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Synthesis of C–C bonded trifluoromethyl-based high-energy density materials *via* the ANRORC mechanism†

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A trifluoromethyl group substituted C–C bonded nitrogen rich energetic material 3-(3-nitro-1*H*-pyrazol-4-yl)-5-(trifluoromethyl)-1,2,4-oxadiazole (**4**), its hydroxyl amine (**5**) and 3,6,7-triamino-7*H*-[1,2,4]triazolo [4,3-*b*][1,2,4]triazol-2-ium (**6**) salts and hydrazinium 5-(3-nitro-1*H*-pyrazol-4-yl)-3-(trifluoromethyl)-1,2,4-triazol-1-ide (**7**) were synthesized and fully characterized using infrared spectroscopy (IR), multinuclear magnetic resonance (NMR) spectroscopy (¹H, ¹³C, and ¹⁹F), high-resolution mass spectrometry (HRMS), elemental analysis (EA) and differential scanning calorimetry (DSC) studies. Furthermore, compounds **4** and **7** were confirmed using single-crystal X-ray diffraction studies (SC-XRD). All compounds possess good density (1.70–1.80 g cm⁻³), detonation velocity (6432–7144 m s⁻¹), pressure (16.38–20.31 GPa), and thermal stability (>170 °C). They are insensitive towards mechanical stimuli, impact (IS > 35 J) and friction (FS > 288 N). Overall, due to their balanced performance, these compounds can be a better replacement for presently used explosives such as trinitrotoluene (TNT).

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Introduction

The study and exploration of novel energetic materials comprise a fascinating field within synthetic chemistry, as evidenced by the steadily growing numbers of studies in recent years, particularly with moieties such as pyrazoles and triazoles.^{1–5} The researchers in this field are keenly focused on developing new derivatives from five-membered heterocyclic rings due to their straightforward synthesis and their potential for substitution at the available carbon atoms.^{6,7} In recent years, compounds rich in nitrogen, fluorine, and oxygen have become crucial components in the field of high-energy density materials (HEDMs), demonstrating their notable energetic properties when combined with core classes of explosives.^{8,9} From thermodynamic considerations, there is a minor difference between oxygen and fluorine as oxidizing moieties. The bond strength of a C–F bond is much higher than that of a C–H

bond; furthermore, fluorine has the benefits of higher electronegativity and small volume that make it more stable and denser than its non-fluorinated analogues. Fluorine or fluorine-containing substituents are often incorporated into energetic compounds to achieve better performance and for applications requiring a longer and flatter pulse. Formation of hydrogen fluoride upon decomposition releases an enormous amount of energy. Recently, the development of halide-based energetic materials has become a prominent theme, owing to their low volatility, ease of synthesis, and versatile modification potential for military and civilian applications.^{10,11} The extensive use of fluorinated triazole-based compounds in medicinal and agricultural fields, as well as in energetic materials, has sparked interest in developing more efficient synthetic procedures to produce molecules having high density and performance.^{12–15} In recent years, Shreeve and co-workers reported the synthesis of –CF₃- and –SF₅-substituted five-membered heterocyclic rings such as pyrazole, triazole, and oxadiazole, showcasing applications in the field of energetic materials.^{16,17} The presence of the trifluoromethyl group can induce high chemical and thermal stability, density, low surface energy and higher electronegativity. However, limited trifluoromethyl-substituted energetic compounds are known due to their multistep synthesis, toxic nature, and low yields. Additionally, fluorine is a crucial atom in the detonation process due to its different processes of bond breaking and decomposition compared to CHNO compounds. CHNO-based

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explosives on initiation yield decomposition products such as carbon dioxide, nitrogen and water, while CHNOF-based compounds give hydrogen fluoride (HF) and fluorine (F₂) gases, thereby accelerating the decomposition and enhancing energy release.^{18–21} It is noteworthy that fluorine-containing energetic compounds and their decomposition products can pose significant hazards to personnel and the environment due to their reactive and toxic nature, necessitating the implementation of safety protocols to minimize potential harm and to mitigate exposure risks. As shown in Fig. 1, the compounds 3',5'-bis(fluorodinitromethyl)-3,5'-bi(1,2,4-oxadiazole) (A),²² 5-(trifluoromethyl)-3-(trinitromethyl)-1H-1,2,4-triazole (B),²³ 3-(dinitromethyl)-5-(trifluoromethyl)-1H-1,2,4-triazole (C),²³ 1,3-bis(4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)propan-2-ol (D), tris(2-(4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)ethyl)amine (E), and 1,1'-(2,2-bis((4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)methyl)propane-1,3-diyl)bis(4-(trifluoromethyl)-1H-1,2,3-triazole) (F)²⁴ have been reported with fluoro and nitro substitution. These compounds show relatively low densities (1.62–1.7 g cm⁻³) and detonation velocities (6338–6429 m s⁻¹) and importantly compounds A–C show very low to moderate thermal decomposition (*T*_d = 78 to 151 °C). These numbers indicate that obtaining balanced properties in a molecule with a combination of fluorine and nitro groups is challenging to energetic materials chemists. Based on the above aspects, we have synthesized compounds 4, 6, and 7 and shown their energetic performance for practical applications in defence. Compound 3-(3-nitro-1H-pyrazol-4-yl)-5-(trifluoromethyl)-1,2,4-oxadiazole (4) was obtained from noncyclic (3-amino-*N*'-hydroxy-1H-pyrazole-4-carboximidamide) (2) through conventional hetero-cyclization reactions using trifluoroacetic anhydride and its energetic salts (5–6) were prepared using inexpensive starting materials. This work also emphasises the formation of hydrazinium 3-(3-nitro-1H-pyrazol-4-yl)-5-(trifluoromethyl)-1,2,4-triazol-1-ide (7) from 4 with the addition of hydrazine monohydrate. This transformation involves rearrangement *via* ring opening and ring closing processes and interestingly, it is less explored with such heterocyclic compounds.

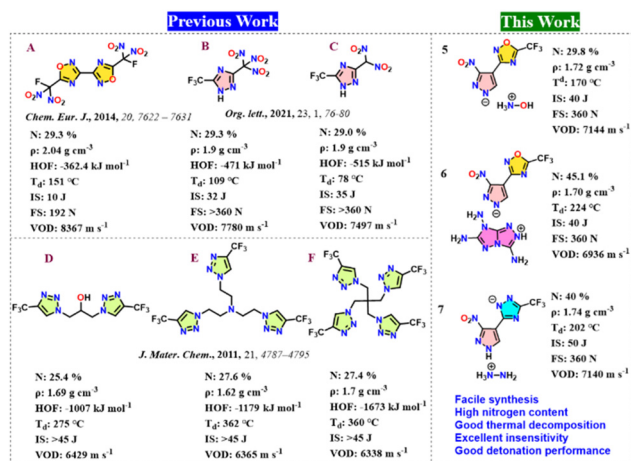
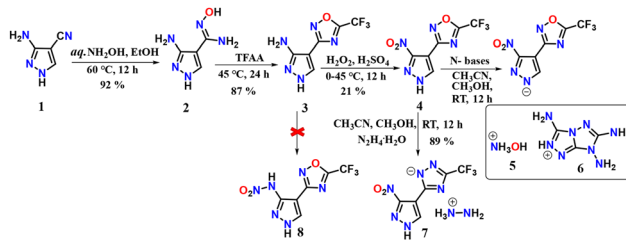


Fig. 1 Selected previously reported fluorinated energetic materials (A–F) and this work (5–7).

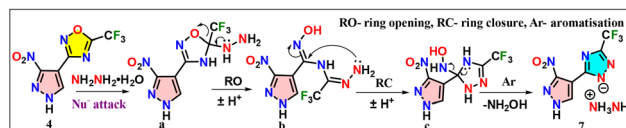
Results and discussion

Synthesis

The synthesis of “amidoxime” from 3-amino-1H-pyrazole-4-carbonitrile (1) is well-reported in the literature.²⁵ As illustrated in Scheme 1, compound 1 was reacted with hydroxylamine hydrate in ethanol at 60 °C for 12 hours, resulting in the formation of compound 3-amino-*N*'-hydroxy-1H-pyrazole-4-carboximidamide (2) in 92% yield. The synthesis of 4-(5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl)-1H-pyrazol-3-amine (3) was carried out with the addition of trifluoroacetic anhydride (TFAA) to compound 2 in a stoichiometric ratio at 0 °C and heating to 45 °C for 12 hours to obtain compound 3 in 87% yield. To this, a 1 : 1 ratio of H₂SO₄/H₂O₂ (2 mL) was added at 0 °C and the reaction was continued at 45 °C for 12 hours to get compound 3-(3-nitro-1H-pyrazol-4-yl)-5-(trifluoromethyl)-1,2,4-oxadiazole (4) in 21% yield. Furthermore, compound 4 was treated with bases such as hydroxylamine hydrate and 3,6,7-triamino-7H-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium (TATOT) to get the nitrogen-rich energetic salts hydroxylammonium-3-nitro-4-(5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl)pyrazol-1-ide (5) and 3,6,7-triamino-7H-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium-3-nitro-4-(5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl)pyrazol-1-ide (6) in quantitative yields. When compound 4 was treated with hydrazine monohydrate, we expected to get the hydrazinium salt, but surprisingly, a triazole rearranged product was formed which is hydrazinium 3-(3-nitro-1H-pyrazol-4-yl)-5-(trifluoromethyl)-1,2,4-triazol-1-ide (7) with the removal of the oxygen atom from the oxadiazole ring. This may be attributed to the strong electron-withdrawing effect of the –CF₃ moiety. Moreover, attempts to obtain compound 8 were unsuccessful despite having multiple nitration conditions at various temperatures. As shown in Scheme 2, the formation of compound 7 suggests that it is going through the domino process *via* nucleophilic addition of hydrazine hydrate, followed by the ring opening and ring closing processes (ANRORC).²⁶ The first step involves the nucleophilic attack of



Scheme 1 Synthesis of –CF₃-based C–C bonded pyrazole–triazole HEDMs.



Scheme 2 Plausible mechanism for the conversion of compounds 4–7.

hydrazine hydrate on the $-\text{CF}_3$ -substituted carbon centre, followed by ring opening (RO), leading to the formation of (*Z*)-*N'*-hydroxy-3-nitro-*N*-((*Z*)-2,2,2-trifluoro-1-hydrazineylideneethyl)-1*H*-pyrazole-4-carboximidamide (**b**) which undergoes ring cyclisation and aromatisation, leading to the formation of compound **7** with the release of hydroxyl amine. It is worth mentioning that this transformation opens a new avenue to prepare high-performance energetic materials.

X-ray crystallography

Single crystals of compounds **4** and **7** were obtained by the slow evaporation of ethyl acetate and methanol at room temperature and atmospheric pressure. The molecular structures of both compounds are shown in Fig. 2 and 3. Compound **4** exhibits the monoclinic space group $P2_1/c$ with four molecules in a unit cell, as depicted in Fig. 2, with a cell volume of 870.93 \AA^3 . This compound featuring a nitro pyrazole unit combined with an oxadiazole demonstrates a twist from planarity with a measured two-plane angle of 50.06° . It shows strong intermolecular hydrogen bonding, contributing to excellent crystal packing, stability, and density (1.90 g cm^{-3} at 100 K). As shown in Fig. S2 (in the ESI†), the molecular structure has disorder in the fluorine atoms of the trifluoromethyl group. The interlayer separation between two planes is 8.82 \AA . The presence of intensive hydrogen bonding enhances the molecular density, which results in an increase in the packing efficiency of the molecule. Compound **7**· H_2O crystallises in the triclinic space group $P2_1/n$ with four molecules per unit cell ($Z = 4$) with a crystal density of 1.77 g cm^{-3} at 100 K, as shown in Fig. 3. The molecular structure is twisted from planarity having a dihedral angle of 21.46° between the triazole and nitro pyrazole rings. The presence of one water molecule and a hydrazinium cation increases the non-covalent interactions within the molecule which assists in stabilizing the crystal system.

The characteristics of the bond critical points (BCPs) in terms of the electron density and their Laplacian in the quantum theory of atoms in molecules (QTAIM) are used to identify hydrogen bonding interactions in compounds **4** and **7**.²⁶ The close interacting sites with the corresponding distances in the dimers of compounds **4** and **7** are summarized

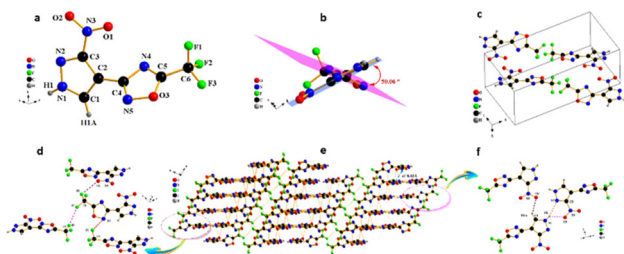


Fig. 2 (a) Asymmetric unit of compound **4**, (b) dihedral angle between the oxadiazole ring (violet) and the nitro pyrazole ring (blue), (c) unit cell packing ($z = 4$), (d) halogen bonding interactions, (e) layer-by-layer packing, and (f) hydrogen bonding interactions (indicated by dotted lines).

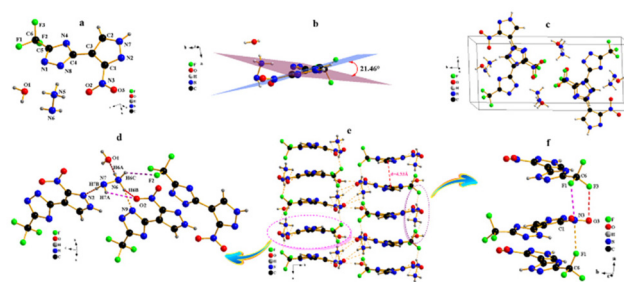


Fig. 3 (a) Asymmetric unit of compound **7**, (b) dihedral angle formed between the triazole ring (violet) and the nitro pyrazole ring (blue), (c) unit cell packing ($Z = 4$), (d) hydrogen bonding interactions in the molecule, (e) multi-layer packing structures showing individual interactions between the molecules along the *c*-axis, and (f) halogen bonding interactions in the molecule.

in Table S20† and the molecular graphs are shown in Fig. S34.† The strength of hydrogen-bonding energy (E_{H}) gradually increases with a decrease in the $\text{H}\cdots\text{F}$, $\text{H}\cdots\text{O}$, and $\text{H}\cdots\text{N}$ distances. The negative values of E_{H} are representative of stronger hydrogen bonds. The total E_{H} of compound **7** ($-155.13 \text{ kJ mol}^{-1}$) is significantly higher than that of compound **4** ($-48.78 \text{ kJ mol}^{-1}$), probably due to the hydrazinium cation, and supports the presence of the hydrogen bond network.

Physicochemical properties

The physicochemical properties of all the synthesized compounds are listed in Table 1. Assessing thermal stability is essential for ensuring the safe handling, storage, transport, and use of energetic materials. Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) measurements were carried out on a ramp of $5 \text{ }^\circ\text{C min}^{-1}$ for determining the thermal stabilities of compounds **4**–**7**. Compounds **4** ($177 \text{ }^\circ\text{C}$), **5** (170 and $254 \text{ }^\circ\text{C}$), **6** ($224 \text{ }^\circ\text{C}$) and **7** ($202 \text{ }^\circ\text{C}$) showed a good onset of thermal decomposition temperature. Among all of them, the values for compounds **6** and **7** are comparable to those for benchmark explosives such as RDX ($204 \text{ }^\circ\text{C}$) and FOX-7 ($220 \text{ }^\circ\text{C}$).²⁷ Most of the energy released by explosives comes from oxidation of carbon, hydrogen, and metals to carbon monoxide, carbon dioxide, water, metal oxide, etc. Oxygen balance is one of the quantifiable factors indicating excess or deficiency of oxygen during the combustion process. The oxygen balance for CHNOF-based energetic compositions was computed using the equation suggested by Muthurajan and Ghee considering N_2 , HF, CO, H_2O and carbon as possible detonation products.²⁷ All the synthesized compounds show a negative oxygen balance (-69.44 to -51.04%) which indicates a deficit of oxygen for their complete combustion. Density plays a crucial role in the packing of energetic materials which in turn affects the energetic performance. Higher density explosives generally release a larger amount of energy per unit volume when initiated. The densities of all the synthesized compounds were measured at room temperature using a gas pycnometer (Ultrapyc 5000 Micro) in a helium environment.

Table 1 Physicochemical properties of compounds 4–7

Compds	T_{dec}^a (°C)	N^b (%)	ρ^c (g cm $^{-3}$)	HOF e (kJ mol $^{-1}$)	VOD f (m s $^{-1}$)	DP g (GPa)	OB h (%)	IS i (J)	FS j (N)
4	177	28.10	1.80/1.90 d	−466.14	6423	16.38	−54.59	35	288
5	170	29.79	1.72	−380.67	7144	20.31	−51.04	40	360
6	224	45.16	1.70	97.59	6936	17.54	−69.44	40	360
7	202	40.00	1.74/1.77 d	−261.31	7140	18.60	−68.53	50	360
Ck	78	29.0	1.90	−515	7497	24.4	−43.46	35	360
Dl	275	25.4	1.69	−1007	6429	13.68	−155.41	45	—
PYXm	357	24.80	1.76	43	7448	24.20	−55.37	10	360
TNTm	300	18.49	1.65	−59.3	6820	19.50	−73.79	15	353

a Onset thermal decomposition temperature in a nitrogen environment at 5 °C min $^{-1}$. b Percentage of nitrogen. c Gas pycnometer density at RT. d Crystal density at 100 K. e Computed heat of formation (solid). f Detonation velocity. g Detonation pressure. h Oxygen balance. i Impact sensitivity. j Friction sensitivity. k Ref. 23. l Ref. 24. m Ref. 30.

The densities of compounds 4–7 range from 1.70 to 1.80 g cm $^{-3}$, which are better than that of TNT (1.65 g cm $^{-3}$).

The heats of formation (HOF) were determined through the Gaussian (G4) composite method and the isodesmic reaction approach using the Gaussian 09 software suite.²⁸ As shown in Table 1, among all the compounds, **6** (97.59 kJ mol $^{-1}$) possesses a positive HOF due to a high energy contribution from the TATOT cation that surpasses that of the benchmark explosives TNT (−59.3 kJ mol $^{-1}$) and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX, 43 kJ mol $^{-1}$). The negative HOFs in compounds **4**, **5**, and **7** arise due to the −CF $_3$ group. With the measured densities and HOFs, the detonation properties, such as detonation velocity (VOD) and detonation pressure (DP), were calculated using EXPLO5 (version 7.01.01) software.²⁹ Compounds 4–7 show VODs of 6423, 7144, 6936, and 7140 m s $^{-1}$ and DPs of 16.38, 20.31, 17.54, and 18.60 GPa, respectively. Among all the compounds, compounds **5** (VOD = 7144 m s $^{-1}$) and **7** (VOD = 7140 m s $^{-1}$) possess better detonation velocities than TNT (6820 m s $^{-1}$). The impact sensitivities (IS) and friction sensitivities (FS) of all the compounds were measured using a BAM fall hammer and a friction tester. The impact sensitivities (IS) for all the newly synthesized compounds are in the range of 35–50 J and the friction sensitivities are >360 N, except for compound **4**, which indicates that they are highly insensitive towards impact and friction. These tests provide essential information about their low susceptibility to accidental detonation and support the low hazard level during preparation, storage, handling, and transportation procedures. Hirshfeld surfaces provide a comprehensive analysis to visualize and quantify intermolecular interactions, close contacts, packing efficiencies, and the percentage of interactions within the molecule. As shown in Fig. 4 and 5, for compounds **4** and **7**, the red colour indicates high strength close contacts, the white colour shows van der Waals distances, and the blue colour indicates longer contacts. Compared to compound **4**, the presence of more red spots on the Hirshfeld surface of compound **7** signifies robust hydrogen bonding interactions. The percentage of total molecular interactions N⋯H, O⋯H and F⋯H is 26% in the case of **4** and 56% in the case of **7**. The contribution of hydrogen bond interactions (O⋯H, N⋯H, and F⋯H) in compound **7** is high, emphasizing their predominant

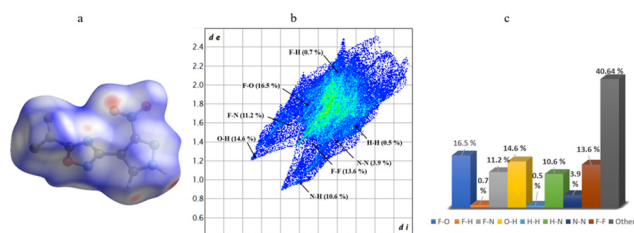


Fig. 4 (a) Hirshfeld surface, (b) 2D fingerprint plot, and (c) bar chart showing different interactions in compound **4**.

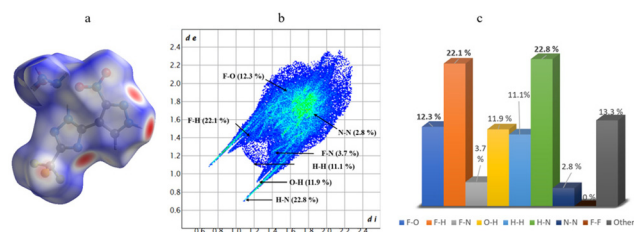


Fig. 5 (a) Hirshfeld surface, (b) 2D fingerprint plot, and (c) bar chart showing different interactions in compound **7**.

role in fortifying the compound's high thermal stability and insensitivity to impact. Similarly, the sum of F⋯N, F⋯O, and F⋯F interactions is 41% in the case of compound **4**, while it is 16% for compound **7**. The substantial prevalence of such interactions renders compound **4** more susceptible to external stimuli and lowers the stability.

Conclusions

This work validates the straightforward synthesis of a trifluoromethyl (−CF $_3$) group substituted C–C bonded five-membered pyrazole ring with oxadiazole and triazole moieties. An interesting transformation took place from the oxadiazole ring of compound **4** to the formation of a new triazole ring using ANRORC rearrangement, which will be highly useful for preparing many such new molecules. All the synthesized com-

pounds showed good density (1.70–1.80 g cm⁻³), moderate VOD (6423–7144 m s⁻¹) and DP (16.38–20.31 GPa), good thermal decomposition (170–224 °C) and excellent insensitivity toward impact (IS > 35 J) and friction (FS > 288 N). The combined effect of O...H, N...H, and F...H hydrogen bond interactions has been found to effectively enhance the thermal stability and reduce the sensitivity of these compounds. The balanced energetic properties make them stable insensitive secondary explosives which can be better replacements for presently used benchmark explosives such as TNT.

Author contributions

Parasar Kumar: conceptualization, methodology, investigation, validation, formal analysis, and writing – original draft. Ramling S. Mathpati: conceptualization, methodology, investigation, validation, formal analysis, and writing – original draft. Vikas D. Ghule: software, review, and editing. Srinivas Dharavath: conceptualization, methodology, validation, supervision, funding acquisition, software, project administration, writing – original draft, and writing – review and editing. The manuscript was written through the 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

The authors declare no competing financial interest.

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