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Intriguing Fluorine Effect：An Important Factor for Effective Construction Insensitive Energetic Materials

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Abstract：The compound 5，7-bis(trifluoromethyl)-2-(dinitromethyl)-[1，2，4]triazolo[1，5-*a*]pyrimidine（**1**）was designed，synthesized，and thoroughly characterized. Thermal properties were determined using Differential Scanning Calorimetry（DSC），while Gaussian 03 and EXPLO5 v6.05 programs were employed to calculate the heat of formation and detonation properties of compound **1**，respectively. In addition，a comparative analysis of Hirschfeld surface，2D fingerprint and electrostatic potentials（ESP）was conducted between compound **1** and other known dinitromethyl-containing compounds in this study. The result demonstrate that compound **1** exhibits exceptional insensitivity（IS > 40 J，FS > 360 N）toward external stimuli compared to other dinitromethyl-containing compounds. Furthermore，the presence of halogen bonding（C—F···X）effectively disrupts the formation of O···O interactions in energetic materials and leads to a favourable distribution of electrostatic potentials. This finding provides valuable insights for the development of novel insensitive energetic materials.

Key words：energetic materials；insensitive explosive；dinitromethyl；halogen bonding；weak interactions

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0 Introduction

Nitrogen-rich high-energy density materials（HEDMs）have been extensively utilized in both defense and civil fields[1]. Over the past few decades，researchers in this field have dedicated their efforts to discovering novel energetic compounds with high density，exceptional detonation performance，excellent thermal stability and low sensitivity[2-6]. The synthesis strategy for nitrogen-rich energetic materials involves the combination of nitrogen-rich heterocyclic rings with energetic units. Commonly used nitrogen-rich heterocyclic rings include pyrazole，triazole，and tetrazole，which contribute to a high enthalpy of formation for energetic materials[7]. Incorporating high-energy nitrogenous groups such as $—NO_2$，$—NHNO_2$，$—N_3$，$—CH(NO_2)_2$，and $—C(NO_2)_3$ can enhance the detonation performance of compounds[8-9].

Dinitromethyl（$—CH(NO_2)_2$）is a highly effective functional group for enhancing the density and improving the oxygen balance of energetic materials[10-13]. However，dinitromethyl-containing heterocyclic compounds，primarily composed of dinitromethyl and pyrazole，triazole，tetrazole rings or fuse rings，exhibit poor stability towards external

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stimuli[14-19]. For instance, in 2023, Pang's group[17] reported the synthesis and performance of 7-(dinitromethyl)-3-nitro-[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4-amine featuring adjacent nitro and amino groups (*o*—NH$_2$—NO$_2$); however its sensitivity (*IS*=30 J; *FS*=252 N) did not meet the standards of insensitive explosives (*IS*>40 J; *FS*>360 N). Therefore, it is crucial to explore key parameters that affects the sensitivity of dinitromethyl energetic materials[20].

In recent years, several research groups have identified that incorporating fluorine atoms or fluorine-containing groups into energetic materials is a reliable method for enhancing sensitivity performance[21]. For instance, compound 3-(dinitromethyl)-5-(trifluoromethyl)-1*H*-1, 2, 4-triazole demonstrates significantly improved insensitivity (*IS*=35 J; *FS*>360 N) compared to 5-(dinitromethyl)-3-(trinitromethyl)-1,2,4-triazole(*IS*=6 J; *FS*>120 N)[22] and compound 1-(dinitromethyl)-3-nitro-1*H*-1,2,4-triazole (*IS* =7 J; *FS*>252 N)[15]. Moreover, the sensitivity of compound 3-Nitro-7-(trifluoromethyl)-1, 2, 4-triazolo[5, 1-*c*]-1, 2, 4-triazine-4-amino[23] surpasses that of DPX-26[24] (*IS*=29 J; *FS*>360 N), with an even higher insensitivity value (*IS*>45 J; *FS*>360 N). In our recent study conducted in 2022, we presented an insensitive explosive named as 3-trifluoromethyl-6-nitroguanyl-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine which exhibits exceptional insensitivity (*IS*>60 J; *FS*>360 N)[25].

Based on the aforementioned studies, this study present here the synthesis of 5,7-bis(trifluoromethyl)-2-(dinitromethyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**1**). The thermal stability, sensitivity and detonation performance of compound **1** were assessed through experimental measurements and computational predictions. Furthermore, elucidating the relationship between the trifluoromethyl group and sensitivity was achieved by employing techniques such as single-crystal X-ray diffraction analysis, Hirschfeld surface analysis, two-dimensional fingerprint plot analysis and electrostatic potential calculations. These findings provide novel insights for future development and design of energetic materials containing dinitromethyl groups.

1 Experimental section

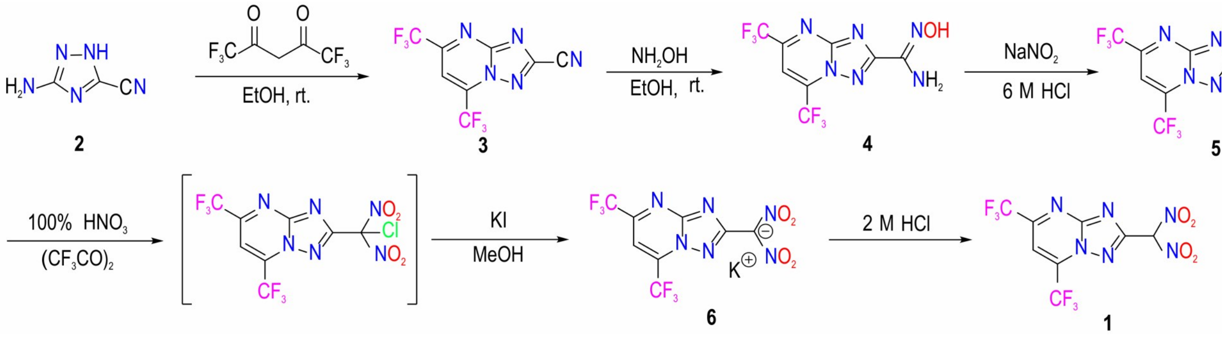
1.1 Chemicals and experimental equipments

Chemicals: Analytical purity 3-amino-1,2,4-triazole-5-carboxylic acid, thionyl chloride, ammoniumhydroxide solution (25%-28% in water), phosphorus pentoxide, 1, 1, 1, 5, 5, 5-hexafluoropentane-2,4-dione, hydroxylamine (50% in water), sodium nitrite, trifluoroacetic anhydride, potassium iodide, ethanol, acetonitrile and methanol were bought from energy-chemical. Hydrochloric acid (2 M and 6 M) and nitric acid (100%) were prepared in our laboratory.

Experimental equipments: Impact sensitivity measurements, HWP18-30S, Young Instruments. Friction sensitivity measurements, HWP17-10S, Young Instruments. Gas pycnometer, AccuPyc II 1345, Micromeritics. Differential scanning calorimeter, DSC-25, TA Instruments. Cube Organic elemental analyzer, elementar vario MACRO, Elementar.

1.2 Synthesis route

The trifluoromethyl-substituted energetic material, **1**, was synthesized following the procedure outlined in Scheme 1. Starting from the previously re-



Scheme 1 Preparation route of compound 1

ported literature[26], 5-amino-1*H*-1, 2, 4-triazole-3-carbonitrile (**2**) was synthesized. Compound **2** underwent a reaction with 1, 1, 1, 5, 5, 5-hexafluoropentane-2, 4-dione in H_2O to afford compound **3** with a yield of 71%. Subsequently treating compound **3** with 50% hydroxylamine yielded compound **4** which was further converted to hydroximoyl chloride **5** through diazotization using 50% HCl. Nitrating compound **5** with a mixture of trifluoroacetic anhydride (TFAA) and 100% HNO_3, followed by treatment with KI in methanol resulted in the formation of potassium salt **6**, obtained as a light yellow solid. Finally, compound **1** was obtained through an acidification reaction using 2 M HCl from compound **6**.

1.3 Experimental process

1.3.1 Synthesis of 5,7-bis(trifluoromethyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine-2-carbonitrile (3)

Compound **2** (0.5 g, 4.58 mmol) and 1,1,1,5,5,5-hexafluoro-pentan-2,4-dione (0.96 g, 4.65 mmol) were stirred in distilled water (10 mL) and few drops of concentrated hydrochloric acid were added at room temperature to maintain pH ~ 2. The resulting mixture was stirred at 80 ℃ for 8 h. After cooling to room temperature, needle-like crystals of compound **3** were collected as a white solid (0.91 g, 71%). ^{1}H NMR (600 MHz, DMSO-d_6, 25 ℃) δ: 8.87(s, 1H, CH); ^{13}C NMR (151 MHz, DMSO-d_6, 25 ℃) δ: 155.1, 154.2 (q, J = 38.1 Hz), 143.3, 137.6 (q, J = 40.2 Hz), 120.0 (q, J = 276.6 Hz), 118.6 (q, J = 275.3 Hz), 112.0, 109.8; IR (KBr, v/cm^{-1}): 3623(m), 3093(m), 2917(m), 1527(s), 1451(s), 1395(s), 1321(s), 1264(vs), 1165(vs), 1102(s), 1020(s), 877(s), 739(m), 682(s), 480(m); Anal. calcd for $C_8HF_6N_5$: C 34.18, H 0.36, N 24.91; Found C 34.32 , H 0.45, N 24.76.

1.3.2 Synthesis of 5,7-bis(trifluoromethyl)-*N*′-hydroxy-[1, 2, 4]triazolo[1, 5-*a*]pyri-midine-2-carboxamidine (4)

50% Hydroxylamine solution(0.132 g, 2.0 mmol) was added into a flask containing compound **3** (0.56 g, 2.0 mmol) and ethanol (5 mL). The resulting mixture was stirred at room temperature for 8 h. After filtering, **4** was obtained as a yellow solid (0.35 g, 56%). ^{1}H NMR (600 MHz, DMSO-d_6, 25 ℃) δ: 10.43 (s, 1H, OH), 8.50 (s, 1H, CH), 6.05(s, 2H, NH_2); ^{13}C NMR (151 MHz, DMSO-d_6, 25 ℃) δ: 162.4, 155.3, 151.2(q, J=37.3 Hz), 144.3, 136.6 (q, J = 39.5 Hz), 120.4 (q, J = 275.7 Hz), 118.9 (q, J = 275.3 Hz), 107.1; IR (KBr, v/cm^{-1}): 3926(m), 3438(vs), 2996(s), 2911(s), 2331(s), 2094(m), 1994(m), 1657(s), 1432(s), 1312(s), 1198(m), 1156(m), 1040(vs), 953(s), 700(s), 669 (m) , 592 (m) ; Anal. calcd for $C_8H_4F_6N_6O$: C 30.95, H 1.28, N 26.75; Found C 30.83, H 1.27, N 27.02.

1.3.3 Synthesis of 5,7-bis(trifluoromethyl)-(chloro(hydroxyimino)methyl)-[1, 2, 4]triazolo[1, 5-*a*]pyrimidine-2-carboxamidine (5)

Compound **4** (1.16 g, 3.7 mmol) was dissolved in 6 M hydrochloric acid solution (14.8 mL). A solution of sodium nitrite (0.644 g, 9.3 mmol) and water (3.7 mL) were added dropwise. The temperature was maintained below 0 ℃ and the flask was stirred for 0.5 h. Then the flask was allowed to remain at ambient temperature for 8 h. Upon filtering, **5** was obtained as a white solid (0.91 g, 74%). ^{1}H NMR (600 MHz, DMSO-d_6, 25 ℃) δ: 13.46 (s, 1H, OH) , 8.60 (s, 1H, CH) ; ^{13}C NMR (151 MHz, DMSO-d_6, 25 ℃) δ: 161.7, 155.6, 152.2 (q, J = 37.6 Hz), 137.0(q, J = 39.4 Hz), 128.3, 120.3(q, J=276.0 Hz), 118.8(q, J=275.1 Hz), 107.7; IR (KBr, v/cm^{-1}): 3439(vs), 2249(s), 2123(s), 1656(s), 1508(m), 1401(m), 1326(m), 1275(s), 1203(s), 1163(s), 1050(vs), 1030(vs), 822(s), 761 (s) , 620 (s) ; Anal. calcd for $C_8H_2ClF_6N_5O$: C 28.81, H 0.60, N 21.00; Found C 28.72, H 0.56, N 21.34.

1.3.4 Synthesis of 5,7-bis(trifluoromethyl)-2-(dinitromethyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (1)

Compound **5** (2.30 g, 6.9 mmol) dissolved in $CHCl_3$ (25 mL) was added dropwise to a stirred mixture of trifluoroacetic anhydride (10.3 mL) and 100% HNO_3 (6 mL), while maintaining the reaction temperature between −5 ℃ and 0 ℃. After the addition was completed, the ice bath was removed, and the mixture was allowed to warm slowly to room temperature and stirred for 2 h. Then the mixture was poured into ice water (60 mL) and extracted with $CHCl_3$ (3×30 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and then concentrated under vacuum to provide the intermediate as a light green solid.

The intermediate was dissolved in methanol (20 mL), to which a solution of potassium iodide (2.29 g, 13.8 mmol) in methanol (30 mL) was added dropwise. The mixture was stirred overnight at room temperature. The precipitate formed was collected by filtration and washed with cold water (3 mL), then methanol (3 mL), and ethyl ether (10 mL) to give **6** (1.64 g, 66.2%) as a light yellow solid. This compound was used directly without further characterization.

The compound **6** (0.80 g, 2 mmol) was added into a 2 M HCl (10 mL) solution. The flask was stirred for 30 min at room temperature. The mixture was extracted with EtOAc (15 mL) three times, dried over Na_2SO_4 and concentrated under reduced pressure. Compound **1** was isolated as a yellow solid (0.68 g, 94%). ^{1}H NMR (600 MHz, DMSO-d_6, 25 ℃) δ: 8.42 (s, 1H, CH), 6.63 (s, 1H, $CH(NO_2)_2$); ^{13}C NMR (151 MHz, DMSO-d_6, 25 ℃) δ: 163.2, 154.8, 151.0 (q, J=37.2 Hz), 136.4 (q, J=39.1 Hz), 126.9, 120.4 (q, J=275.9 Hz), 119.0 (d, J=274.8 Hz), 107.0; IR (KBr, v/cm^{-1}): 2995(m), 1770(s), 1758(s), 1373(m), 1245(vs), 1054(m), 667(m); Anal. calcd for $C_8H_2F_6N_6O_4$: C 26.68, H 0.56, N 23.34; Found C 26.74, H 0.73, N 23.06.

1.4 Characterization

The saturated solution of compound **1** was prepared using methanol as the solvent, and the single crystal was obtained through volatilization at room temperature. A single crystal of 0.150 mm×0.130 mm×0.110 mm was selected and placed on the SuperNova single crystal diffractometer using CuKα (λ = 0.71073 Å) as the ray source. The single crystal diffraction data were collected at 149.99(10) K. Using shell XT and Shell 2017 program[27], the atoms were refined and the crystal cell structure was optimized.

The thermal properties of compound **1** were investigated by employing differential scanning calorimetry (DSC) with a heating rate of 5 ℃·min^{-1}. The theoretical enthalpy of formation of compound **1** was calculated by utilizing the B3LYP group and the density functional theory. EXPLO5 (V6.05)[28] was employed to calculate the detonation velocity and detonation pressure of compound **1**.

According to BAM test standard[29], the impact sensitivity and friction sensitivity of compound **1** were tested under the corresponding test conditions: (30±1) mg, drop weight 10 kg, ambient temperature 10−35 ℃, relative humidity not more than 80%.

2 Results and Discussion

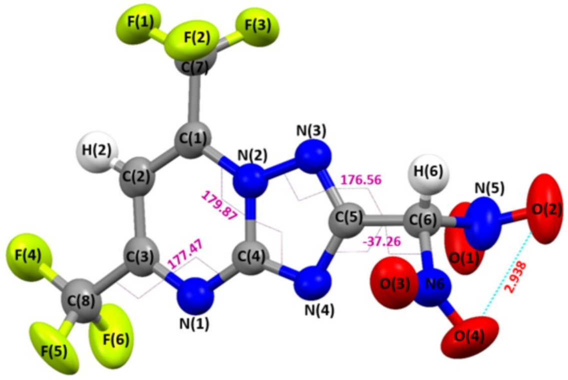
2.1 Crystal structure analysis

Compound **1** crystallizes from methanol at room temperature adopting an orthorhombic space group (*Pbca*) with *Z*=4 (Fig.1), and its crystal density is 1.799 g·cm^{-3} at 149.99(10) K. The structure of fused-ring has good coplanarity, which can be verified by the torsion angles of C(1)—N(2)—C(4)—N(4) (179.87°), C(8)—C(3)—N(1)—C(4) (177.47°) and C(6)—C(5)—N(3)—N(2) (176.56°). However, the dinitromethyl group is not planar with the fused-ring, and the corresponding dihedral angle N(4)—C(5)—C(6)—N(6) is −37.26°. An intramolecular O⋯O interaction could be observed from O(2) to O(4) (2.938 Å). Each molecule interacts with eight other molecules through three hydrogen bonding (2.172−2.183 Å) and six C—F⋯O/N/F halogen bonding (2.779−3.208 Å). Under the influence of intermolecular hydrogen and halogen bonding, this compound adopts a cross-stacking arrangement. Evidently, the dinitromethyl group in compound **1** is encompassed by trifluoromethyl group from neighbouring molecules, as depicted in the crystal stacking diagram (Fig.1c).

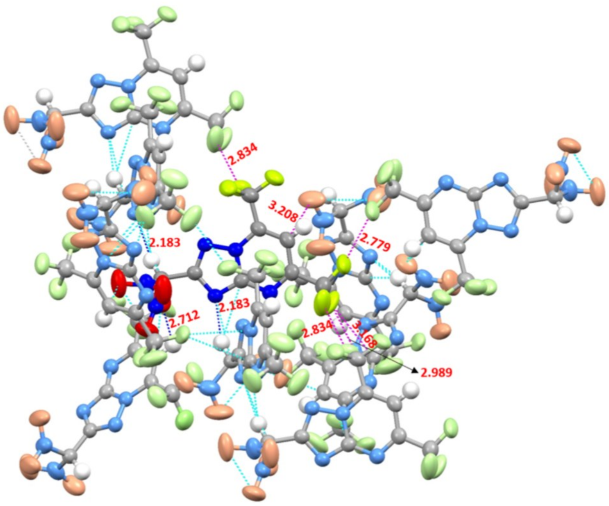
2.2 Physicochemical and energetic properties

The thermal properties of compound **1** were surveyed using TG-DSC with a heating rate of 5 ℃·min^{-1}.

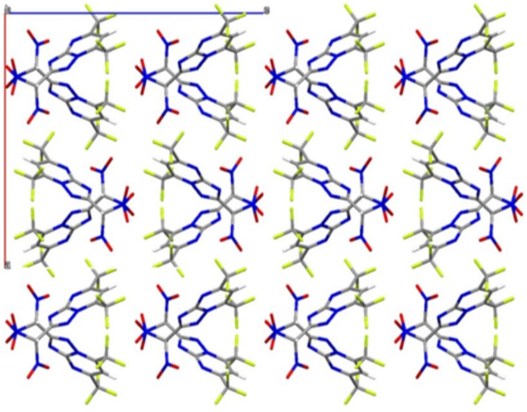
Compound **1** displays an onset decomposition temperature at 122.0 ℃(Fig.2). The measured density for **1** is 1.791 g·cm^{-3}. The heat of formation was determined using isodesmic reactions (see as Scheme S1 in Supporting Information) and Gaussian 03 software[30]. Due to the presence of trifluoromethyl groups, compound **1** exhibits a negative heat of formation with −415.67 kJ·mol^{-1} (−1.15 kJ·g^{-1}).



a. molecular structure



b. intermolecular weak interactions



c. packing diagram viewed up the *b* axis

Fig.1 Molecular structure, intermolecular weak interactions and packing diagram of compound **1**

Based on the above density and enthalpy of formation, the detonation performances of compound **1** were calculated using EXPLO5 (v 6.05)[28]. As shown in Table 1, the theoretical detonation velocity and pressure were 6748 m·s^{-1} and 20.4 GPa, respectively. These values are close to those of known explosives such as TNT and Pb(N$_3$)$_2$[18]. The sensitivities towards external stimuli including impact and friction were determined using BAM technology[29]. Compound **1** exhibits good sensitivity performance (*IS* > 40 J, *FS* > 360 N), surpassing that of TNT[18] (*IS* > 15 J, *FS* > 353 N).

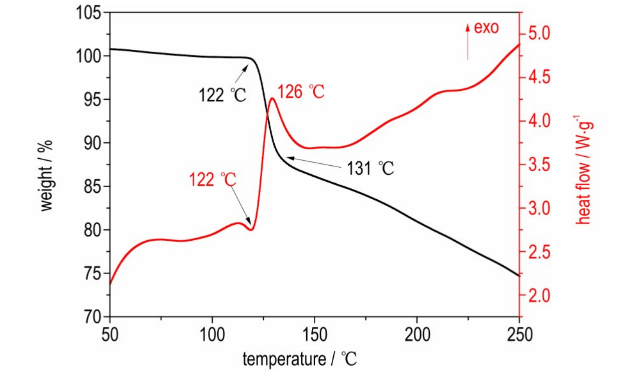


Fig.2 TG-DSC curves of compound **1**

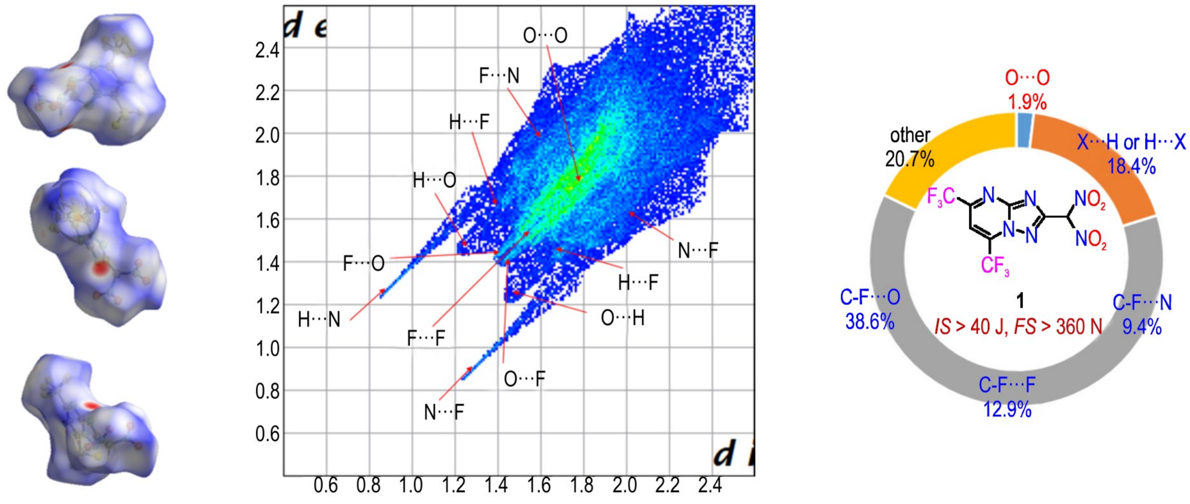
Table 1 Physicochemical and energetic properties of compounds **1**

comp.	T_{dec} /℃	ρ /g·cm^{-3}	ΔH_f /kJ·mol^{-1}/ kJ·g^{-1}	v_D / m·s^{-1}	p /GPa	*IS* / J	*FS* / N
1	122	1.79	−415.67/−1.15	6748	20.4	>40	>360
TNT[18]	295	1.65	−59.4/−0.26	7303	21.3	15	>353
Pb(N$_3$)$_3$[18]	315	4.80	450.1/1.55	5877	33.4	2.5−4.0	0.1−1.0

Note: T_{dec} is decomposition temperature (onset), ρ is density (measured by gas pycnometer at 25 ℃), ΔH_f is calculated molar enthalpy of formation (solid state), v_D is detonation velocity, p is detonation pressure, *IS* is impact sensitivity, *FS* is friction sensitivity.

2.3 Factors on sensitivity performance

To elucidate the correlation between structural attributes and sensitivity performance of dinitromethyl-containing compounds, this study employed Hirshfeld surfaces and 2D fingerprint plots[31] to investigate intermolecular interactions in compound **1**, as well as several known compounds. As depicted in Fig. 3a, a prominent protrusion is observed at the dinitromethyl group site in compound **1**. Two distinct red dots were identified on the edges of triazole and dinitromethyl group due to hydrogen bonding (O/N/F—H), while white spots surrounding the trifluoromethyl groups indicate halogen bonding (CF—F/O/N). The contributions of these strong and weak intermolecular interactions are further elucidated through fingerprint plots (Fig. 3b). Hydrogen bonding collectively accounts for 18.4% contribution (Table 2 and Fig. S8 in Supporting Information), whereas halogen bonding significantly contributes up to 60.9% (CF···F=12.9%, CF···O=38.6%, CF···N=9.4%). Surprisingly, the population of O···O intermolecular interactions is only 1.9%, which is significantly lower than the corresponding values observed in known dinitromethyl-containing energetic materials (see as Table 2 and Fig.4), such as 4-(dinitromethyl)-5-nitro-1*H*-pyrazole (**7**) (30.5%)[14], 2-(dinitromethyl)-4-nitro-2*H*-1, 2, 3-triazole (**8**) (31.3%)[32], fused-ring energetic material *N*-(3-(dinitromethyl)-[1, 2, 4]triazolo[5, 1-*c*][1, 2, 4]triazin-4(1*H*)-ylidene)nitramide (**9**) (20.4%)[33], multi-heterocycles energetic material 4, 4′-oxybis (3-(dinitromethyl)-1,2,5-oxadiazole)(**10**)(41.0%)[34], bis(3-(dinitromethyl)-1*H*-1, 2, 4-triazol-1-yl) methane (**11**) (21.4%)[35], (*E*)-1, 2-bis(4-(5-(dinitro-



a. b. c.

Fig. 3 (a) Hirshfeld surfaces that use color coding to represent the proximity of close contacts around **1** (white, *d* = van der Waals (vdW) distance; blue, *d* > vdW distance; red, *d* < vdW distance), (b) fingerprint plots in crystal stacking found, (c) contributions of some strong and other weak intermolecular interactions

Table 2 Contributions of these strong and weak intermolecular interactions, as well as the sensitivity value of compounds **1** and several known dinitromethyl-containing energetic materials[14, 22, 32-37]

comp.	O···O / %	X···H(X=O, N, F) / %	CF···Y(Y=N, O, F) / %	other / %	*IS* / N	*FS* / J
1	1.9	18.4	60.9	20.7	>40	>360
7[14]	30.5	44.1	0	25.4	17	144
8[32]	31.3	33.1	0	35.6	10	192
9[33]	20.4	36.5	0	53.1	15	144
10[34]	41.0	19.6	0	39.4	2	no data
11[35]	21.4	21.3	0	26.3	7	120
12[36]	19.0	23.7	0	57.3	5	80
13[37]	47.5	13.5	0	39.0	9	160
14[35]	37.3	35.5	0	27.2	6	240
15[22]	14.1	17.8	47.5	20.6	32	>360

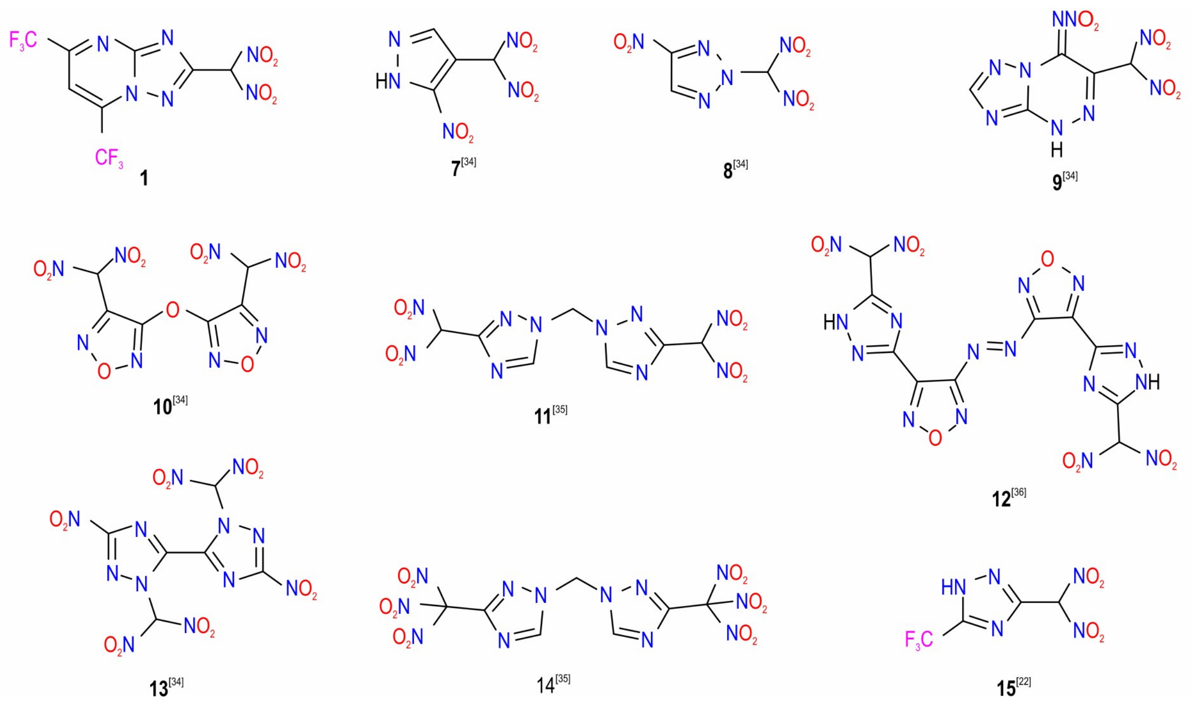
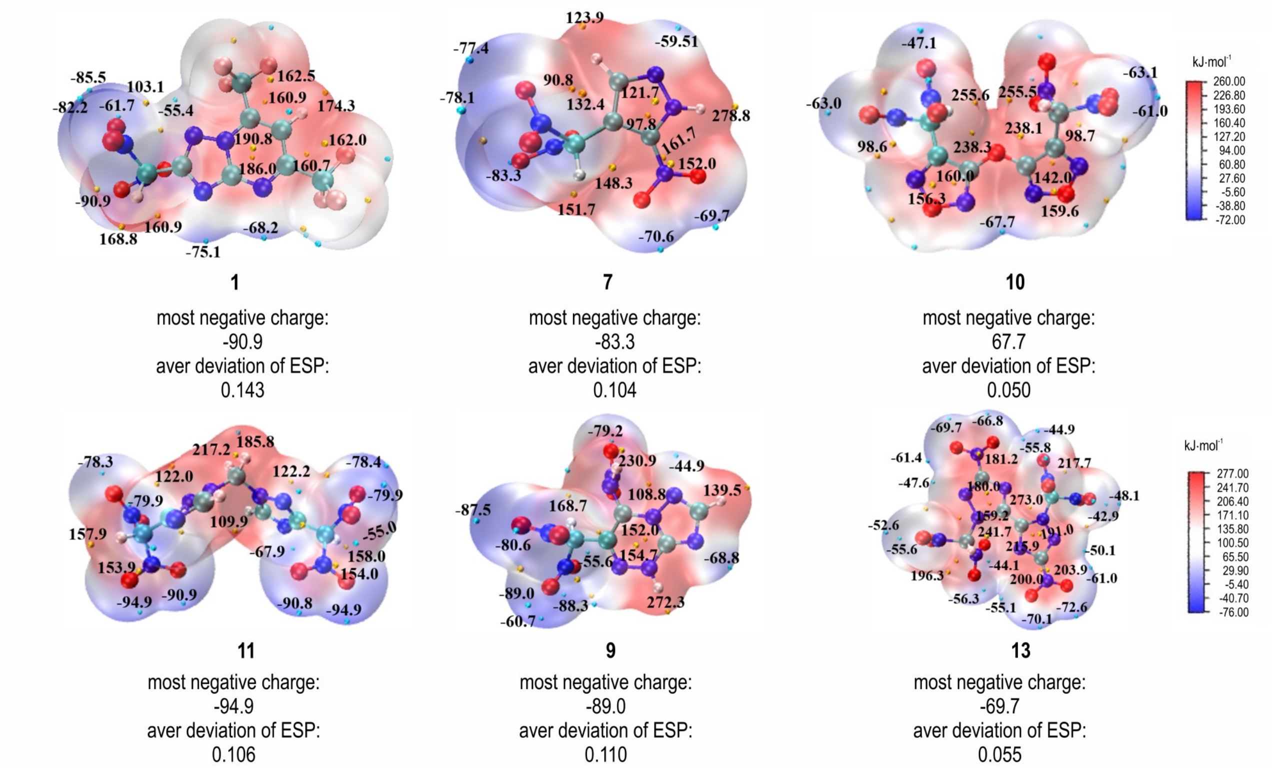


Fig.4 Chemical structures of compounds 1 and several known dinitromethyl-containing energetic materials[14, 22, 32-37]

methyl)-1*H*-1, 2, 4-triazol-3-yl)-1, 2, 5-oxadiazol-3-yl) diazene (**12**) (19.0%)[36] and 1-(dinitromethyl)-4, 4′, 5, 5′-tetranitro-1*H*, 1′*H*-2, 2′-biimidazole (**13**) (47.5%)[37]. Based on these data and crystal stacking of compound **1**, it can be inferred that halogen bonds effectively disrupt the formation of $O\cdots O$ interactions. To validate this finding, we also analyzed the intermolecular interactions of trinitromethyl-containing compounds bis(3-(trinitromethyl)-1*H*-1, 2, 4-triazol-1-yl) methane (**14**)[35] and 5-(trifluoromethyl)-3-(trinitromethyl)-1*H*-1, 2, 4-triazole (**15**)[22]. As depicted in Table 2, compound **14** exhibits $O\cdots O$ intermolecular interactions accounting for 37.3% of the total weak interactions. However, in compound **15**, this value is reduced to 14.1% due to the presence of $CF\cdots O$ halogen bonds (39.1%). Considering that the $O\cdots O$ intermolecular interactions are crucial factors contributing to extreme sensitivity development, it is evident that compound **1** demonstrates superior sensitivity performance (IS > 40 J; FS >360 N) compared to common dinitromethyl-containing compounds.

To gain a deeper understanding of the relationship between molecular structure and impact sensitivity, study computed the electrostatic potentials (ESP)[38] of representative dinitromethyl-containing compound **1**, single-ring compound **7**, bridged-ring compounds **10**-**11**, fused-ring energetic material **9**, and bicyclic energetic material **13** using the Multiwfn software. Typically, an energetic material with more negative ESP values and an average deviation of ESP (around 0.25) exhibits greater insensitivity. As depicted in Fig.5, the electrostatic potential values for these compounds range from −94.9 kJ·mol^{-1} to −69.7 kJ·mol^{-1} with only slight differences observed among them. However, due to the appearance of trifluoromethyls which possesses strong electron-withdrawing ability, compound **1** demonstrates a superior average deviation of ESP (0.143) compared to other compounds (−0.110−0.106). Notably, in compound **1**, the most positive ESP regions are localized within the aromatic rings while in other compounds these regions are situated at the molecular edges making them more susceptible to external stimuli. Consequently, compound **1** exhibits enhanced insensitivity towards impact stimuli compared to other compounds. This result further corroborates the rationality underlying the assessed experimental impact sensitivity.



1
most negative charge: -90.9
aver deviation of ESP: 0.143

7
most negative charge: -83.3
aver deviation of ESP: 0.104

10
most negative charge: 67.7
aver deviation of ESP: 0.050

11
most negative charge: -94.9
aver deviation of ESP: 0.106

9
most negative charge: -89.0
aver deviation of ESP: 0.110

13
most negative charge: -69.7
aver deviation of ESP: 0.055

Fig. 5 Electrostatic potential of compounds **1**, **7**[14], **9**[33], **11**[35], **12**[36] and **13**[37]

3 Conclusion

5, 7-Bis (trifluoromethyl)-2-(dinitromethyl)-[1, 2,4]triazolo[1,5-*a*]pyrimidine (**1**) was successfully synthesized using 5-isocyano-2*H*-1, 2, 4-triazol-3-amine as the starting material. It was fully characterized through various techniques such as IR, NMR analysis, elemental analyses and single crystal X-ray diffraction. The following conclusions are obtained:

(1) Compound **1** demonstrates an onset decomposition temperature of 122.0 ℃ along with moderate calculated detonation performance (v_D=6748 m·s^{-1}, p = 20.4 GPa) and excellent sensitivity performance (IS > 40 J, FS > 360 N).

(2) The crystal stacking diagram reveals that the dinitromethyl group in compound **1** is surrounded by trifluoromethyl groups from other molecules, effectively reducing the formation of O⋯O interactions.

(3) Compound **1** exhibits superior sensitivity compared to common dinitromethyl-containing compounds due to a lower population of O⋯O intermolecular interactions and a more favorable average deviation of ESP.

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奇特氟效应：一个有效构筑不敏感含能材料的重要因素

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摘　要： 研究设计、合成并表征了化合物5,7-二(三氟甲基)-2-(二硝甲基)-[1,2,4]三唑[1,5-*a*]嘧啶(1)。采用差示扫描量热仪、高斯03及EXPLO5 v6.05软件分别测试或计算了其热性能、生成焓和爆轰性能，并通过Hirschfeld表面分析、2D指纹图谱、静电势(ESP)对化合物1和已报道的偕二硝甲基含能化合物进行了对比研究。结果表明，化合物1具有较低的机械感度，其撞击感度>40 J，摩擦感度>360 N，这与已报道的CHON型偕二硝甲基含能化合物的敏感性有很大不同。单晶堆积及分子间作用力的计算结果表明化合物1中的卤键(C—F…X)能够有效打断分子之间O…O相互作用的生成。此外，由于三氟甲基的存在，化合物1展示出较为优越的静电势值和静电势偏移值，从而使其比其它偕二硝甲基含能化合物更加稳定。

关键词： 含能材料；不敏感炸药；偕二硝甲基；卤键；弱相互作用

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