicative of a melting process. The peak temperature at the melting point of **3** was 157.5 °C. The second stage was an exothermic decomposition process, while the extrapolated onset temperature (T_d) and peak temperature (T_p) were 307.1 and 329.6 °C, respectively. The decomposition enthalpy of the process was 320.1 J/g. In the DSC curve of 4 (Fig. 4), there are two endothermic peaks near 130 °C, which is the melting process of **4**. The decomposition process commenced at 160 °C, with an extrapolated onset temperature (T_d) of 160.2 °C, a peak temperature (T_p) of 205.7 °C and an enthalpy of decomposition of 273.7 J/g. The results showed that compound **4** exhibited excellent thermal stability at elevated temperatures, with a higher T_d than both 1,3,5-trinitrohydro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT). In comparison with **5**, which exhibits structural similarity to **3**, there is a substantial enhancement of T_d when the methyl group is replaced by a

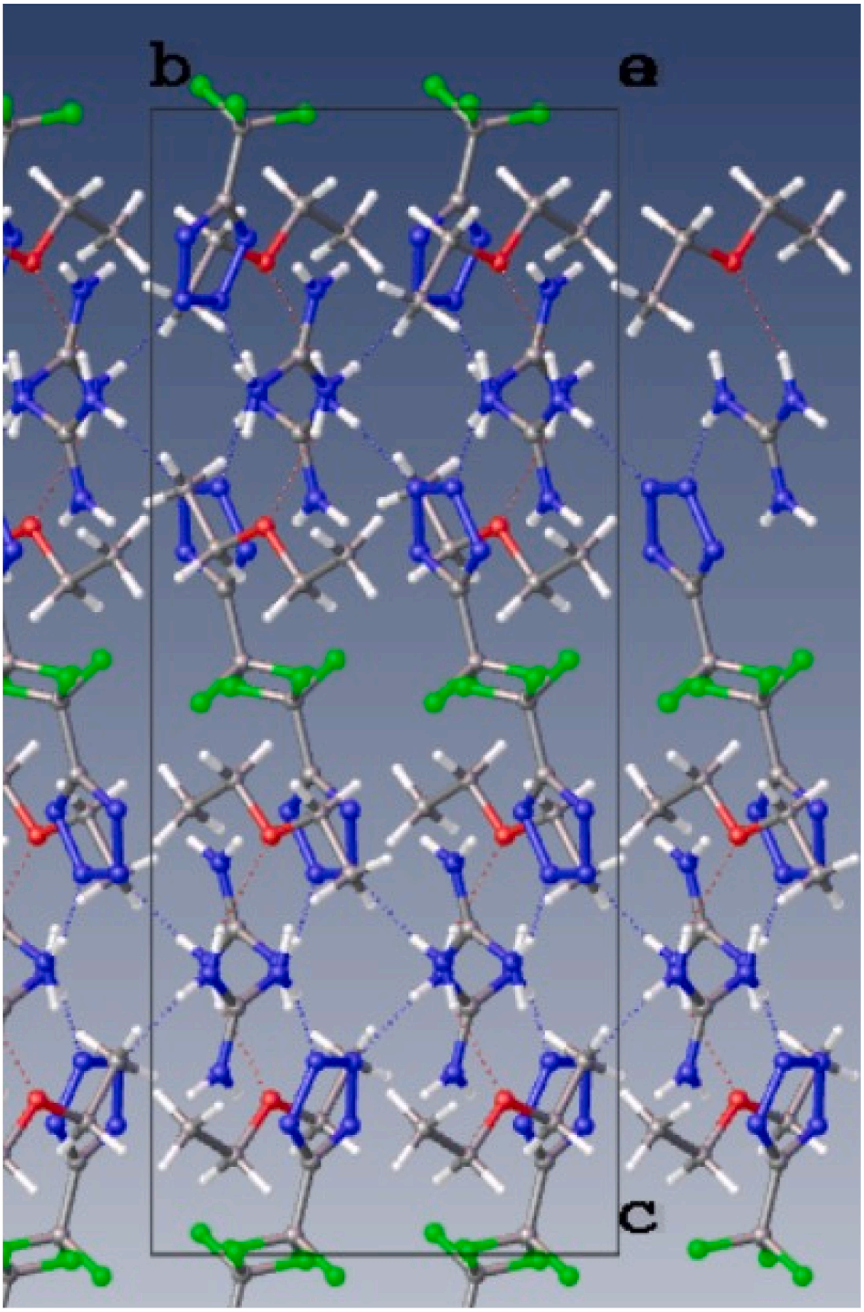


Fig. 2. Crystal packing of 3 showing molecular stacking planes.

trifluoromethyl group. This phenomenon may be attributed to the incorporation of a trifluoromethyl group, which has been shown to mitigate localized heating from external stimuli, thereby enhancing the thermal stability of the energy-containing compound **3**. At the same time, due to the introduction of the trifluoromethyl group, the stability is improved while sacrificing some of the explosive properties (suboptimal detonation pressure and pressure due to low HOF). Furthermore, the true densities of all compounds were measured using a gas pycnometer. The results show that compounds **3** and **4** have densities of 1.64 and 1.59 g cm^{-3}, respectively. These values are both greater than the structurally similar compounds **5** and **6**.

We investigate the physicochemical and detonation properties (Table 1) of the energy-containing compounds **3** and **4**. The heat of formation (HOF) of **3** −**6** were calculated with Gaussian 09 program [55]. And based on the values of the density and HOF, the detonation properties were calculated by the Kamlet−Jacobs equation [56–58]. The heat of formation for compounds **3** and **4** are negative, with values of −1004 and −792.9 kJ mol^{-1}, respectively, due to the presence of the trifluoromethyl group with low oxygen balance. Compound **3** has a detonation velocity of 4599 m s^{-1}. Compound **4** has a detonation velocity of 8606 m/s, which is higher than TNT and close to RDX (8795 m s^{-1}). The detonation pressure of compounds **3** and **4** were 10.1 GPa and 32.1 GPa, respectively, and the detonation pressure of **4** was higher than that of TNT (21.3 GPa). Impact sensitivity (IS) and friction sensitivity (FS) were measured using BAM sensitivity testers. The results showed that compounds **3** and **4** had lower sensitivities (IS $>$ 40 J, FS = 144 N; IS $>$ 40 J, FS = 252 N) relative to RDX (IS = 7.5 J, FS = 120 N) and that the introduction of the trifluoromethyl group increased the friction sensitivities. The new compounds **4** are less sensitive to impact and friction and have the potential to be developed into insensitive energetic materials.

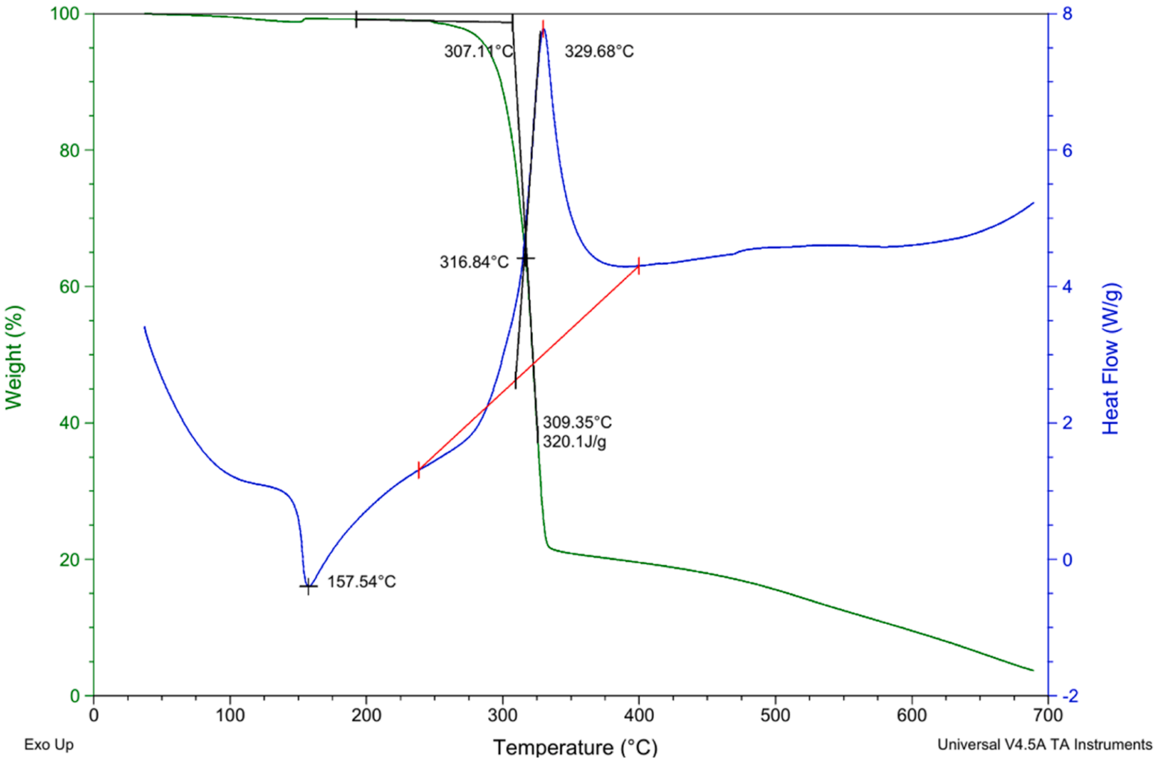


Fig. 3. DSC-TGA of 3.

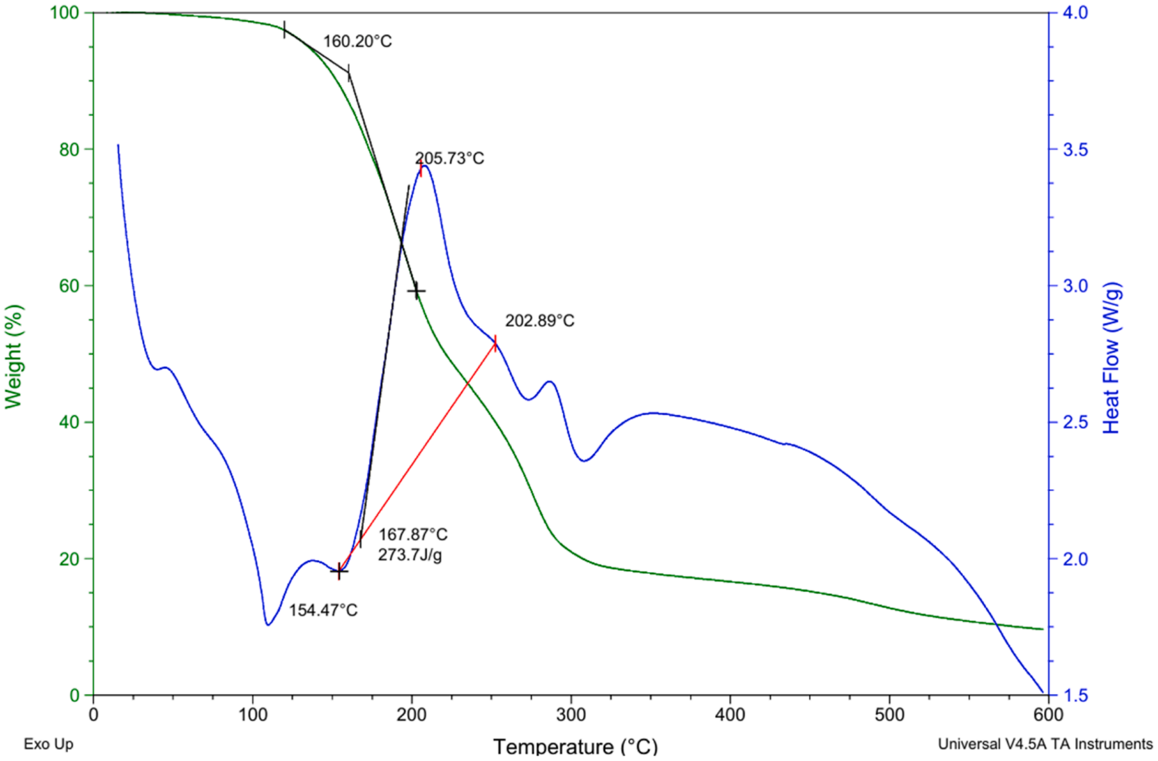


Fig. 4. DSC-TGA of 4.

3. Conclusions

Through rational molecular design, we synthesized a novel class of trifluoromethyltetrazole-based energetic compounds and developed a cost-effective synthetic route using readily available precursors, successfully preparing trifluoromethyltetrazolate salts **3** and **4**. To systematically evaluate the structural effects of the trifluoromethyl group, methyltetrazolate analogs were synthesized as a comparative system. Experimental results demonstrated that the introduction of the trifluoromethyl moiety significantly enhanced the thermal stability of the

Table 1
Physicochemical and Detonation Properties of Compounds 3–6 in Comparison to RDX and TNT.

Compound	T_d[a] (°C)	ρ[b] (g cm^{-3})	OB[c] (%)	$\Delta_f H$[d] (kJ mol^{-1}/kJ g^{-1})	D_v[e] (m s^{-1})	P[f] (GPa)	IS[g] (J)	FS[h] (N)
3	307	1.59	−48.7	−1004/−5.3	4599	10.1	>40	144
4	160	1.64	−35.8	−792.9/−3.5	8606	32.1	>40	252
5	269	1.40	−83.7	−394.9/−2.7	–	–	>40	128
6	207	1.61	−61.4	−144.5/−0.85	–	–	>40	144
RDX [59]	205	1.80	0	70.7/0.32	8801	33.6	7.5	120
TNT [60,61]	295	1.65	−74.0	−59.3/−0.26	6824	19.4	39.2	353
TFX [49]	300	1.88	−25.7	−184.7/−0.74	7492	26.4	>40	>360
TFNH-1 [45]	275	1.69	−58.1	−1006.9/−3.04	6429	13.68	>40	–

[a] Thermal decomposition temperature (onset) under nitrogen gas (DSC at 10 °C min^{-1}).
[b] Measured densities, with a gas pycnometer at room temperature.
[c] Oxygen balance assuming the formation of CO_2.
[d] Calculated heat of formation.
[e] Calculated detonation velocity.
[f] Calculated detonation pressure.
[g] Impact sensitivity.
[h] Friction sensitivity.

compounds. Although compound **3** exhibited relatively moderate detonation performance, its exceptional thermal stability ($T_d = 307$ °C) and reduced sensitivity (IS > 40 J) highlight its potential for specialized applications requiring high thermal tolerance. In contrast, compound **4** achieved a balanced combination of theoretical detonation parameters ($D = 8606$ m s^{-1}; $P = 32.1$ GPa) and insensitivity, validating the fluorine-functionalization strategy as a viable approach to harmonize energy output and safety performance. This work provides a new direction for developing safety-enhanced energetic materials with practical engineering applicability, emphasizing the critical role of molecular engineering in advancing energetic material design.

4. Experimental section

Caution! Although we have no explosions or hazards in preparing and handling these new energetic materials, proper protective precautions must be used. All compounds should be handled with care using the best safety practices.

4.1. General

The ^1H, ^{13}C and ^{19}F NMR spectra were recorded on 400 MHz NMR spectrometers (400 MHz for ^1H, 101 MHz for ^{13}C and 375 MHz for ^{19}F respectively). Coupling constants (J) are reported in Hz. The following abbreviations were used to explain the multiplicities: *s* = singlet, *d* = doublet, *t*= triplet, *q* = quartet, *m* = multiplet, sept = septet. All reactions were monitored by ^{19}F NMR or ^1H NMR. Low-resolution mass spectrum (MS) was obtained on LC-MS (ESI), and high-resolution mass spectrometry (HRMS) data were measured on a Thermo Scientific Q Exactive HF Orbitrap-FTMS instrument with electrospray ionization (ESI) mode. Melting points were determined by DSC Q2000 differential scanning calorimeter. IR spectra were measured by Nicolet 380 FT-IR infrared spectrophotometer from Thermo Fisher Scientific. Thermal decomposition temperatures were collected on a DSC823 differential scanning calorimeter from Mettler Toledo, USA, with a scanning rate of 10 °C min^{-1}. TGA spectra were determined using a TGA/ADTA851 thermogravimetric analyser under N_2 flow with a ramp rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) thermograms were analyzed using Advantage Software (Version 5.5.22) with standardized baseline correction protocols. Impact and friction sensitivities were obtained using standard BAM Fallhammer and BAM friction tester. Density was determined at room temperature using an Anton paar ultrapyc 5000 gas concentrator. Crystal structures were generated using Olex2 software.

4.2. Synthesis

4.2.1. Compound 1 [sodium 5-(trifluoromethyl)tetrazol-1-ide] [52]

In a 250 ml round-bottomed flask, trifluoroacetamide (12.4 g, 0.1 mol) was mixed thoroughly with phosphorus pentoxide (46 g, 0.3 mol). The setup was connected to a three-necked flask containing sodium azide (0.58 g, 14 mmol) via tetrafluoroethylene tubing, with an anti-siphonage device positioned between the two flasks. The entire system was purged with nitrogen to establish an inert atmosphere, and dry DMF (40 mL) was added to the three-necked flask. The round-bottomed flask was then immersed in an oil bath preheated to 120 °C, with the tetrafluoroethylene tubing submerged below the DMF level. Upon the appearance of trifluoroacetonitrile bubbles, the oil bath temperature was gradually increased to 150 °C. After 2 hours, the reaction mixture transitioned from a suspension to a clear solution. Following the completion of the reaction, the solution was carefully transferred to a distillation apparatus, and the crude product was collected by distilling off the DMF at 65 °C under reduced pressure. The crude product was then dissolved by heating it with 10 mL of tetrahydrofuran (THF) in an oil bath at 65 °C until complete dissolution was achieved. Recrystallization was initiated by adding 90 mL of dichloromethane (DCM), resulting in the formation of a white solid. The final product was isolated, yielding 1.77 g (79 %) of the desired compound. ^{19}F NMR (376 MHz, CD_3OD) δ −63,4 (s, 3F); ^{13}C NMR (101 MHz, CD_3OD) δ 155.5 (q, $J = 36.4$ Hz), 122.7 (q, $J = 267.8$ Hz). IR(KBr):3663 3351 3256 1686 1673 1508 1419 1234 1173 1144 1046 749.

4.2.2. Compound 2 [1H-tetrazol-5-amine hydrochloride]

Aminotetrazole (1.06 g, 12.5 mmol) was dissolved in 20 ml of methanol. Thereafter, 5 ml of concentrated hydrochloric acid (0.06 mol) was added to the solution in order to initiate a reflux reaction. The mixture was refluxed for 20 min. After the reflux period, the solvent was removed by concentration at 40 °C. The resulting residue was then saturated with a few drops of petroleum ether, prompting recrystallization and yielding 1.5 g (98 %) of white crystalline product. ^1H NMR (400 MHz, CD_3OD) δ 6,14 (s,4H). ^{13}C NMR (101 MHz, CD_3OD) δ 151.8. IR(KBr): 3348 3153 2504 2070 1694 1285 1024 995 709 552.

4.2.3. Compound 3 [diaminomethaniminium 5-(trifluoromethyl)tetrazol-1-ide]

In a 50 ml flask, a solution of compound **1** (1.60 g, 10 mmol) in ethyl acetate (50 mL) was gradually added to a solution of Guanidine Hydrochloride (0.95 g, 10 mmol) in ethyl acetate (50 mL). The mixture was stirred in an oil bath at 65 °C for two hours. Upon completion of the reaction, the insoluble white solid was removed by filtration. The filtrate was then concentrated to 20 ml and recrystallised by the addition of 230 ml of DCM, yielding 1.59 g of white solid (81 %). ^{19}F NMR (376 MHz, CD_3OD) δ −63,4 (s, 3F); ^{1}H NMR (400 MHz, CD_3OD) δ 4.96 (s, 6H); ^{13}C NMR (101 MHz, Methanol) δ 158.7, 154.2 (q, $J = 36.2$ Hz), 121.2 (q, $J = 268.0$ Hz). IR(KBr): 3368 3173 2045 1664 1504 1229 1163 1038 749 533. HRMS (ESI) Calcd for $CN_3H_6^+$ [Cation of this salt]: 60.0556, Found: 60.0560; Calcd for $C_2F_3N_4^-$ [Anion of this salt]: 137.0081, Found: 137.0069.

4.2.4. *Compound **4** [5-amino-1H-tetrazol-4-ium 5-(trifluoromethyl) tetrazol-1-ide]*

Compound **1** (1.60 g, 10 mmol) and compound **2** (0.95 g, 10 mmol) were each dissolved completely in 50 ml of ethyl acetate respectively. The ethyl acetate solution of compound **1** was slowly poured into the solution of compound **2** and the resulting mixture was stirred in an oil bath at 65 °C for 2 h. After completion of the reaction, the insoluble white solid was removed by filtration. After removing the solvent from the filtrate, 1.61 g of white solid was obtained (72 %). ^{19}F NMR (376 MHz, CD_3OD) δ −63,4 (s, 3F); ^{1}H NMR (400 MHz, CD_3OD) δ 5.09 (s, 4H). ^{13}C NMR (101 MHz, D_3OD) δ 154.1, 153.5 (q, $J = 35.4$ Hz), 119.2 (q, $J = 268.9$ Hz). IR(KBr): 3399, 3192, 1636, 1263, 1044, 1034, 908, 728. HRMS (ESI) Calcd for $CN_5H_4^+$ [Cation of this salt]: 86.0461, Found: 86.0465; Calcd for $C_2F_3N_4^-$ [Anion of this salt]: 137.0081, Found: 137.0075.

4.2.5. *Compound 5 [diaminomethaniminium 5-methyltetrazol-1-ide]*

Into a solution of 5-Methyltetrazole (0.84 g, 10 mmol) in 20 ml of anhydrous methanol was added NaOH (0.40 g, 10 mmol) at 0 °C, followed by warming up to room temperature. The reaction mixture was stirred for 2 h. The solvent was removed to obtain a white solid, which was then dissolved in methanol (15 mL). Into the solution was added a solution of guanidine hydrochloride (0.95 g, 10 mmol) in 15 ml of methanol. After the mixture was stirred for 2 h, the insoluble solid was removed by filtration and the filtrate was concentrated to give 1.4 g of white solid (98 %). ^{1}H NMR (400 MHz, CD_3OD) δ 4.94 (s, 6H), δ 2.40 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.0, 159.1, 10.1. IR(KBr): 3420, 3152, 2194, 1648, 1567, 1478, 1373, 1123, 692, 610. HRMS (ESI) Calcd for $CN_3H_6^+$ [Cation of this salt]: 60.0556, Found: 60.0564; Calcd for $C_2H_3N_4^-$ [Anion of this salt]: 83.0363, Found: 83.0354.

4.2.6. *Compound 6 [5-amino-1H-tetrazol-4-ium 5-methyltetrazol-1-ide]*

Into a solution of 5-Methyltetrazole (0.84 g, 10 mmol) in 20 ml of anhydrous methanol was added NaOH (0.40 g, 10 mmol) at 0 °C, followed by warming up to room temperature. The reaction mixture was stirred for 2 h. The solvent was removed to obtain a white solid, which was then dissolved in methanol (15 mL). Into the solution was added a solution of **2** (1.21 g, 10 mmol) in 15 ml of methanol. After the mixture was stirred for 2 h, the insoluble solid was removed by filtration and the filtrate was concentrated to give 1.6 g of white solid (97 %). ^{1}H NMR (400 MHz, CD_3OD) δ 5.00 (s, 4H), δ 2.55 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 158.1, 154.0, 8.4. IR(KBr): 3726, 3381, 2795, 2021, 1897, 1651, 1587, 1284, 1070, 994, 911, 740, 687, 551. HRMS (ESI) Calcd for $CN_5H_4^+$[Cation of this salt]: 86.0461, Found: 86.0469; Calcd for $C_2H_3N_4^-$ [Anion of this salt]: 83.0363, Found: 83.0354.

Declaration of competing interest

All of the authors declare no conflict of interest.

CRediT authorship contribution statement

Jiawen Deng: Writing – original draft, Methodology, Investigation, Formal analysis. **Lukang Lin:** Investigation. **Yahan Zhang:** Methodology, Investigation, Formal analysis. **Xu Yao:** Project administration. **Jun Zhang:** Investigation. **Jin-Hong Lin:** Supervision, Project administration, Investigation. **Wenbin Yi:** Methodology, Formal analysis. **Xing Zheng:** Supervision, Formal analysis. **Ji-Chang Xiao:** Writing – review & editing, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no competing financial interests.

Acknowledgements

The authors thank the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB0590000), the National Natural Science Foundation of China (22271181), the Natural Science Foundation of Hunan Province (2023JJ60212), Hunan Provincial Hengyang Joint Fund (2020JJ6052) and the Science and Technology Commission of Shanghai Municipality (22ZR1423600). Computing resources were provided by the National Supercomputing Center of China in Shenzhen.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2025.110427.

References

[1] O.T. O'Sullivan, M.J. Zdilla, Properties and promise of catenated nitrogen systems As high-energy-density materials, Chem. Rev. 120 (12) (2020) 5682–5744.

[2] G. Li, C. Zhang, Review of the molecular and crystal correlations on sensitivities of energetic materials, J. Hazard. Mater. 398 (2020) 122910.

[3] J.C. Gálvez-Ruiz, G. Holl, K. Karaghiosoff, T.M. Klapötke, K. Löhnwitz, P. Mayer, H. Nöth, K. Polborn, C.J. Rohbogner, M. Suter, et al., Derivatives of 1,5-diamino-1H-tetrazole: A new Family of energetic heterocyclic-based salts, Inorg. Chem. 44 (12) (2005) 4237–4253.

[4] N. Liu, Y.-J. Shu, H. Li, L.-J. Zhai, Y.-N. Li, B.-Z Wang, Synthesis, characterization and properties of heat-resistant explosive materials: polynitroaromatic substituted difurazano[3,4-b:3′,4′-e]pyrazines, RSC Adv. 5 (54) (2015) 43780–43785.

[5] Q. Wang, S. Wang, X. Feng, L. Wu, G. Zhang, M. Zhou, B. Wang, L. Yang, A heat-resistant and energetic metal–Organic framework assembled by chelating Ligand, ACS Appl. Mater. Interfaces 9 (43) (2017) 37542–37547.

[6] M. Zhang, W. Fu, C. Li, H. Gao, L. Tang, Z. Zhou, E)-1,2-bis(3,5-dinitro-1H-pyrazol-4-yl)diazene – Its 3D potassium metal–Organic framework and organic salts with super-heat-resistant properties, Eur. J. Inorg. Chem. 2017 (22) (2017) 2883–2891.

[7] Y. Wang, Y. Liu, S. Song, Z. Yang, X. Qi, K. Wang, Y. Liu, Q. Zhang, Y. Tian, Accelerating the discovery of insensitive high-energy-density materials by a materials genome approach, Nat. Commun. 9 (1) (2018) 2444.

[8] D.L. Williams, K.D. Kuklenz, A determination of the Hansen solubility parameters of hexanitrostilbene (HNS), Propellants, Explos., Pyrotech 34 (5) (2009) 452–457.

[9] C. Zhang, Investigation of the slide of the single layer of the 1,3,5-triamino-2,4,6-trinitrobenzene crystal: sliding potential and orientation, J. Phys. Chem. B. 111 (51) (2007) 14295–14298.

[10] P. Pagoria, M.X. Zhang, N. Zuckerman, G. Lee, A. Mitchell, A. DeHope, A. Gash, C. Coon, P. Gallagher, Synthetic studies of 2,6-diamino-3,5-dinitropyrazine- 1-oxide (LLM-105) from discovery to multi-kilogram scale, Propellants, Explos., Pyrotech 43 (1) (2017) 15–27.

[11] D. Kumar, C. He, L.A. Mitchell, D.A. Parrish, J.M. Shreeve, Connecting energetic nitropyrazole and aminotetrazole moieties with N,N′-ethylene bridges: a promising approach for fine tuning energetic properties, J. Mater. Chem. A 4 (23) (2016) 9220–9228, https://doi.org/10.1039/C6TA02387H.

[12] D. Kumar, G.H. Imler, D.A. Parrish, J.M. Shreeve, N-acetonitrile functionalized nitropyrazoles: precursors to insensitive asymmetric N-methylene-C linked azoles, Chem. Eur. J. 23 (33) (2017) 7876–7881.

[13] S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang, S. Pang, 3D Energetic metal–Organic frameworks: synthesis and properties of high energy materials, Angew. Chem., Int. Ed. 52 (52) (2013) 14031–14035.

[14] Y. Tang, C. He, L.A. Mitchell, D.A. Parrish, J.M. Shreeve, Potassium 4,4′-bis (dinitromethyl)-3,3′-azofurazanate: a highly energetic 3D metal–Organic framework as a promising primary explosive, Angew. Chem., Int. Ed. 55 (18) (2016) 5565–5567.

[15] J. Tang, H.-W. Yang, G.-B. Cheng, Nitrogen-rich tetracyclic-based heterocyclic energetic materials, Energ. Mater. Front. 4 (2) (2023) 110–122.

[16] B. Chen, H. Lu, J. Chen, Z. Chen, S.-F. Yin, L. Peng, Qiu, R. Recent progress on nitrogen-rich energetic materials based on tetrazole skeleton, Top Curr. Chem. 381 (5) (2023) 25.

[17] X. Wang, G. Hao, L. Xiao, Y. Hu, G. Zhang, S. Wang, J. Yang, W. Jiang, Review on the thermal decomposition of dihydroxylammonium 5,5′- bistetrazole-1,1′-diolate (TKX-50), Thermochim. Acta. 719 (2023) 179393.

[18] Y. Tang, C. He, G.H. Imler, D.A. Parrish, J.M. Shreeve, Aminonitro Groups Surrounding a Fused Pyrazolotriazine Ring: A Superior Thermally Stable and Insensitive Energetic Material, 2, ACS Appl. Energy Mater, 2019, pp. 2263–2267.

[19] P. Yin, L.A. Mitchell, D.A. Parrish, J.M. Shreeve, Energetic N-nitramino/N-oxyl-functionalized pyrazoles with versatile π–π stacking: structure–Property

relationships of high-performance Energetic materials, Angew. Chem., Int. Ed. 55 (46) (2016) 14409–14411.

[20] Y. Tang, C. He, G.H. Imler, D.A. Parrish, J.M. Shreeve, Energetic derivatives of 4,4′,5,5′-tetranitro-2H,2′H-3,3′-bipyrazole (TNBP): synthesis, characterization and promising properties, J. Mater. Chem. A 6 (12) (2018) 5136–5142.

[21] Y. Zhang, Y. Li, J. Hu, Z. Ge, C. Sun, S. Pang, Energetic C-trinitromethyl-substituted pyrazoles: synthesis and characterization, in: Dalton Trans., 48, 2019, pp. 1524–1529.

[22] Y. Tang, Y. Liu, G.H. Imler, D.A. Parrish, J.M. Shreeve, Green synthetic approach for high-performance energetic nitramino azoles, Org. Lett. 21 (8) (2019) 2610–2614.

[23] J. Singh, V. Thaltiri, R.J. Staples, J.M. Shreeve, Understanding the stability of highly nitrated sensitive pyrazole isomers, Org. Lett. 26 (28) (2024) 5946–5950.

[24] H. Gu, H. Xiong, H. Yang, G. Cheng, Tricyclic nitrogen-rich cation salts based on 1,2,3-triazole: chemically stable and insensitive candidates for novel gas generant, Chem. Eng. J. (2021) 408.

[25] P. Yin, D.A. Parrish, J.M. Shreeve, Bis(nitroamino-1,2,4-triazolates): n-bridging strategy toward insensitive energetic materials, Angew. Chem., Int. Ed. 53 (47) (2014) 12889–12892.

[26] V. Thottempudi, H. Gao, J.M. Shreeve, Trinitromethyl-substituted 5-nitro- or 3-azo-1,2,4-triazoles: synthesis, characterization, and energetic properties, J. Am. Chem. Soc. 133 (16) (2011) 6464–6471.

[27] S. Lal, R.J. Staples, J.M. Shreeve, Nitroiminotriazole (NIT) based potential solid propellants: synthesis, characterization, and applications, Dalton Trans. 53 (3) (2024) 903–907.

[28] Y.H. Joo, B. Twamley, S. Garg, J.M. Shreeve, Energetic nitrogen-rich derivatives of 1,5-diaminotetrazole, Angew. Chem., Int. Ed. 47 (33) (2008) 6236–6239.

[29] M. Zhang, H. Gao, C. Li, W. Fu, L. Tang, Z. Zhou, Towards improved explosives with a high performance: n-(3,5-dinitro-1H-pyrazol-4-yl)-1H-tetrazol-5-amine and its salts, J. Mater. Chem. A 5 (4) (2017) 1769–1777.

[30] B. Wang, X. Qi, W. Zhang, K. Wang, W. Li, Q. Zhang, Synthesis of 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole and its derivatives from 5-aminotetrazole and cyanogen azide: a promising strategy towards the development of C–N linked bistetrazolate energetic materials, J. Mater. Chem. A 5 (39) (2017) 20867–20873.

[31] G. Zhao, C. He, P. Yin, G.H. Imler, D.A. Parrish, J.M. Shreeve, Efficient construction of energetic materials via nonmetallic catalytic carbon–Carbon cleavage/oxime-release-coupling reactions, J. Am. Chem. Soc. 140 (10) (2018) 3560–3563.

[32] H. Xia, W. Zhang, Y. Jin, S. Song, K. Wang, Q. Zhang, Synthesis of thermally stable and insensitive energetic materials by incorporating the tetrazole functionality into a fused-ring 3,6-dinitropyrazolo-[4,3-c]pyrazole framework, ACS Appl. Mater. Interfaces 11 (49) (2019) 45914–45921.

[33] A.K. Chinnam, J. Singh, R.J. Staples, J.M. Shreeve, Manipulating sensitivities of planar oxadiazole-based high performing energetic materials, J. Heterocycl. Chem. 61 (3) (2024) 506–513.

[34] J. Ma, G. Cheng, X. Ju, Z. Yi, S. Zhu, Z. Zhang, H. Yang, Amino-nitramino functionalized triazolotriazines: a good balance between high energy and low sensitivity, Dalton Trans. 47 (41) (2018) 14483–14490.

[35] J. Ma, Y. Tang, G. Cheng, G.H. Imler, D.A. Parrish, J.M. Shreeve, Energetic derivatives of 8-nitropyrazolo[1,5-a][1,3,5]triazine-2,4,7-triamine: achieving balanced explosives by fusing pyrazole with triazine, Org. Lett. 22 (4) (2020) 1321–1325.

[36] K. Li, W. Huang, Z. An, X. Wei, Y. Tang, Efficient synthesis of a superior heat-resistant energetic material based on fused pyrazolotriazine ring, Cryst. Growth Des. 21 (12) (2021) 6872–6878.

[37] H. Xue, B. Twamley, J.M. Shreeve, Energetic salts of substituted 1,2,4-triazolium and tetrazolium 3,5-dinitro-1,2,4-triazolates, J. Mater. Chem. 15 (34) (2005) 3459–3465.

[38] C. Ye, J.-C. Xiao, B. Twamley, J.M. Shreeve, Energetic salts of azotetrazolate, iminobis(5-tetrazolate) and 5, 5′-bis(tetrazolate), Chem. Commun. (21) (2005) 2750–2752.

[39] Y. Guo, H. Gao, B. Twamley, J.M. Shreeve, Energetic nitrogen rich salts of N,N-bis [1(2)H-Tetrazol-5-yl]amine, Adv. Mater. 19 (19) (2007) 2884–2888.

[40] H. Gao, Y. Huang, C. Ye, B. Twamley, J.M. Shreeve, The synthesis of di (aminoguanidine) 5-nitroiminotetrazolate: some diprotic or monoprotic acids as precursors of energetic salts, Chem. Eur. J. 14 (18) (2008) 5596–5603.

[41] F.R. Benson, The chemistry of the tetrazoles, Chem. Rev. 41 (1) (1947) 1–61.

[42] G.-H. Tao, Y. Guo, Y.-H. Joo, B. Twamley, J.M. Shreeve, Energetic nitrogen-rich salts and ionic liquids: 5-aminotetrazole (AT) as a weak acid, J. Mater. Chem. 18 (45) (2008) 5524–5530.

[43] S. Lal, R.J. Staples, J.M. Shreeve, Design and synthesis of high-performance planar explosives and solid propellants with tetrazole moieties, Org. Lett. 25 (27) (2023) 5100–5104.

[44] Z. Guo, Q. Yu, Y. Chen, J. Liu, T. Li, Y. Peng, W. Yi, Fluorine-containing functional group-based energetic materials, Chem. Rec. 23 (9) (2023) e202300108.

[45] S. Garg, J.M. Shreeve, Trifluoromethyl- or pentafluorosulfanyl-substituted poly-1,2,3-triazole compounds as dense stable energetic materials, J. Mater. Chem. 21 (13) (2011) 4787.

[46] M. Xu, Z. Ge, X. Lu, H. Mo, Y. Ji, H. Hu, Fluorinated glycidyl azide polymers as potential energetic binders, RSC Adv. 7 (75) (2017) 47271–47278.

[47] S.K. Valluri, M. Schoenitz, E.L. Dreizin, Combustion of aluminum-metal fluoride reactive composites in different environments, Propellants, Explos., Pyrotech 44 (10) (2019) 1327–1336.

[48] Y. Kang, Y. Dong, Y. Liu, H. Gao, Y. Wang, J.M. Shreeve, Halogen bonding (C-F⋯X) and its effect on creating ideal insensitive energetic materials, Chem. Eng. J. 440 (2022) 135969.

[49] Z. Yan, T. Lu, Y. Liu, W. Liu, B. Zhao, Y. Wang, Z. Ge, High thermal stability and insensitive fused triazole-triazine trifluoromethyl-containing explosives (TFX), ACS Omega 6 (29) (2021) 18591–18597.

[50] A.K. Chinnam, R.J. Staples, J.M Shreeve, HFOX–1-amino-1-hydrazino-2,2-dinitroethylene as a precursor to trifluoromethyl, dinitro, or trinitro-based energetic 1,2,4-triazoles, Org. Lett. 23 (1) (2020) 76–80.

[51] K.G. Balachandar, A. Thangamani, Novel high performance energetic materials of fluorine-containing 2,6-dinitro-4-(trifluoromethyl)phenol derivatives with substituted azoles, J. Fluorine Chem. 247 (2021) 109801.

[52] W.P. Norris, 5-Trifluoromethyltetrazole and its derivatives, J. Org. Chem. 27 (9) (1962) 3248–3251.

[53] A.P. Cox, M.C. Ellis, A.C. Legon, A. Wallwork, Microwave spectra, hyperfine splittings and average structures of 3,3,3-trifluoropropyne, CF3C=CH and trifluoroacetonitrile, CF3CN, J. Chem. Soc., Faraday Trans. 89 (16) (1993) 2937–2944.

[54] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J. Appl. Crystallogr. 42 (2009) 339.

[55] G.W. Frischmjt, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R.Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, Gaussian 09, Revision D. 01. Gaussian, Inc, Wallingford, CT. Gaussian, Inc. Wallingford, CT. 2013.

[56] M.J. Kamlet, J.E. Ablard, Chemistry of detonations. II. Buffered equilibria, J. Chem. Phys. 48 (1968) 36.

[57] M.J. Kamlet, C. Dickinson, Chemistry of detonations. III. Evaluation of the simplified calculational method for Chapman-Jouguet detonation pressures on the basis of available experimental information, J. Chem. Phys. 48 (1968) 43.

[58] M.J. Kamlet, S.J. Jacobs, Chemistry of detonations. I. A simple method for calculating detonation properties of C–H–N–O explosives, J. Chem. Phys. 48 (1968) 23.

[59] Y. Tang, D. Kumar, J.M. Shreeve, Balancing excellent performance and high thermal stability in a dinitropyrazole fused 1,2,3,4-tetrazine, J. Am. Chem. Soc. 139 (39) (2017) 13684–13687.

[60] A.K. Chinnam, Q. Yu, G.H. Imler, D.A. Parrish, J.M. Shreeve, Azo- and methylene-bridged mixed azoles for stable and insensitive energetic applications, Dalton. Trans. 49 (33) (2020) 11498–11503.

[61] S. Zeman, V.B. Patil, Towards to some published misconceptions about TNT and ε-CL20, FirePhysChem. 5 (1) (2025) 68–73.