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High Thermal Stability and Insensitive Fused Triazole-Triazine Trifluoromethyl-Containing Explosives (TFX)

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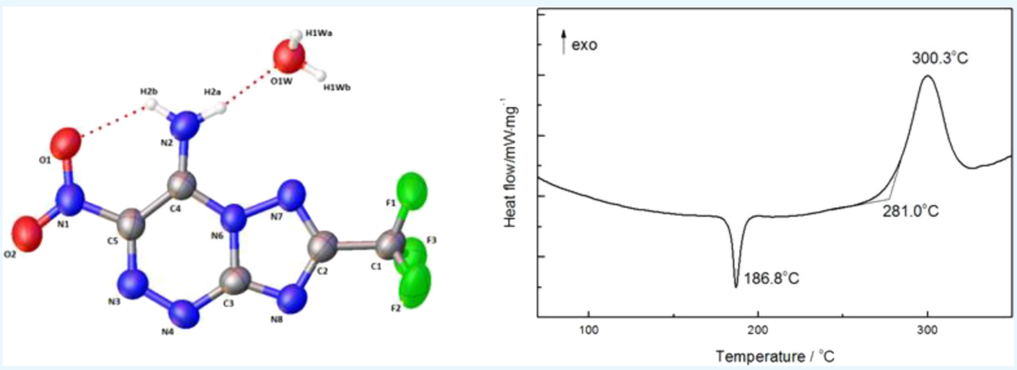

ABSTRACT: A trifluoromethyl-containing fused triazole-triazine energetic molecule, 3-nitro-7-(trifluoromethyl)-1,2,4-triazolo[5,1-*c*]-1,2,4-triazin-4-amine (TFX), has been synthesized in three steps from amino guanidine bicarbonate and trifluoroacetic acid. The process was found to be effective, nontoxic, and simple. The X-ray structure analysis of TFX finds that there are inter- and intramolecular hydrogen bonds and $\pi-\pi$ interactions in the crystal lattice. TFX with a high density (1.88 g·cm^{-3}) at room temperature, excellent thermal stability (T_p = 300.3 °C), moderate energetic performance, and with insensitivity to mechanical stimulation has potential as heat-resistant energetic materials.

■ INTRODUCTION

Energetic materials have contributed tremendously to the process and prosperity of human beings.[1−3] Apart from high performance and insensitivity, increasing thermal stability appears to be a prime goal in the evolution of next-generation energetic materials, especially in the field of heat-resistant explosives.[4−9] Relying on the nitro aromatic ring, traditional heat-resistant explosives (TATB,[10−12] HNS,[13−16] and LLM-105;[17−19] Scheme 1) are often flat molecules that display high thermal stabilities, hydrogen bonding, and $\pi-\pi$ interactions. However, they have to face many environmental issues during the process of manufacture.[4] With the development of nuclear weapons, space explorations, and deep sea missions, especially the requirements of hypersonic weapons, the exploitation of energetic materials with high thermal stability and extreme insensitivity is in great demand.[4]

Recently, the azole-azine bicycle system became an attractive backbone for energetic materials due to its planar structure and high nitrogen content. A series of derivations such as 4-amino-3,7,8-trinitropyrazolo[5,1-*c*]-1,2,4-triazine (PTX),[20] 4-amino-3,7-dinitro-1,2,4-triazole[5,1-*c*]-1,2,4-triazine (TTX),[21,22] and 3-nitro-7-(1*H*-tetrazol-5-yl)-1,2,4-triazolo[5,1-*c*]-1,2,4-triazin-4-amine[23] (Scheme 1) were synthesized with good detonation performance, moderate thermal stability, and with insensitivity. However, their thermal decomposition temperatures (T_o) are low (TTX: T_o = 232 °C; PTX: T_o = 246 °C), which is still a big challenge that needs to be addressed for application in this field.

The trifluoromethyl group (CF_3) can introduce properties into organic compounds that include high thermal stability, high chemical resistance, low surface energy, and high electronegativity.[24−27] Furthermore, the CF_3 group is more dense than the nitro group (2.25 g·cm^{-3} for $-CF_3$ vs 2.17 g·cm^{-3} for $-NO_2$).[24] Therefore, it may be an effective approach to develop novel thermally stable and insensitive energetic materials by introducing CF_3 in the energetic molecule. Within the last decades, lots of CF_3-containing energetic materials were synthesized as sources of oxidizers, explosives, and propellants (TANH-2 and TANH-4; Scheme 1).[24,25] How-

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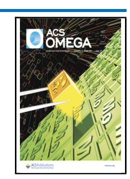
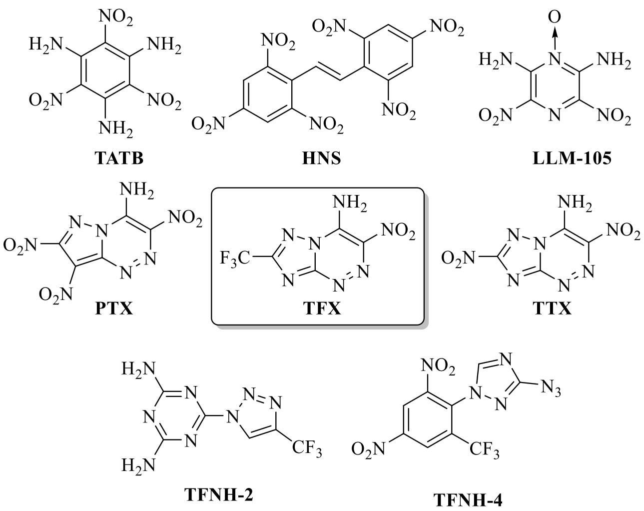


Scheme 1. Structure of PTX, TTX, and TFX



ever, the application of CF_3-containing energetic materials is limited to numerous steps of the synthesis, poor yield, and high toxicity of materials.

In this work, a new conjugated CF_3-containing energetic molecule, 3-nitro-7-(trifluoromethyl)-1,2,4-triazolo[5,1-*c*]-1,2,4-triazine-4-amino (TFX), was synthesized starting from the cyclization reaction of amino guanidine bicarbonate and trifluoroacetic acid followed by ring-expansion reaction with nitroacetonitrile. The crystal studies showed that the backbone of TFX was planar. Thermal stability, density, and sensitivity were studied. The detonation performances were calculated.

EXPERIMENTAL SECTION

Caution! Although no explosions or hazards were observed during the preparation and handling of these compounds, all the compounds investigated are potentially explosive materials. Mechanical actions involving scratching or scraping must be avoided. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times.

Materials and Instrument. A Nicolet 6700 spectrophotometer was used for Fourier transform infrared (FT-IR) spectra using a potassium bromide (KBr) matrix. Elemental analyses were performed with a VARIO-EL-3 spectrometer from Elementar. The ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature with a Bruker Advance 500 MHz spectrometer. All samples for NMR were dissolved in dimethylsulfoxide (DMSO-d_6). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) tests were conducted with a TA Instruments MDSC2910 using aluminum pans. Scans were executed at scan rates of 10 °C·min^{-1} under nitrogen flux. The crystal structure of TFX was determined by single-crystal X-ray diffraction. The data collection was performed on a Bruker APEX-II CCD X-ray diffractometer (Bruker Germany) with highly oriented graphite crystal monochromated GaK/α radiation (λ = 1.34138 nm). The crystal was kept at 150(2) K during data collection. Using Olex2,[28] the structure was solved with the XT[29] structure solution program using intrinsic phasing and refined with the XL[30] refinement package using least-squares minimization.

Synthetic Procedures. *Synthesis of 3-(Trifluoromethyl)-1H-1,2,4-triazol-5-amine (TFAT).* The compound was prepared according to an improved procedure from Boechat et al.[31] and Phillips et al.[32] Amino guanidine bicarbonate (10 g, 73.5 mmol) was suspended into 80 mL of toluene. Trifluoroacetic acid (9 mL) was added to the mixture dropwise at room temperature till effervescence ceased. The reaction mixture was refluxed for 12 h using a Dean−Stark condenser. The precipitated solid was filtered and then dissolved into 20 mL of water. The solution was neutralized with 10% sodium bicarbonate solution and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by a rotary evaporator under reduced pressure to get TFAT as a white solid (10.5 g, 93.7%). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ = 12.69 (1H, s), 6.40 (2H, s). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ = 158.03, 150.23 (q, $^2J_{C-F}$ = 37.2 Hz), 119.88 (q, $^1J_{C-F}$ = 268.8 Hz);

Synthesis of Potassium Salt of Ethyl 2-Cyano-2-nitroacetate. The compound was prepared according to a procedure reported by Voinkov et al.[33] A solution of KOH (2.8 g, 0.05 mol) in water (50 mL) was prepared. The solution of KOH was added into a solution of ethyl 2-cyano-2-(hydroxyimino)acetate (21.3 g, 0.15 mol) in water (400 mL) at room temperature. Then, $KMnO_4$ (15.8 g, 0.10 mol) was added into the reaction mixture as a solid stepwise, maintaining a temperature not higher than 40 °C. The mixture was stirred at 30 °C for 0.5 h, and then the precipitate was filtered off. The filtrate was concentrated under reduced pressure at T < 40 °C. The dry residue was washed with ethanol and recrystallized from 90% ethanol. White crystals were obtained (20.2 g, 68.7%). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ = 4.02 (2H, q), 1.16 (3H, t). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ = 162.12, 118.56, 93.82, 58.65, 15.04.

Synthesis of 3-Nitro-7-(trifluoromethyl)-1,2,4-triazolo[5,1-c]-1,2,4-triazin-4-amine (TFX). The potassium salt of ethyl 2-cyano-2-nitroacetate (1.96 g, 10 mmol) was suspended into a solution of KOH (0.56 g, 10 mmol) in water, and the mixture was stirred at 30 °C for 2.5 h. Then, the mixture was cooled below 0 °C followed by treatment of NaOAc (2.46 g, 30 mmol) to get the sodium salt of nitroacetonitrile. Meanwhile, a solution of sodium nitrite (0.76 g, 11 mmol) in water was added dropwise to a solution of TFAT (1.52 g, 10 mmol) in 3.0 M HCl (10 mL) cooled to −5 to 0 °C. The obtained white slurry was maintained below 0 °C for 0.5 h with constant stirring, resulting in the azide of TFAT. Then, the sodium salt of nitroacetonitrile was added into the azide of TFAT, maintaining a temperature below 5 °C. The resulting yellow solution was heated to 80 °C and stirred for 8 h. When cooling to room temperature, a yellow precipitate formed. The reaction mixture was filtered yielding TFX (1.92 g, 77.1%). M.p. 182 °C. IR: υ = 3462, 3340, 1664, 1648, 1570, 1516, 1490, 1412, 1381, 1335, 1291, 1255, 1233, 1212, 1181, 1141, 981, 919, 848, 779, 697, 559, 547 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ = 10.71 (1H, s), 10.00 (1H, s). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ = 156.94, 156.94 (q, $^2J_{C-F}$ = 39.6 Hz), 140.41, 138.97, 119.13 (q, $^1J_{C-F}$ = 271.3 Hz). Elemental analysis calculated (%) for $C_5H_2F_3N_7O_2$: C 24.11, H 0.81, N 39.36; found: C 24.18, H 0.88, N 39.45. The theoretical absolute mass of $C_5HF_3N_7O_2$ was calculated to be 248.01493. The m/z value measured from HRMS was 248.01443.

RESULTS AND DISCUSSION

TFX was synthesized starting from amino guanidine and bicarbonate and trifluoroacetic acid (Scheme 2). Since the

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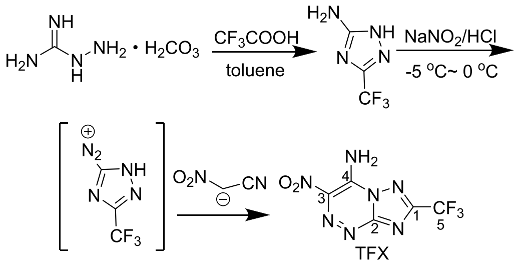
Scheme 2. Synthesis of Compound TFX



structure of TFX was similar to TTX,[21] their ^{1}H NMR and ^{13}C NMR were compared. In contrast with a broad peak at 10.45 ppm for TTX, ^{1}H NMR of $-NH_2$ in TFX showed two peaks at δ = 10.71 and 10.00 ppm. The reason may be the conjugation between the nitrogen atom and fused conjugated structure. In addition, the intramolecular hydrogen bond between $-NH_2$ and adjacent $-NO_2$ may lead to different chemical shifts. In the ^{13}C NMR spectrum of TFX, the carbon atoms (C1−C4) in the 1,2,4-triazolo[5,1-*c*]-1,2,4-triazine backbone appeared at δ = 156.94, 156.94, 140.41, and 138.97, respectively, which were consistent with those of TTX.[21] The signal corresponding to carbon C5 of the trifluoromethyl group was observed at 119.3 ppm. Due to the coupling effect of fluorine atoms, the signals of C4 and C5 were split into quartet peaks with coupling constants of 271.3 and 39.6 Hz, respectively. The high-resolution mass spectrum of TFX had a quasi-molecular ion $[M-H]^-$ at 248.01443, corresponding to the expected chemical formula of $C_5H_2F_3N_7O_2$.

Suitable crystals for single-crystal X-ray diffraction were obtained from the solution of TFX in methanol/water (1:1). The crystallographic data in CIF of TFX·H_2O are available in the Supporting Information. The details of data collection and refinement are given in Table 1. As can be seen from Figure 1a, TFX crystallizes as a H_2O adduct (TFX·H_2O) in the orthorhombic space group $P2_12_12_1$ with four formula units per unit cell (Z = 4) and a crystal density of 1.868 g·cm^{-3} at 150 K. The amino group (N2) and nitro group (N1) were essentially held co-planar with the bicyclic system, with torsional angles between the mean plane through the triazolo-triazine system and amino group (∠N1−C5−C4−N2) and nitro group (∠O1−N1−C5−C4) of 3.46 and −1.15°, respectively (Figure 1b).

In the packing diagram of Figure 2a, strong intramolecular N−H···O hydrogen bonds (N2−H2b···O1) were formed between the adjacent amino and nitro group with a distance between H2b and O1 of 2.09 Å. In the meantime, intermolecular hydrogen bonds (N2−H2b···F1) were also observed between the amino and trifluoromethyl group. As can be seen from Figure 2b, the crystal packing of TFX showed four molecular stacking plane orientations, which were similar to PTX (Figure 2).[20] This showed the molecular stacking planes that resulted from the $\pi-\pi$ interaction with an interplanar distance of 3.09 Å, which was smaller than PTX (3.45 Å). The density of TFX was lower than PTX (1.946 g·cm^{-3}). The reason may be the steric hindrance effect of the trifluoromethyl group. The mixed molecular stacking caused by four orientations prevented interlayer sliding within the crystal lattice. Interlayer sliding within a crystal lattice is a feature that contributes to the insensitivity of TATB and DAAF, which have graphite-like stacking that allow such sliding.[4,20] Hence, the steric hindrance effect of the trifluoromethyl group may

Table 1. Crystal Data and Structure Refinement for TFX

	TFX
empirical formula	$C_5H_2F_3N_7O_2 \cdot H_2O$
CCDC number	1998452
formula weight	267.15
temperature (K)	150(2)
crystal system	orthorhombic
space group	$P2_12_12_1$
a (Å)	5.2854(14)
b (Å)	12.560(3)
c (Å)	14.308(4)
α (°)	90
β (°)	90
γ (°)	90
volume (Å^3)	949.8(4)
Z	4
T (K)	150(2)
P_{calc} (mg·mm^3)	1.868
F [0 0 0]	536
2θ range for data collection (°)	8.16−106.26
index ranges	$-6 \le h \le 6, -11 \le k \le 14, -8 \le l \le 17$
reflections collected	3606
independent reflections	1613 [R_{int} = 0.0526]
goodness-of-fit on F^2	1.105
final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0713, wR_2 = 0.2058
final R indexes [all data]	R_1 = 0.0741, wR_2 = 0.2129
largest diff peak and hole (e·Å^{-3})	0.36/−0.37

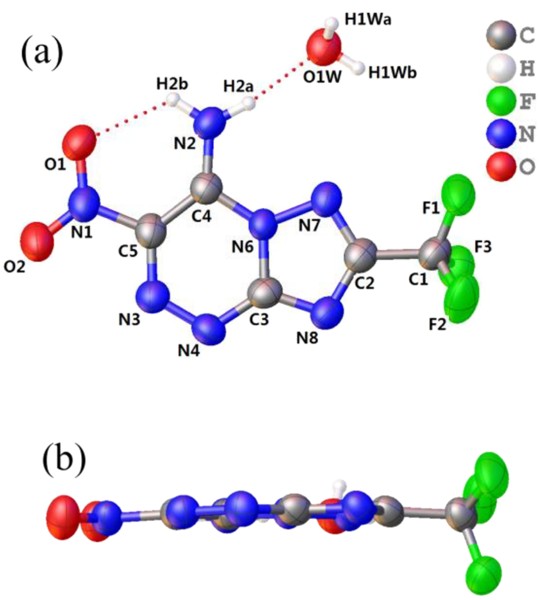


Figure 1. (a) Molecular structure and labeling for TFX·H_2O. (b) Edge view showing the planarity of the backbone of TFX·H_2O.

increase the mechanical sensitivity of TFX. However, with the help of hydrogen bonds and $\pi-\pi$ interactions, TFX is insensitive.

Thermal stability is important for energetic materials as the military explosives that can withstand high temperature. The DSC and TG-DTG measurements were applied to analyze the thermal stability of TFX. The DSC curve indicated that the thermal behavior of TFX could be divided into two stages (Figure 3). The first stage showed a sharp endothermic peak, which was a melting process. The peak temperature and melting enthalpy were 186.8 °C and −87.11 J·g^{-1}, respectively.

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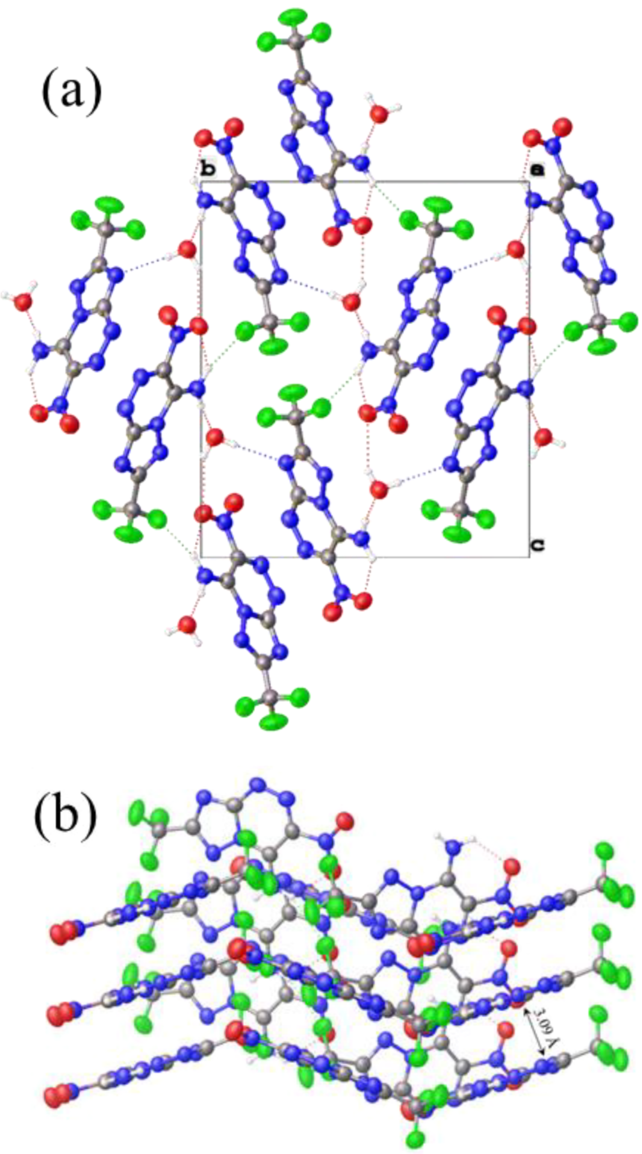

Figure 2. (a) Molecular packing diagram of TFX·H_2O along the *a* axis (dash lines indicated hydrogen bond interactions). (b) Crystal packing of TFX showing molecular stacking planes (H_2O was omitted for clarity).

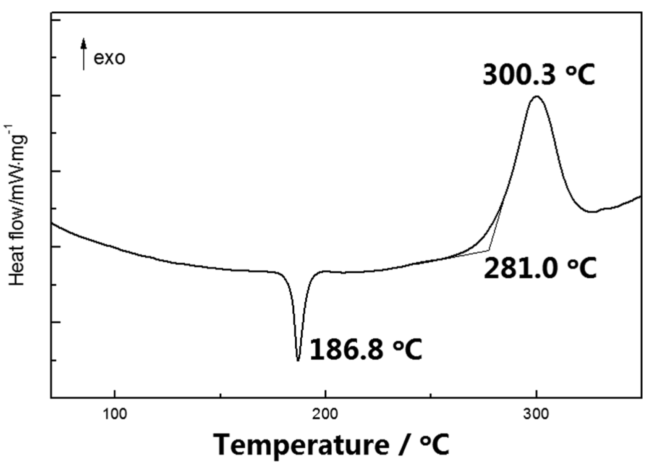

Figure 3. DSC curve of TFX.

The second stage was an exothermic decomposition process, while the extrapolated onset temperature (T_o) and peak temperature (T_p) were 281.0 and 300.3 °C, respectively. The decomposition enthalpy of the process was 538.5 $J{\cdot}g^{-1}$. The results demonstrated that TFX can exist steadily at high temperature. The T_p of TFX was higher than those of TTX (T_p = 232 °C)[21,22] and PTX (T_p = 288 °C),[20] indicating that the hydrogen bonds of the trifluoromethyl group indeed improve the thermal stability. The trigger bond dissociation enthalpy (TBDE), which represents the lowest energy to break the first bond during thermal decomposition, was investigated to explain the thermal behavior of TFX. The TBDE value of TFX is 276.3 $kJ{\cdot}mol^{-1}$, which is a little lower than that of TATB (287.2 $kJ{\cdot}mol^{-1}$) and higher than those of LLM-105 (251.7 $kJ{\cdot}mol^{-1}$) and PTX (246.4 $kJ{\cdot}mol^{-1}$).

The TG curve of TFX showed that the mass loss was only 0.97% from 50 to 187 °C, which demonstrated that the first stage of the DSC curve was the melting process. It was shown that the decomposition of TFX began at 281.0 °C, and there was a sudden drop in the weight at 302.7 °C (Figure 4). The mass loss arrived at 100% when the temperature was 362 °C. The peak temperature on the derivative thermogravimetric (DTG) curve coincided with that on the DSC curve, which means that TFX did not evaporate before its decomposition. It was worth noting that the decomposition residue of TFX was −20% when the temperature reached 550 °C. The reason may be the reaction that occurred between the aluminum crucible and TFX.

TFX had a good density of 1.88 $g{\cdot}cm^{-3}$, as measured by a gas pycnometer. The heat of formation (HOF) of TFX was determined by the Gaussian09 program.[34] Based on the values of the density and HOF, detonation properties were calculated by the Kamlet−Jacobs equation.[35−37] These data were compared to previously reported CF_3-substituted nitrogen heterocycle energetic materials (Scheme 3). The results are listed in Table 2.

The molecules bearing the CF_3 group showed negative HOFs owing to the presence of F atoms. The HOF of TFX was −184.74 $kJ{\cdot}mol^{-1}$. The introduction of the fused nitrogen heterocycle backbone increases the energy of the molecules, leading to an enhanced HOF. Benefitting from the fused triazole-triazene heterocycle, the density of TFX was higher than the CF_3-substituted endocyclic compounds (Table 2). It was indicated that the fused triazole-triazene heterocycle was an effective backbone that contributes to high density energetic compounds.

TFX showed good thermal stability (T_p > 300 °C). The detonation properties revealed that TFX exhibited better detonation performance than the normal CF_3-substituted energetic compounds and HNS (Table 2). TFX can be useful as high thermal stability fluorine-containing explosives. The detonation properties of TFX were lower than those of TTX (D = 8580 $m{\cdot}s^{-1}$ and P = 31.2 GPa). The contrastive analysis showed that the presence of the trifluoromethyl group was beneficial to thermal stability and density, nevertheless depressed the detonation properties of compounds. In pursuit of fluorine-containing energetic compounds with high detonation properties and thermal stability, we would attempt to turn the amino group into the nitro group or turn the trifluoromethyl group into the fluorodinitromethyl group in the future.

The impact sensitivity (IS) and fraction sensitivity (FS) of TFX were also characterized to evaluate safety by a BAM drop

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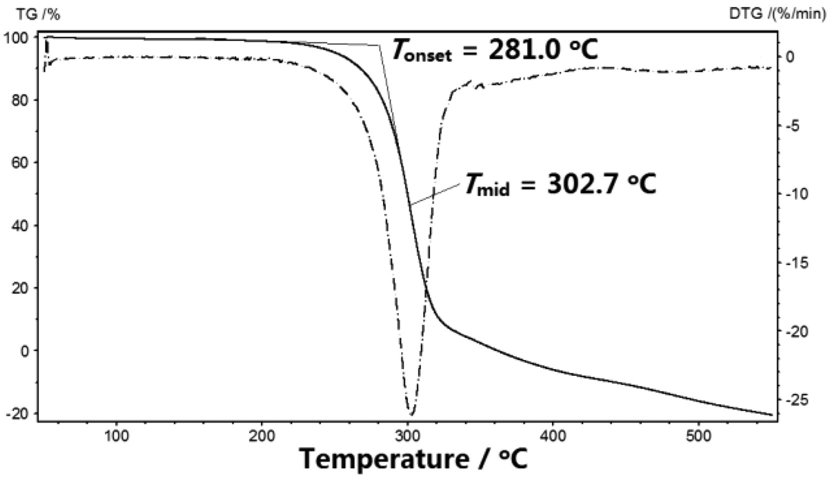
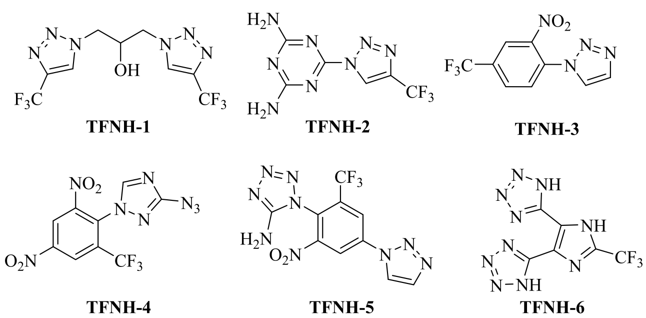


Figure 4. TG-DTG curves of TFX.

Scheme 3. CF_3-Containing Nitrogen Heterocyclic Energetic Compounds (TFNH)



hammer apparatus and BAM friction tester, respectively. Surprisingly, TFX was insensitive to both impact and friction (IS: >45 J; FS: > 360 N), which were lower than those of PTX. The presence of intermolecular hydrogen bonding of CF_3 could account for lower sensitivity, despite the lack of interlayer sliding in the crystal lattice.

■ CONCLUSIONS

In summary, a new trifluoromethyl-containing, highly stable, and insensitive fused triazole-triazine energetic material, TFX, was synthesized in three steps. Given the high thermal stability, moderate detonation performance, and low sensitivity, TFX has potential application in heat-resistant energetic materials. This work provides new insight for the development of F-containing thermally stable insensitive energetic compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01018.

The crystallographic data in CIF of TFX·H_2O (CIF)

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Table 2. Detonation and Safety Properties of CF_3-Containing Nitrogen Heterocyclic Energetic Compounds and HNS

compounds	N^a (%)	D^b (g·cm^{-3})	HOF^c (kJ·mol^{-1})	HOF^c (kJ·g^{-1})	$T_p{}^d$ (°C)	D^e (m·s^{-1})	P^f (GPa)	IS^g(J)	FS^h(N)
TFX	39.36	1.88	−184.7	−0.74	300.3	7492	26.4	>45	>360
TANH-1	25.45	1.69	−1006.9	−3.05	275	6429	13.68	>45	-[i]
TANH-2	45.52	1.68	−251.5	−1.02	290.6	6879	15.39	>45	-[i]
TANH-3	21.70	1.62	−266.5	−1.03	237	6252	16.67	-[i]	-[i]
TANH-4	32.56	1.80	−71.8	−0.21	213	7279	23.47	-[i]	-[i]
TANH-5	36.95	1.68	100.4	0.29	261	6552	18.22	-[i]	-[i]
TANH-6	51.47	1.80	90.3	0.33	271	6866	20.9	-[i]	-[i]
HNS	18.67	1.74	−58.2	−0.13	316	7019	-[i]	5	240

[a]Nitrogen content. [b]Density. [c]Calculated heat of formation. [d]Thermal decomposition temperature (determined by the DSC exothermal peak, 10 °C·min^{-1}). [e]Calculated detonation velocity. [f]Calculated detonation pressure. [g]Impact sensitivity. [h]Friction sensitivity. [i]Not available in the original literature.

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Notes

The authors declare no competing financial interest.

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