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The New Role of 1,1-Diamino-2,2-dinitroethylene (FOX-7)：Two Unexpected Reactions

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Abstract: Two novel derivatives of FOX-7, 2-methyl-5-nitro-1,2,3-triazole-4-amine (MNTzA) and 1,5-bis(1-amino-2,2-dinitrovinyl)carbonohydrazide (BADCh), were synthesized by two unexpected reactions of FOX-7 and hydrazino compounds, and the two reaction processes were analyzed. The reaction for MNTzA is infrequent to the syntheses of 2,4,5-trisubstituted 1,2,3-triazole compounds. The structures of the two compounds were studied by NMR, single crystal X-ray crystallography and theoretical calculation. MNTzA crystallizes in monoclinic $P_{2(1)/n}$ space group with four molecules per unit cell, and each molecule exhibits good coplanarity. But BADCh presents a serious structural distortion of 'W' shape and possesses two highly polarized C-C double bonds. DSC analysis and detonation properties of the two compounds were compared with those of FOX-7 and RDX, and the results indicated that MNTzA is an available intermediate to synthesize other complicated 2,4,5-trisubstituted 1,2,3-triazole compounds, and BADCh is an excellent energetic material and exhibits good thermal stability (thermal decomposition peak temperature >250 ºC), lower sensitivity (impact sensitivity >19.6 J and friction sensitivity 16 %) and similar detonation properties (detonation pressure 32.1 GPa and detonation velocity 8.6 km) to FOX-7 and RDX.

Keywords: 1,1-Diamino-2,2-dinitroethylene (FOX-7); 2-Methyl-5-nitro-1,2,3-triazole-4-amine (MNTzA); 1,5-Bis(1-amino-2,2-dinitrovinyl)carbonohydrazide (BADCh); Synthesis；Energetic materials

1. Introduction

The design and synthesis of new high-energy insensitive compounds are still an important research direction of energetic materials.[1] 1,1-Diamino-2,2-dinitroethylene (FOX-7) as a new high-energy insensitive material has been considered as the applied component of insensitive ammunitions and solid propellants in future, possessing a density of 1.885 g cm^{-3}, a heat of formation of 133.7 kJ mol^{-1}, a same insensitivity to

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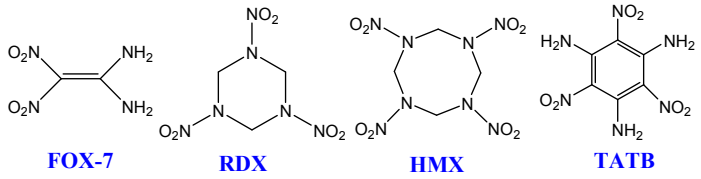
1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and a similar energy-density with 1,3,5-trinitro-1,3,5-triazinane (RDX) and cyclotetramethylenetetranitramine (HMX) (**Scheme 1**).[2] Many researches on FOX-7 have been reported every year since first synthesized by Latypov in 1998.[2a, 3] Recently, Zhou et al [4] studied the mechanical anisotropy of the FOX-7's crystal, Lempert et al [5] explored the energy potential of solid composite propellants based on FOX-7 and Wang et al [6] also studied the configuration and stability of FOX-7 embedded in graphene.



Scheme 1 Chemical structures of FOX-7, RDX HMX and TATB

FOX-7 is a magic compound for its surprising chemical reactivity. Though the molecular composition and structure of FOX-7 is very simple, its chemical reactivity is abundant, including acid-base reaction, coordination reaction, nucleophilic substitution reaction, acetylate reaction, oxidiating reaction, reduction reaction and electrophilic addition reaction.[7] More than 130 derivative compounds of FOX-7 have been reported through the above reactions. These reactions were systematically summarized and analyzed in the two reviews just published in this year.[7]

Lately, Vo et al reported their exciting discovery of the first cations based on FOX-7 and its derivative 1-amino-1-hydrazino-2,2-dinitroethylene, and amphoteric properties of the two compounds were demonstrated.[8] Gao et al also reported some complicated multinitro derivatives of FOX-7, and those compounds exhibit good thermal stability, high density, positive HOF, acceptable oxygen balances and excellent detonation properties.[9] He et al theoretically studied two potential derivatives of FOX-7, 5-(dinitromethylene)-1,4-dinitramino-tetrazole(NNAT) and 1,1'-dinitro-4,4'-diamino-5,5'-bitetrazole (DNABT), and found they all presents good detonation properties.[10] The study on reactivity of FOX-7 is still an active field of energetic materials.

In this paper, we also report two unexpected reactions of FOX-7, and the structure and properties of two reaction products will be meticulously studied. The work further

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enriches the research of FOX-7.

2. Experimental Section

2.1. Materials

FOX-7 was obtained form *Xi'an Modern Chemistry Research Institute*, and the purity is over 99%. Methylhydrazine aqueous solution and carbohydrazide were purchased from commercial sources and used as received.

2.2. Physical Measurements

NMR spectra were recorded with a AV500 NMR spectrometer (BRUKER). IR spectra were determined on NEXUS870 (THERMO NICOLET) with KBr pellets. Elemental analyses were performed on a Vario EL III elemental analyzer (ELEMENTAR). MS spectra were recorded on a GCMS-QP2010 mass spectrometer (SHIMADZU). SEM images were recorded using a Zeiss SIGMA scanning electron microscope. DSC experiments were performed using a DSC200 F3 apparatus (NETZSCH, German) under a nitrogen atmosphere at a flow rate of 80 mL min^{-1}. TG-DTG experiment was performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min^{-1}. The combustion energy was determined by using a IKA C5000 oxygen-bomb calorimeter (German). The impact and friction sensitivities were determined by using a ZBL-B impact sensitivity instrument (NACHEN, China) and a MGY-2 friction sensitivity instrument (NACHEN, China), respectively. The mass of drop hammer is 5.0 kg. The swing angle and gauge pressure are 50 º and 0.6 MPa. The mass for each test is 30 mg. All other reagents were purchased from commercial sources and used without further purification.

2.3. Crystal Structure Determinations

Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo-*K*α radiation (λ=0.071073 nm). The structures were solved by the direct methods (*SHELXTL-97*) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[11] The hydrogen atoms were added according to the

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theoretical models.

2.4. Theoretical Calculation Investigation

A molecular unit of BADCh generated from Chem3D software was optimized by minimize energy of MOPAC method repeatedly to non-change, and then selected as the initial model, while B3LYP/6-31+G method in Gaussian 03 package was used to further optimize the structure and compute its frequencies at different temperatures.[12] Meanwhile, the optimized parameters were used to further compute molecular volume for 100 times, and the average value was regarded as the credible molecular volume. All convergent precisions were the system default values, and all calculations were carried out on the *Lenovo* T260 server.

2.5. Preparation

2-Methyl-5-nitro-1,2,3-triazole-4-amine (MNTzA) was prepared according to the following method: FOX-7 (0.02 mol, 2.96 g) was dispersed in 12 mL of water and to it methylhydrazine aqueous solution (about 0.05 mol, 18 mL) was added dropwise. After stirred reaction at 100 ºC for 1.5 h, the resulting solution was slowly cooled to ambient temperature, then diluted with water, filtered, washed with water and dried under vacuum to obtain the pale yellow crystals of MNTzA. These pale yellow crystals present regularly rodlike as shown in **Figure 1**. Yield 1.78 g (62%). m.p.167-169 ºC. IR (KBr, *v*, cm^{-1}), 3440(vs), 3321(vs), 3237(w), 3188(m), 3047(w), 2685(w), 1643(vs), 1574(vs), 1473(w), 1448(w), 1354(m), 1299(s), 1207(m), 1114(w), 1070(m), 866(m). ^{13}C NMR(DMSO, 500MHz, δ, ppm) 149.745, 137.845, 43.472. ^{1}H NMR(DMSO, 500MHz, δ, ppm) 4.057, 6.773. MS (m/z, %) 143(M^+, 60), 53(M^+, 35), 43(M^+, 100), 30(M^+, 30). Anal. Calcd. for $C_3H_5O_2N_5$ (%): C 25.18, N48.94, H 3.52. Found. C 25.11, N 48.87, H 3.59.

1,5-Bis(1-amino-2,2-dinitrovinyl)carbonohydrazide (BADCh) was prepared according to the following method: FOX-7 (0.01 mol, 1.48g) was dispersed in 30 mL of H_2O and to it carbohydrazide (0.02mol, 1.82 g) was added. After reaction at 105 ºC for 28 h, the resulting solution was slowly cooled to ambient temperature and diluted with proper amount of water. Many brown solid were formed, which were filtered, washed with water, and dried under vacuum, yielding 0.472 g (26.8 %). **Figure 1**

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indicates that the crystalline solids of BADCh are irregular blocky structure. The try for the single crystal all failed. ^{1}H NMR(DMSO, 400MHz, ppm), δ=8.788, 3.346, 2.509. ^{13}C NMR(DMSO, 400MHz, ppm), δ=43.477, 137.005, 149.745. IR(KBr) υ: 3421, 2360, 1635($\nu_{C=O}$), 1396, 1132, 752, 619 cm^{-1}. MS [m/z(%), 351(M+, 30), 307(M+, 100), 263(M+, 35), 105(M+, 30)]. Anal. Calcd. for $C_5H_8N_{10}O_9$: C 17.05, H 2.290, N 39.77 %; found: C 17.09, H 2.263, N 39.49 %.

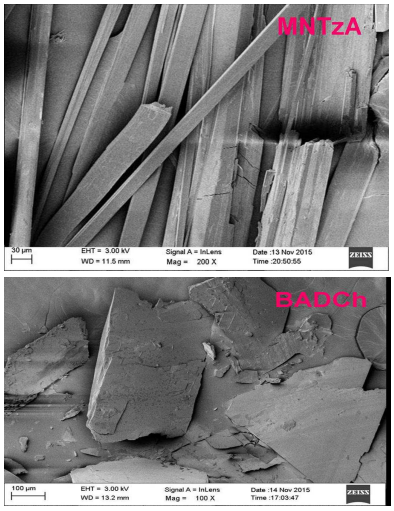

Figure 1. SEM images of MNTzA and BADCh

3. Results and Discussion

3.1. Synthesis of MNTzA

1-Amino-1-hydrazino-2,2-dinitroethylene (AHDNE) as a nucleophilic substitution derivative of FOX-7 exhibits high reactivity for its special adjacent amino-hydrazino group.[7b,13] AHDNE can react with potassium nitrite in organic acid solution to synthesize a rich-nitrogen compound 5-(dinitromethylene)-tetrazole (DNMT) (**Scheme 2**).[14] However, AHDNE and DNMT are unstable, even AHDNE can self-explode or self-ignite at ambient temperature.[9, 13b, 13c] So we design to substitute methylhydrazine for hydrazine to prepare a stable energetic compound. However, the result is unexpected. The designed compound was not got, but an unusual 2,4,5-trisubstituted 1,2,3-triazole compound, 2-methyl-5-nitro-1,2,3-triazole-4-amine, (MNTzA) was surprisingly synthesized (**Scheme 2**). 1,2,3-Triazole compounds were largely reported every year since the publication of "Click Chemistry" by Sharpless in 2001,[15] and the main "Click Reaction" (Cycloaddition) is to use azide and acetylide

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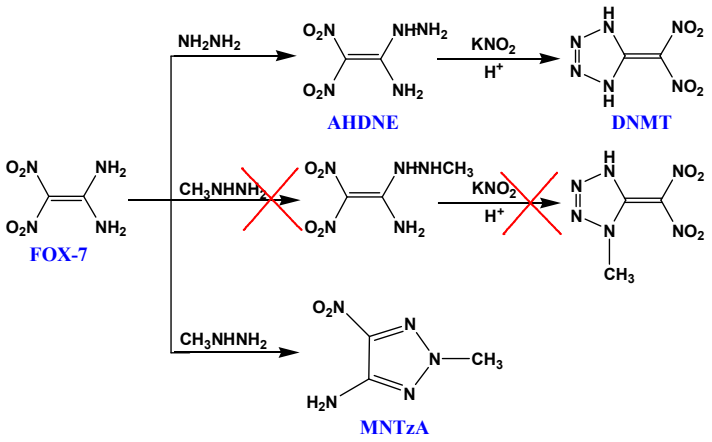
with the action of catalysts to obtain 1,2,3-triazole or tetrazole compounds. However, getting 1,4,5-trisubstituted or 2,4,5-trisubstituted 1,2,3-triazole compounds needs much more complicated multistep reactions and the yield is very low.[16] However, a 2,4,5-trisubstituted 1,2,3-triazole compound can be easily synthesized in this work, not involving in "Click Chemistry". Though the compound was reported by Zhang et al in 2013,[17] whose synthesis method was very complicated and needed about 13 step reactions, using acetic anhydride as initial raw material. MNTzA is not a complicated compound, but its amino group, nitro group and methyl group are active groups and can be further substituted or reacted to prepare other complicated 1,2,3-triazole compounds.[17] The reaction for MNTzA may be a good way to synthesize complicated 2,4,5-trisubstituted 1,2,3-triazole compounds, and MNTzA may be an available intermediate to synthesize other complicated 2,4,5-trisubstituted 1,2,3-triazole compounds.



Scheme 2. Syntheses of FOX-7's derivative

The conjectural reaction process for MNTzA is shown in **Scheme 3**. Firstly, FOX-7 reacts with methylhydrazine to form an unstable intermediate, 1-amino-1-methylhydrazino-2,2-dinitroethylene. Secondly, 1-amino-1-methylhydrazino-2,2-dinitroethylene becomes the format of tautomers and resonances (**1-3**).[3a-3c] Thirdly, with the action of electron-donating CH_3- group, the H atom of –NH– dissociates to the adjacent O^- atom, so the middle N atom of methylhydrazino group exhibits obvious electronegativity (**4**). Finally, N^- atom with lone pair electrons attacks adjacent N^+ atom to form stable 1,2,3-triazole ring in the

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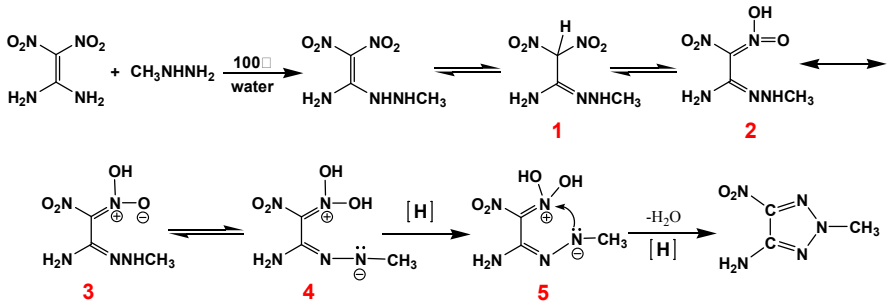
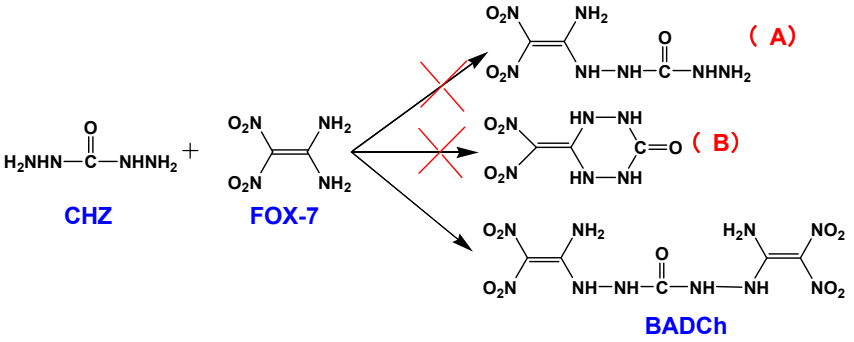
strong reduction system of methylhydrazine, along with the leaving of the two hydroxyl group to become water.



Scheme 3. Reaction process for MNTzA

3.2. Synthesis of BADCh

Based on the nucleophilic reactions of FOX-7,[7a] carbohydrazide (CHZ) was used as a nucleophile to prepare new energetic compound. The result indicates that only a seemingly symmetrical compound 1,5-bis(1-amino-2,2-dinitrovinyl)carbonohydrazide (BADCh) was found through the reaction of one CHZ molecule and two FOX-7 molecules with a yield of 26.8 %, but other two expected compounds (**A** and **B**) were not found, regardless of how to change the reaction conditions (**Scheme 4**). Compound **B** is attractive, and we ever doubted that the product should be compound **B**, because the compound possesses a stable six-member ring and should have big competitive advantage compared with other two compounds. The rule also was found in other double nucleophilic substitution derivatives.[2b, 7a] However, the results of ^{1}H NMR (three chemical shifts: 8.788, 3.346, 2.509 ppm) and MS [351(M+, 30)] deny our guess, and BADCh is the only product. The try for compound **B** all failed.



Scheme 4 Synthesis of BADCh

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3.3. Structure analysis of MNTzA

The single crystal of MNTzA was obtained from the reaction solution cooled very slowly. The orderly rodlike crystal of MNTzA is pale yellow (**Figure 1**), and structured by single crystal X-ray crystallography. MNTzA crystallizes in monoclinic $P_{2(1)/n}$ space group with four molecules per unit cell (**Supporting materials**). The structure of MNTzA is simple, consisting of a triazole ring and three small substituent groups as shown in **Figure 2(a)**. From selected bond lengths, N2-C2 bond (1.346 Å) is a typical conjugated N-C double bond, but N4-C3 bond (1.456 Å) is a typical C-N single bond. In triazole ring, N3-N4 bond (1.299 Å), N3-C1 bond (1.341 Å), N4-N5 bond (1.348 Å), N5-C2 bond (1.339 Å) and C1-C2 bond (1.403 Å) are all conjugated double bond. Moreover, N2-C2 bond also involves in the conjugative effect of triazole ring to form a larger conjugated system, which reduces the energy and increases the stability of molecule. From selected bond angles (N4-N3-C1, 102.667°; N3-N4-N5, 116.56°; N4-N5-C2, 103.82°; N3-C1-C2, 110.37° and N5-C2-C1, 106.58°), it can be seen that the triazole ring was greatly effected by substituent groups, especially to amino group. Despite of the influence of substituent groups, all non-hydrogen atoms in triazole ring and three substituent groups have good coplanarity. The two biggest torsion angles are 177.86° (C1-N3-N4-C3) and -177.75° (C3-N4-N5-C2), and the two smallest are 0° (N4-N5-C2-C1) and -0.3° (N3-N4-N5-C2), respectively. Each MNTzA molecule contacts with two surrounding molecules by four hydrogen-bond interactions [only two kinds; N2-H…N5#1 (d(D…A)=3.102 Å, ∠DHA=168.06°), N2-H…O2#2 (d(D…A)=3.313 Å, ∠DHA=142.65 °); symmetry transformations: #1: -x+1, -y, -z+2; #2: x+1/2, -y+1/2, z+1/2] (**Figure 2(a)**), which infinitely extend out to form an ordered 3D packing of MNTzA as shown in **Figure 2(b)**.

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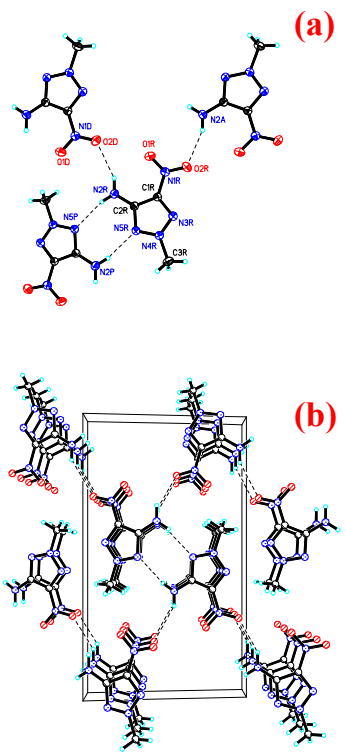

Figure 2. Thermal ellipsoids plots shown at 30% and their hydrogen-bond interactions (a), and packing diagram of MNTzA along the *a*-axis (b)

Selected bond lengths(Å): N2-C2, 1.346(3); N3-N4, 1.299(2); N3-C1, 1.341(3); N4-N5, 1.348(2); N4-C3, 1.456(3); N5-C2, 1.339(3); C1-C2, 1.403(3). Selected bond angles(°): N4-N3-C1, 102.66(17); N3-N4-N5, 116.56(17); N4-N5-C2, 103.82(16); N3-C1-C2, 110.37(19); N3-C1-N1, 121.62(19); C2-C1-N1, 128.0(2); N5-C2-N2, 123.0(2); N5-C2-C1, 106.58(18); N2-C2-C1, 130.4(2).

3.4. Theoretical Calculation Results of BADCh

Vibration analysis showed that the optimized structure is in accord with the minimum points on the potential energy planes, proving that the optimized structure is stable and the calculation results are reliable.[12] The optimized structure of BADCh and some selected bond lengths are shown in **Figure 3**. One CHZ molecule connects with two FOX-7 molecules by mucleophilic substitution to form a new bigger molecule with the leave of two amino groups. The new molecule (BADCh) presents a serious structural distortion of 'W' shape around the central CHZ group, which is much different from the similar plane structure of FOX-7's molecule and highly ordered single-layer space construction.[18] The structural distortion also can be supported by those seemingly symmetric chemical bonds, such as bond C5-C7 (1.431 Å) and C15-C17 (1.430Å), C1-N24 (1.407Å) and C1-N2 (1.399Å), N14-N24 (1.391 Å) and

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N2-N4 (1.387Å), and C15-N14 (1.368Å) and C5-N4 (1.368Å) **(see Supporting Materials)**. From the bond lengths, bond C5-C7 and C15-C17 still are conjugated double bonds. Bond C15-N14, C15-N16, C5-N4 and C5-N6 are conjugated double bonds. Comparing with related bond lengths of CHZ [C-N (1.348 Å), N-N (1.411 Å)],[19] C-N bond was elongated, but N-N bond was shortened in BADCh. So, a big conjugated system forms from C7 to C17 including all middle atoms, which should be the main reason for BADCh having better thermal stability than FOX-7. The distribution of atomic net charges indicated that C5 (0.7581*e*) and C15 (0.6476 *e*) have more positive charges than C7 (0.1377 *e*) and C17 (0.2604 *e*), also indicating that BADCh possesses two highly polarized C-C double bonds. Carbonyl group reduces the activities of N-N bond and C-N bond of both sides, which may be another reason for BADCh having better thermal stability than FOX-7.

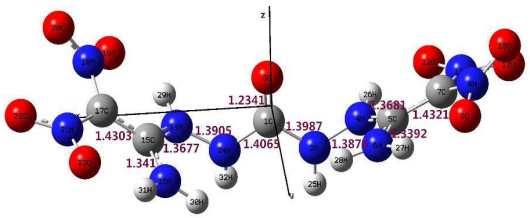

Figure 3 Optimized structure of BADCh and some selected bond lengths

3.5. DSC analysis

Typical DSC and TG/DTG curves in **Figure 4** indicate that the thermal behavior of MNTzA presents two obvious stages. The first is an intense endothermic melting-decomposition process with a mass loss of about 92.8%, and the onset temperature, peak temperature and decomposition enthalpy at a heating rate of 10 ℃ min^{-1} are 169.56, 170.41 ℃ and 140.9 J g^{-1}, respectively. The second is a slow endothermic decomposition process with a mass loss of only about 4.5 %. The final residue at 300 ℃ is about 3.3 %. No exothermic process can be found in the whole DSC curve of MNTzA. The introduction of a methyl group and the losing of a nitro group make the thermal behavior of compound change greatly, compared with that of parent compound (FOX-7) in **Figure 5**.

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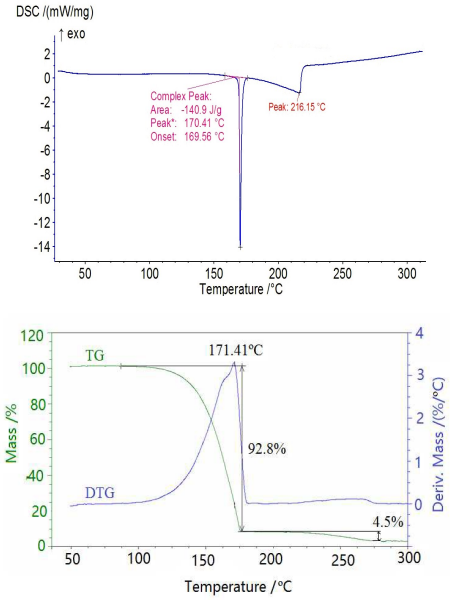

Figure 4. Typical DSC and TG/DTG curves of MNTzA at a heating rate of 10 °C min^{-1}

Figure 5 indicates that thermal behavior of BADCh can be divided into four stages. The first two stages are crystal-phase transition processes, and the peak temperatures are 116.51 and 169.13 ºC at the heating rate of 5.0 ºC min^{-1}, respectively. The last two stages are a continuous exothermic decomposition process with a mass lose of about 76 %, and the peak temperatures are 252.82 and 286.49 ºC at the heating rate of 5.0 ºC min^{-1}, respectively. It is surprising that the thermal behavior of BADCh was very similar to that of FOX-7 including two crystal-phase transition processes, and the difference for the two compounds is the thermal decomposition temperature of BADCh is higher than that of FOX-7 (229.70 and 294.33 ºC). The same phenomenon also can be found in another derivative of FOX-7----1-amino-1-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene (APHDNE),[20] indicating that 1-amino-2,2-dinitrovinyl group plays the key role in molecules. The sequence of thermal stability for the three compounds is BADCh > APHDNE > FOX-7. The introduction of stable group can raise the thermal stability of compound. Moreover, the two continuous exothermic decomposition processes of BADCh can easily become a big and wide exothermic process with the rise of heating rate (10 °C min^{-1}), but FOX-7 still presents two exothermic decomposition processes (**Figure 6**).

A multiple heating method was employed to obtain the kinetic parameters [the

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apparent activation energy (E) and pre-exponential factor (A)]. The DSC data and results obtained by Kissinger method and Ozawa method of the decomposition process for BADCh are listed in **Table 1**.[21] The apparent activation energy obtained by Kissinger method agrees well with that by Ozawa method. The linear correlation coefficients (r) are very close to 1. So, the results are credible. Moreover, the apparent activation energy is lower, indicating that BADCh easily decomposes at high temperature.

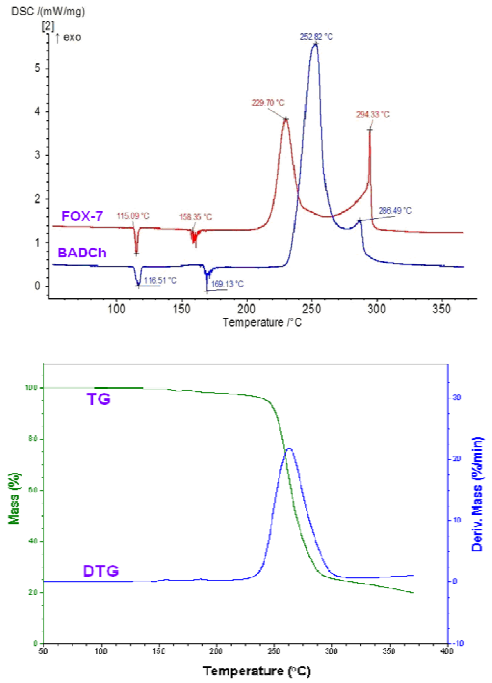

Figure 5 Typical DSC and TG/DTG curves of BADCh at a heating rate of 5 °C min^{-1}

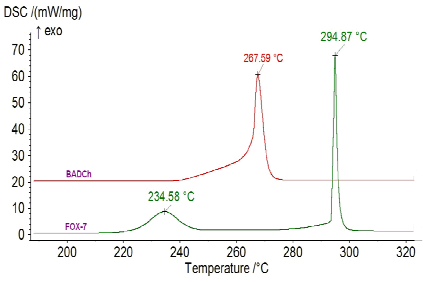

Figure 6 DSC curves of BADCh and FOX-7 at a heating rate of 10 °C min^{-1}

Table 1. DSC data and results of kinetic parameter at different heating rates (β)

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β/ (ºC min^{-1})	T_e /ºC	T_p /ºC	E_k /(kJ mol^{-1})	log(A_k/s^{-1})	r_k	E_O / (kJ mol^{-1})	r_O
5.0	235.1	252.8	113.6	8.90	0.9905	116.5	0.9918
7.5	238.8	260.8					
10.0	255.3	267.6					
12.5	257.7	269.7					

Subscript k is data obtained by Kissinger method, Subscript *O* is data obtained by Ozawa method

The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are two important parameters required to ensure safe storage and process operations for energetic materials and then to evaluate the thermal stability. T_{SADT} and T_b for BADCh are calculated as 213.7 and 222.1 ºC respectively,[22] which all are much higher than those of FOX-7 as 206.0 and 207.1 ºC,[3g] also indicating BADCh has higher thermal stability than FOX-7.

3.6 Detonation Properties

The detonation properties of MNTzA, BADCh and the properties of FOX-7 and RDX for comparison are summarized in **Table 2**.[2d, 8] MNTzA, as an energetic material, exhibits bad detonation properties comparing with FOX-7 and RDX, though having high nitrogen content (48.9 %) and good insensitivity (>16.9 J, 24 %). The reason should be the losing of one nitro group and the introduction of a methyl group, which makes the energy and density of compound decline greatly (the crystal density declines from 1.88 g cm^{-3} of FOX-7 to 1.58 g cm^{-3} of MNTzA).[18] However, detonation properties of BADCh are good, whose detonation velocity and detonation pressure are close to that of FOX-7 and RDX, but the sensitivities are much lower than that of RDX.

Table 2. Detonation properties

sample	M[a] /g mol^{-1}	T_m[b] /°C	d[c] /g cm^{-3}	OB[d] /%	$-\Delta_c H_c$[e] /kJ g^{-1}	$\Delta_f H^0_m$[f] /kJ mol^{-1}	IS[g] /J	FS[h] /%	P[i] /GPa	D[j] km s^{-1}
MNTzA	143.12	167.8	1.58	-72.7	12.38	-130.1	16.9	24	20.7	7.1
BADCh	352.18	-	1.75[k]	-22.7	8.11	-260.9	19.6	16	32.1	8.6
FOX-7	148.08	-	1.88	-21.6	7.83	-133.7	24.7	10	36.1	8.3
RDX	222.12	204.5	1.82	-21.6	9.55	96.2	7.4	76	33.7	8.7

[a] Molecular mass, [b] Melting point; [c] Crystal density; [d] Oxygen balance; [e] Combustion energy; [f] Enthalpy of formation; [g] Impact sensitivity; [h] Friction sensitivity; [i] Detonation pressure based on *Kamlet-Jacobs* (K-J) equations; [j] Detonation velocity based on *Kamlet-Jacobs* (K-J) equations; [k] Theoretical calculation result.

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4. Conclusions

In conclusion, we reported two new reactions of FOX-7 in this work, and two reaction products, 2-methyl-5-nitro-1,2,3-triazole-4-amine (MNTzA) and 1,5-bis(1-amino-2,2-dinitrovinyl)carbonohydrazide (BADCh), are unexpected. The reaction for MNTzA is infrequent to the syntheses of 2,4,5-trisubstituted 1,2,3-triazole compounds, and may be a selectable way to synthesize other complicated 2,4,5-trisubstituted 1,2,3-triazole compounds by the reaction without involving in well-known "Click Chemistry". 1-Amino-2,2-dinitrovinyl group plays the key role to the thermal behavior of compound, but the introduction of a methyl group and the losing of a nitro group make the thermal behavior of FOX-7 change greatly. MNTzA is not a good energetic compound for its bad detonation properties, but BADCh still exhibits excellent thermal stability, lower sensitivity and similar detonation properties to FOX-7 and RDX and has a good application potential as energetic material. This work further enriches the reactivity of FOX-7.

Supporting Information

CCDC-1044208 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.ac.uk/data_repuset/cif.

Crystallographic data, optimized bond lengths, bond angles and atomic net charges, and energies of combustion.

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References

1. (a) D.M. Badgujar, M.B. Talawar, S.N. Asthana, and P.P. Mahulikar, Advances in Science and Technology of Modern Energetic Materials: An Overview, *J. Hazard. Mater.,* 2008, **151**, 289. (b) H. Gao, J. M. Shreeve, Azole-based Energetic Salts, *Chem. Rev.*, 2011, **111**, 7377.

View Article Online
DOI: 10.1039/C6NJ03370A

2. (a) V. N. Latypov and J. Bergman, Synthesis and Reactions of 1,1-Diamino-2,2-Dinitroethylene, *Tetrahedron,* 1998, **54**, 11525; (b) A. J. Bellamy, P. Goede, C. Sandberg and N. V. Latypov, Substitution Reactions of 1,1-Diamino-2,2-Dinitroethylene (FOX-7), The Proceedings of the 33th International Annual Conference ICT, Karlsruke, Germany, 2002; (c) B. Buszewski, M. Michel, S. Cudzilo and Z. Chylek, High Performance Liquid Chromatography of 1, 1-Diamino-2,2-dinitroethene and Some Intermediate Products of Its Synthesis, *J. Hazard. Mater.,* 2009, **164**, 1051. (d) Y. D. Tian, F. Q. Zhao and J. H. Liu, *Handbook of Energetic Materials and the Related Compounds*, National Defense Industry Press, Beijing, 2011 (in Chinese).

3. (a) G. Hervé, G. Jacob and N. Latypov, The Reactivity of 1,1-Diamino-2,2-dinitroethene (FOX-7), *Tetrahedron,* 2005, **61**, 6743; (b) M. Anniyappan, M. B. Talawar, G. M. Gore, S. Venugopalan and B. R. Gandhe, Synthesis, Characterization and Thermolysis of 1,1-Diamino-2,2-dinitroethylene (FOX-7) and Its Salts, *J. Hazard. Mater.,* 2006, **137**, 812; (c) G. Hervé, G. Jacob and N. Latypov, Novel Illustrations of the Specific Reactivity of 1,1-Diamino-2,2-dinitroethene (DADNE) Leading to New Unexpected Compounds, *Tetrahedron* 2007, **63**, 953; (d) C. R. Chang, K. Z. Xu, J. R. Song, B. Yan, H. X. Ma, H. X. Gao and F. Q. Zhao, Preparation, Crystal Structure and Theoretical Calculation of 1-Amino-1-hydrazino-2, 2-dinitroethene, *Acta Chim. Sinica*., 2008, **66**, 1399; (e) K. Z. Xu, J. R.Song, F. Q. Zhao, H. X. Ma, H. X. Gao, C. R. Chang, Y. H. Ren and R. Z. Hu,Thermal Behavior, Specific Heat Capacity and Adiabatic Time-to-Explosion of G(FOX-7), *J. Hazard. Mater.,* 2008, **158**, 333; (f) K. Z. Xu, F. Wang, Y. H. Ren, W. H. Li, F. Q. Zhao, C. R. Chang and J. R. Song, Structural Characterization and Thermal Behavior of 1□Amino□1□methylamino□2, 2□dinitroethylene, *Chin. J. Chem.,* 2010, **28**, 583; (g) H. X. Gao, F. Q. Zhao, R. Z. Hu, Q. Pan, B. Z. Wang, X. W. Yang, Y. Gao, S. L. Gao and Q. Z. Shi, Thermochemical Properties, Thermal Behavior and Decomposition Mechanism of 1,1□Diamino□2, 2□dinitroethylene (DADE), *Chin. J. Chem.,* 2006, **24**, 177; (h) S. Garg, H. X. Gao, Y. H. Joo, D. A. Parrish, Y. Huang and J. M. Shreeve, Taming of the Silver FOX, *J. Am. Chem. Soc.,* 2010, **132**, 8888; (i) T. T. Vo, D. A. Parrish and J. M. Shreeve, 1,1-Diamino-2,2-dintroethene (FOX-7) in Copper and Nickel Diamine Complexes and Copper FOX-7, *Inorg. Chem.,* 2012, **51**, 1963; (j) Z. Gao, J. Huang, K. Z. Xu, W. T. Zhang, J. R. Song and F. Q. Zhao, Synthesis, Structural Characterization, and Thermal Properties of a New Energetic Zinc-FOX-7 Complex, *J. Coord. Chem.,* 2013, **66**, 3572; (k) T. T. Vo, J. Zhang, D. A. Parrish, B. Twamley and J. M. Shreeve, New Roles for 1,1-Diamino-2,2-dinitroethene (FOX-7): Halogenated FOX-7 and Azo-bis (diahaloFOX) as Energetic Materials and Oxidizers, *J. Am. Chem. Soc.,* 2013, **135**, 11787. (l) X. Fang and W. G. Mcluckie, Laser Ignitibility of Insensitive Secondary Explosive 1,1-Diamino-2,2-dinitroethene (FOX-7), *J. Hazard. Mater.,* 2015, 285, 375. (m) H. M. Shin,

View Article Online
DOI: 10.1039/C6NJ03370A

H. S. Kim and K. K. Koo, Molecular Modeling on Supersaturation-Dependent Growth Habit of 1,1-Diamino-2,2-dinitroethylene, *Cryst. Growth Des*. 2015, **15**, 1833; (n) M. Civis, S. Civis, K. Sovova, K. Dryahina, P. Spanel and M. Kyncl, Laser Ablation of FOX-7: Proposed Mechanism of Decomposition, *Anal. Chem.*, 2011, **83**, 1069; (o) V. G. Kiselev and N. P. Gritsan, Unexpected Primary Reactions for Thermolysis of 1,1-Diamino-2,2-dinitroethylene (FOX-7) Revealed by Ab Initio Calculations, *J. Phys. Chem. A,* 2014, **118**, 8002; (p) M. M. Bishop, N. Velisavljevic, R. Chellappa and Y. K. Vohra, High Pressure–Temperature Phase Diagram of 1, -Diamino-2,2-dinitroethylene (FOX-7), *J. Phys. Chem. A,* 2015, **119**, 9739.

4. X. Zhou, Z. Lu, D. Chen, H. Li, F. Nie and C. Zhang, Mechanical Anisotropy of the Energetic Crystal of 1, 1-Diamino-2, 2-dinitroethylene (FOX-7): A Study by Nanoindentation Experiments and Density Functional Theory, *J. Phys. Chem. C*, 2016, **120**,13434.
5. D. B. Lempet, E. M. Dorofeenko and Y. Shu, Energy Potential of Solid Composite Propellants Based on 1,1-Diamino-2,2-dinitroethylene, *Russ. J. Phys. Chem. B*, 2016, **10**, 483.
6. Y. Q. Wang and G. X. Wang, Configuration and Stability of 1,1□Diamino□2,2□dinitroethylene (FOX□7) Embedded in Graphene, *Bull. Korean Chem. Soc.*, 2016, **37**, 1571.
7. (a)Y. Zhang, Q. Sun, K. Z. Xu, J. R. Song and F. Q. Zhao, Review on the Reactivity of 1,1□Diamino□2,2□dinitroethylene (FOX□7), *Propellants Explos. Pyrotech.,* 2016, **41**, 35; (b) H. Gao and J. M. Shreeve, Recent Progress in Taming FOX-7 (1,1-Diamino-2,2-dinitroethene), *RSC Adv.,* 2016, **6**, 56271.
8. T. T. Vo and J. M. Shreeve, 1,1-Diamino-2,2-dinitroethene (FOX-7) and 1-Amino-1-hydrazino-2,2-dinitroethene (HFOX) as Amphotères: Bases with Strong Acids, *J. Mater. Chem. A*, 2015, **3**, 8756.
9. H. X. Gao and J. M. Shreeve, The Many Faces of FOX□7: A Precursor to High□Performance Energetic Materials, *Angew. Chem. Int. Ed.,* 2015, **54**, 6335.
10. P. He, J. G. Zhang, K. Wang, X. Yin, X. Jin and T. L. Zhang, Extensive Theoretical Studies on Two New Members of the FOX-7 Family: 5-(Dinitromethylene)-1,4-dinitramino-tetrazole and 1,1′-Dinitro-4,4′-diamino-5,5′-bitetrazole as Energetic Compounds, *Phys. Chem. Chem. Phys.*, 2015, **17**, 5840.
11. (a) G. M. Sheldrick, *SHELXS*, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL*, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany, 1997.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M.A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J.C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. azyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P.

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DOI: 10.1039/C6NJ03370A

Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03. Revision B.01. Gaussian. Inc. Pittsburgh PA, 2003.

13. (a) A. J. Bellamy, FOX-7 (1, 1-Diamino-2, 2-dinitroethene), *Struct. Bond.* 2007, **125**, 1; (b) A. J. Bellamy and A. E. Contini, 1- Amino- 1- hydrazo- 2, 2- dinitroethene–a Hazard Warning, *Propellants Explos. Pyrotech.* 2008, **33**, 87; (c) H. X. Gao, Y. H. Joo, D. A. Parrish, T. Vo and J. M. Shreeve, 1- Amino- 1- hydrazino- 2, 2- dinitroethene and Corresponding Salts: Synthesis, Characterization, and Thermolysis Studies, *Chem. Eur. J.,* 2011, **17**, 4613.
14. (a) J. N. She, K. Z. Xu, H. Zhang, J. Huang, F. Q. Zhao and J. R. Song, Preparation, Crystal Structure and Thermal Behavior of 1,4-Dihydro-5H-(dinitromethylidene)-tetrazole (DNMT), *Acta Chim. Sinica* 2009, **67**, 2645. (b) K. Z. Xu, H. Zhang, P. Liu, J. Huang, Y. H. Ren, B. Z. Wang and F. Q. Zhao, Structural and Thermal Characterization of a Novel High Nitrogen Energetic Material:$(NH_4)_2$DNMT, *Propellants Explos. Pyrotech.,* 2012, **37**, 653.
15. H. C. Kolb, M. G. Finn and K. B. Sharpless, Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angew. Chem. Int. Ed.,* 2001, **40**, 2004.
16. (a) G. A. Romeiro and L. R. Pereira, A New and Efficient Procedure for Preparing 1,2,3-Triazoles, *Tetrahedron Lett.,* 1997, **38**, 5103; (b) A. Krasinski, V. V. Fokin and K. B. Sharpless, Direct Synthesis of 1,5-Disubstituted-4-magnesio-1,2,3-triazoles, Revisited, *Org. Lett.,* 2004, **6**, 1237; (c) Y. M. Wu, J. Deng, Y. Li and Q.Y. Chen, Regiospecific Synthesis of 1,4,5-Trisubstituted-1,2,3-triazole via One-Pot Reaction Promoted by Copper (I) Salt, *Synthesis,* 2005, **8**, 1314; (d) Y. Liu, W. Yan, Y. Chen, J. L. Petersen and X. Shi, Efficient Synthesis of N-2-Aryl-1,2,3-triazole Fluorophores via Post-Triazole Arylation, Org. *Lett.,* 2008, **10**, 5389; (e) D. Kumar, V. B. Reddy and R. S. Varma, A Facile And Regioselective Synthesis of 1,4-Disubstituted 1,2,3-Tiazoles Uing Cick Cemistry, *Tetrahedron Lett.,* 2009, **50**, 2065; (f) L. J. T. Danence, Y. Gao, M. Li, Y. Huang and J. Wang, Organocatalytic Enamide–Azide Cycloaddition Reactions: Regiospecific Synthesis of 1,4,5- Trisubstituted- 1,2,3- triazoles, *Chem. Eur. J.,* 2011, **17**, 3584; (g) W. Liu, Y. Li, B. Xu and C. Kuang, Palladium-Catalyzed Olefination and Arylation of 2-Substituted 1,2,3-Triazole N-Oxides, *Org. Lett.,* 2013, **15**, 2342; (h) S. Koguchi and K. Izawa, Ionic Liquid-Phase Synthesis of 1,5-Disubstituted 1,2,3-Triazoles, *ACS Comb. Sci.,* 2014, **16**, 381; (i) L. J. Li, Y. Q. Zhang, Y. Zhang, A.L. Zhu, and G. S. Zhang, Synthesis of 5-Functionalized-1,2,3-triazoles via a One-Pot Aerobic Oxidative Coupling Reaction of Alkynes and Azides, *Chin. Chem. Lett.,* 2014, **25**, 1161.
17. Y. Zhang, Damon A. Parrish and J. M. Shreeve, Derivatives of

View Article Online
DOI: 10.1039/C6NJ03370A

5-Nitro-1,2,3-2*H*-Triazole–High Performance Energetic Materials, *J. Mater. Chem. A*, 2013, **1**, 585.

18. U. Bemm and H. Öestmark, 1,1-Diamino-2,2-dinitroethylene: a Novel Energetic Material with Infinite Layers in Two Dimensions, *Acta Cryst. Sect. C.,* 1998, **54**, 1997.
19. J. G. Zhang, T. L. Zhang and K. B. Yu, The Preparation, Molecular Structure, and Theoretical Study of Carbohydrazide (CHZ), *Struc. Chem.,* 2006, **17**, 249.
20. X. L. Ren, X. G. Zuo, K. Z. Xu, Y. H. Ren, J. Huang, J. R. Song, B. Z. Wang and F. Q. Zhao, Structural Characterization and Thermal Behavior of a Novel Energetic Material: 1-Amino-1-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene, *Bull. Korean Chem. Soc.,* 2011, **32**, 2267.
21. (a)H. E. Kissinger, Reaction Kinetics in Differential Thermal Analysis, *Anal. Chem.,* 1975, **29**, 1702; (b) T. Ozawa, A New Method of Analyzing Thermogravimetric Data, *Bull. Chem. Soc. Jpn.,* 1965, **38**, 1881.
22. (a) R. Z. Hu, S. L. Gao, F. Q. Zhao, Q. Z. Shi, T. L. Zhang and J. J. Zhang, *Thermal Analysis Kinetics* (2^{th}), Science Press, 2008. (in Chinese); (b)T. L. Zhang, R. Z. Hu, Y. Xie and F. P. Li, The Estimation of Critical Temperatures of Thermal Explosion for Energetic Materials Using Non-isothermal DSC, *Thermochim. Acta,* 1994, **244**, 171.

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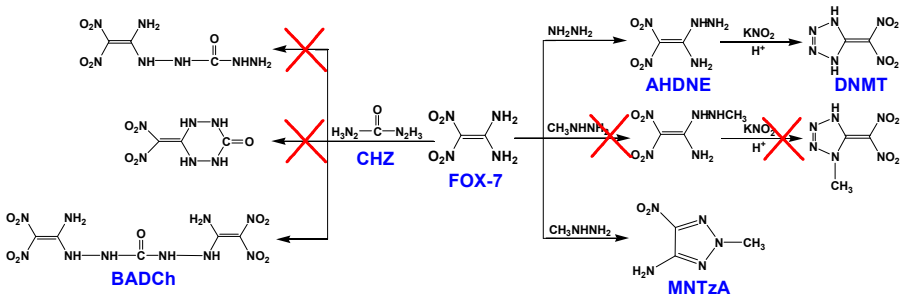
DOI: 10.1039/C6NJ03370A



Two unexpected reactions of FOX-7 were studied. The reaction for MNTzA is infrequent to the synthesis of 2,4,5-trisubstituted 1,2,3-triazole compounds.