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A series of *N*-trinitromethyl-substituted polynitropyrazoles: high-energy-density materials with positive oxygen balances[†]

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An *N*-trinitromethyl strategy was employed for the synthesis of polynitro-pyrazole based high-energydensity compounds with great potential as energetic materials. The new compounds were characterized by ¹H and ¹³C NMR, IR spectroscopy, elemental analysis, differential scanning calorimetry, and singlecrystal X-ray diffraction. Compound **10** exhibits high energetic properties, has a positive oxygen balance (OB) of +2.1%, and an excellent specific impulse (272.4 s), making it a potential high-energy dense oxidizer to replace AP in solid rocket propellants. The nitration of **7** with HNO₃/H₂SO₄ yielded the green primary explosive **12**, which showed higher density, higher performance, better oxygen balance and lower sensitivities to those of currently used diazodinitrophenol. Compound **13** is a nitrogen and oxygen rich secondary explosive with a high OB (+5.0%), comparable energy (D = 9030 m s⁻¹; P = 35.6 GPa; η = 1.03) to HMX, and much lower mechanical sensitivity (IS = 12 J, FS = 240 N).

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Introduction

Energetic materials represent an important class of compounds that can rapidly release a large amount of energy when subjected to appropriate external stimuli to accomplish propulsion, damage and other purposes, and are widely used in civil and military applications.¹ Creating new nitrogen-rich, energetic compounds has been a long-standing goal of chemists and has attracted considerable interest due to the technical challenges involved in synthesis and isolation.² New high-energy-density materials (HEDMs) must meet increasing energy requirements, also considering oxygen balance, thermal stability and sensitivity.

In recent years, five-membered nitrogen-rich heterocyclic compounds (azoles) have emerged as the most promising skeleton for the design and synthesis of advanced HEDMs.³ The azoles have a large number of N–N and C–N bonds and aromatic heterocycles, and their energy is released from the high positive heat of formation rather than by the oxidation of the carbon backbone as in traditional explosives (eg: TNT, TATB).⁴

Therefore, azoles tend to have high energy density and good thermal stability. Among them, pyrazole is easy to carry out electrophilic substitution reactions such as nitration and halogenation due to the compactness, stability and modifiability of its own structure, and the density and nitrogen content of nitro-substituted pyrazole increase with the increase of the nitro group on the ring.⁵ It can improve the detonation performance of the target compound. In recent years, many valuable nitropyrazole energetic compounds have been synthesized successively, such as 4-amino-3,5-dinitropyrazole (LLM-116), 3,6-dinitro-1,5-dihydropyrazolo[4,3-*c*]pyrazole (DNPP), and 3,4,5-trinitropyrazole (TNP).⁶

However, they have not yet found use as energetic materials due to the presence of strongly acidic N-H protons. Salt formation,7 N-hydroxylation,8 N-dinitromethylation,9 N-trinitromethylation,¹⁰ N-nitromethylation,¹¹ N,N'-alkyl bridge,¹² Nmethylation,¹³ N-amination¹⁴ are among the various approaches that have been used to address this problem (Fig. 1). However, except for hydroxylation and di/tri-nitromethylation, the oxygen balances of nitropyrazoles cannot be improved, and the energy performances of the modified compounds are often reduced. Unfortunately, N-hydroxy derivatives were found to be generally very sensitive to impact, for example 3,4,5-trinitropyrazole-1-ol15 was tested to be IS = 1 J. Therefore, in this work, we report the Ntrinitromethylation of four nitropyrazoles, and the obtained six di/trinitromethyl-substituted energetic compounds. Most of these compounds were found to have detonation performances superior to that of RDX, positive oxygen balances and specific impulses higher than that of HMX.

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Fig. 1 Various approaches to remove the acidic N–H proton in nitropyrazole (X, Y: $-NO_{2}$, $-NH_{2}$, $-N_{3}$, -H, *etc.*).

Results and discussion

Synthesis

The synthetic routes are shown in Scheme 1. Compounds 1–4 were synthesized according to the literature.^{5b,6c,12b} By the reaction of 1, 2, and 4 with bromoacetone under alkaline conditions, *N*-alkyl-functionalized nitropyrazoles 6, 5, and 9 were easily obtained in the yields of 86.5, 81.3, and 75.2%, respectively. While compounds 7 and 8 were obtained by reaction of 3 and 4 with KBr and chloroacetone in DMF at 70 °C. Compounds 5–8 were nitrated with a mixture of 98% H₂SO₄ and 98% HNO₃ for 2–5 h at 60 °C to give the corresponding trinitromethyl compounds 10–12 and 14. Interestingly, when 7 was nitrated by the same mixed acid system at room temperature for 6 h, 13 was obtained in 44.9% yield. While 9 was treated similarly, *N*-dinitromethyl substituted 15 was obtained.

Single crystal X-ray diffraction

Crystals of **2**, **6**, **7**, and **10–15** suitable for single-crystal X-ray diffraction were obtained *via* the slow evaporation of their methanol or diethyl ether solution at room temperature, and their structures are shown in Fig. 2, and Fig. S1–S6.† Their crystallographic data, bond lengths, bond angles, and hydrogen bonds are given in the ESI.†

Compound 2 crystallizes in a monoclinic crystal system (space group *Pc*). Compound 6 and 7 all crystallizes in the monoclinic $P2_1c$ space group. Their C–C, C–N, and N–N bond lengths are normal in pyrazoles. Many hydrogen bonds can be clearly observed from their packing diagrams (Fig. S2, S4 and S6†).

Compound **10** crystallizes in the orthorhombic space group *Pbca* with a density of 1.894 g cm^{-3} at 150 K and eight molecules per unit cell. Its density is much higher than that of *N*-(3,5-



Scheme 1 Synthetic routes for compounds 10–15



Fig. 2 Crystal structures of 10-15 (a-f). Thermal ellipsoids are drawn at the 50% probability level.

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dinitro-1*H*-pyrazol-4-yl)-*N*-methylnitramide^{5b} (1.74 g cm⁻³). Only the nitro group attached to C3 is substantially coplanar with the pyrazole ring, which could be seen from the torsional angle of O6-N6-C3-N5 (2.59°) and O5-N6-C3-C2 (3.43°). The adjacent trinitromethyl group is staggered so that its two nearer nitro groups straddle the ring plane fairly symmetrically (see Fig. 2a). The nitrogen atom N9 of the other nitro group is almost in line with C1 and N4 on the pyrazole ring (N9-N4-C1: 172.39°), and the distance from N4 is 2.561 Å. Even in this optimal conformation, several nonbonding distances are significantly less than their corresponding van der Waals (e.g., $O6\cdots N7 = 2.702$ Å, $O6\cdots N8 = 2.757$ Å, van der Waals $O\cdots N =$ 2.90 Å), which is a good indicator of repulsive strain. A comparison of bond angles provides further evidence of strain as bond angles near the close contact region are several degrees larger than the corresponding types of bond angles further away; e.g., the closer trinitromethyl N-C-N angle is 112.32° (N7-C5-N8), while the farther ones are 105.85° (N7-C5-N9) and 104.65° (N8-C5-N9). Combining with the literature,¹⁶ it is shown that the similar arrangement is formed when the trinitromethyl group is in the ortho position of the nitro group.

Compounds 11-13 all crystallize in the monoclinic space group $P2_1/n$. Their calculated densities are 1.960 g cm⁻³ (173 K), 1.927 g cm^{-3} (170 K), and 1.895 g cm^{-3} (193 K), higher than that of 10 (1.894 g cm⁻³ at 150 K). All substituents except trinitromethyl group in 11-13 are nearly coplanar with the pyrazole ring. The structural features of the trinitromethyl group in the three compounds are similar to those of 10. Compared with 4diazo-5-nitro-pyrazol-3-one,17 the C=O bond in Ntrinitromethyl-substituted compound 12 is shorter, but both the C–NO₂ and C–N $_2^+$ bonds are longer.

Compound 14 crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell and a calculated density of 1.859 g cm⁻³ at 296 K. Compound 15 crystallizes with two water molecules in the triclinic $P\bar{1}$ space group with two molecules per unit cell. The C1 and C2 positions of the pyrazole ring in compounds 14 and 15 are adjacent nitro groups, and the C3 position is an electronegative single atom (chlorine and oxygen). Due to steric hindrance, the nitro group at C2 twists slightly out of the plane of the pyrazole ring, while the nitro group at C1 has a larger twist angle.

A series of short intermolecular O…O and O…N contacts could be observed in the crystals, indicating the presence of weak interactions between the single molecules in the solid state. However, only a few hydrogen bonding interactions were found in 10, 13 and 15 · 2H₂O (Fig. 3).

To gain more insight into the intermolecular interactions, two-dimensional (2D) fingerprints of crystals and the associated Hirshfeld surfaces (Fig. 4) were analyzed using Crystalexplorer 17.5 (ref. 18). The red and blue areas on the Hirshfeld surfaces represent high and low close contact populations, respectively. Fig. 4 shows red dots scattered in many orientations, mainly near the oxygen atoms of the trinitromethyl, nitro, and carbonyl groups, thus indicating strong intermolecular O···O, N···O, O··· N, and O…C interactions. In addition to these interactions, compounds 11 and 14 have apparent Cl--O interactions between the chlorine and the oxygen atoms of the nitro groups



Fig. 3 Packing diagrams of 10–15 (a–f). Unit cell indicated and dashed lines represent hydrogen bonding.

in the adjacent molecule. Compounds 10, 13 and 15 also have H…O interactions, that is, hydrogen bonds. Furthermore, in the 2D fingerprint plots of crystal 13 (Fig. 4k), a pair of spikes on bottom left (H…O & O…H interactions) indicate intermolecular hydrogen bonds. While, there is only one spike in 15, because its molecule contains no hydrogen and only acts as hydrogen bond acceptors. According to the di + de values of the spikes, it can be seen that the O···H hydrogen bonds in 15 are stronger than the N···H hydrogen bonds in 13. In fact, there are also weak $O \cdots H$ interactions in **10**, and their proportion (28.2%) is even higher than those (22.8%) in 13. Except for compound 15, the proportions of O···O interactions are more than 50%, indicating that compounds 10-14 are high dense. Since the oxygen atoms are in the trinitromethyl and nitro groups, higher proportion of close O···O contacts indicates that more nitro groups exposed on the molecular surface, may leading to an increased possibility of unexpected explosion.

Physicochemical and energetic properties

To identify the decomposition temperatures of high energy density compounds 10-15, differential scanning calorimetry

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Fig. 4 (a–c) Hirshfeld surface, 2D fingerprint plot, and pie graph of the individual atomic contact percentage for 10. (d–f) Hirshfeld surface, 2D fingerprint plot, and pie graph of the individual atomic contact percentage for 11. (g–i) Hirshfeld surface, 2D fingerprint plot, and pie graph of the individual atomic contact percentage for 12. (j–l) Hirshfeld surface, 2D fingerprint plot, and pie graph of the individual atomic contact percentage for 13. (m–o) Hirshfeld surface, 2D fingerprint plot, and pie graph of the individual atomic contact percentage for 14. (p–r) Hirshfeld surface, 2D fingerprint plot, and pie graph of the individual atomic contact percentage for 14. (p–r) Hirshfeld surface, 2D fingerprint plot, and pie graph of the individual atomic contact percentage for 14. (p–r)

(DSC) with a heating rate of 5 °C min⁻¹ was used. The results are shown in Fig. 5 and Table 1.

Among the six title compounds, only compounds **11** and **14** containing chlorine substituents have obvious endothermic peaks before decomposition, and the corresponding melting points were 72 °C (**11**) and 69 °C (**14**), respectively. All other compounds are directly decomposed without going through the melting process (Fig. 5). The decomposition temperatures of



Fig. 5 DSC curves of compounds 10-15 measured with a heating rate of 5 °C min⁻¹.

10–14 range from 128 to 145 °C, which are consistent with the decomposition temperatures of most trinitromethyl functionalized compounds.¹⁹ Compound **14**, as an isomer of **11**, has a decomposition temperature nearly 10 °C higher than that of **11**. *N*-dinitromethyl substituted nitropyrazole **15** are more thermally stable than all *N*-trinitromethyl substituted nitropyrazoles.

The mechanical sensitivities of compounds 10-15 toward impact (IS) and friction (FS) were determined by using a BAM drop hammer apparatus and BAM friction tester, respectively. The results are summarized in Table 1. Compound 12 (IS = 3 J, FS = 50 N) is the most sensitive among them, due to the structure of its diazonium inner salt. N-trinitromethyl makes its impact sensitivity higher than that of the unsubstituted 4-diazo-5-nitro-pyrazol-3-one (IS = 4.5 J),¹⁷ but the friction sensitivity is slightly reduced. Six nitro groups are in one molecule of 10, resulting in its impact and friction sensitivities of 5 J and 100 N. Other compounds have sensitivities ranging from 10-20 J and 180-240 N, which are more insensitive than RDX (7.5 J, 120 N) and HMX (7 J, 112 N).20 It is worth mentioning that 13 has a "NO2-NH2-NO2" structure similar to TATB and LLM-105, which may be an important reason for its lower sensitivity than 1-trinitromethyl-3,4,5-trinitropyrazole (7 J, 120 N).10a

The electrostatic potential (ESP) on the molecular surface here is used to analyze the relationship between molecular structure and impact sensitivity. The ESP-mapped vdW surfaces of **10–15** are shown in Fig. 6, with electron-rich areas marked blue and electron-deficient marked red. Surface local maxima and minima of ESP are represented as orange and cyan spheres, respectively. We can see that the positive electrostatic potential is mainly distributed near the pyrazole ring and the methyl, chlorine, amino and diazo groups. The negative electrostatic

Table 1 Physicochemical properties of 10, 11, 12, 13, 14 and 15

Compound	Formula	$T_{d}^{a} [^{\circ}C]$	$ ho^{b} \left[\mathrm{g \ cm^{-3}} \right]$	$\Delta H_{\rm f}^{\ c} \left[{\rm kJ} \ {\rm mol}^{-1} \right]$	$D^d \left[{ m m \ s^{-1}} ight]$	P ^e [GPa]	$\mathrm{IS}^{f}[\mathrm{J}]$	$FS^{g}[N]$	$OB(CO_2)^h$ [%]	N^{i} [%]	$N + O^{j} [\%]$	$I_{\mathrm{sp}}^{ k} [\%]$	η^l
10	C ₅ H ₃ N ₉ O ₁₂	139	1.853	516.67	9082	36.3	5	100	+2.1	33.08	83.45	272.4	1.04
11	C ₄ ClN ₇ O ₁₀	136	1.924	457.47	8438	31.5	10	220	+11.7	28.71	75.55	251.4	0.98
12	$C_4N_8O_9$	128	1.891	479.75	9023	35.2	3	50	+5.3	36.85	84.20	263.7	1.04
13	$C_4H_2N_8O_{10}$	143	1.866	389.92	9030	35.6	12	240	+5.0	34.79	84.46	266.5	1.03
14	$C_4 ClN_7 O_{10}$	145	1.859	456.38	8184	29.0	15	200	+11.7	28.71	75.55	251.4	0.95
15	$C_4N_6O_9$	179	1.861	386.55	8821	33.7	20	180	+5.8	30.44	82.60	264.6	1.04
RDX^{20}	$C_3H_6N_6O_6$	210	1.806	86.3	8801	33.6	7.5	120	-21.61	37.84	81.06	258	0.96
HMX ²⁰	$\mathrm{C_4H_8N_8O_8}$	279	1.904	116.1	9193	37.8	7	112	-21.61	37.84	81.06	258	1.00

^{*a*} Decomposition temperature (onset temperature from DSC at a heating rate of 5 °C min⁻¹). ^{*b*} Density, measured at 25 °C by a gas pycnometer. ^{*c*} Heat of formation. ^{*d*} Detonation velocity calculated by EXPLO5 V6.05.04. ^{*e*} Detonation pressure calculated by EXPLO5 V6.05.04. ^{*f*} Impact sensitivity. ^{*g*} Friction sensitivity. ^{*h*} Oxygen balance for C_aH_bO_cN_d, 1600(c-2a-b/2)/M_{wi}; M_w = molecular weight. ^{*i*} Nitrogen content. ^{*j*} Nitrogen and oxygen content. ^{*k*} Specific impulse calculated by EXPLO5 V6.05.04. ^{*l*} Calculated metal acceleration ability by Muravyev–Wozniak–Piercey method.



Fig. 6 The ESP-mapped vdW surfaces of 10-15 (a-f). ESP colour (blue-white-red) range from -0.04 to +0.04 Hartrees (a.u.).

potential is mainly distributed around the oxygen atoms of the nitro or carbonyl groups. According to the results of the Multiwfn²¹ analysis, the average values of the positive electrostatic potential of the six compounds are greater than those of the negative electrostatic potential. The charge distribution of the molecular surface of impact-sensitive compounds corresponds to electron-poor areas above C–NO₂ bonds. Molecules that are more sensitive to impact have a larger electron deficiency (larger maxima of ESP) in this region than molecules that are less sensitive.²² Compounds **12** and **10** show extremely intense electropositive areas, and the contrast is considerably stronger

than others, which corresponds to the higher impact sensitivities and fits with the results of studies by Murray and Politzer.²³ It is worth mentioning that, the area of the positive potential region (128.7 Å²) in **13** is slightly smaller than the negative potential region (129.4 Å²), which is contrary to the general phenomenon in high energy density compounds. This may be an important reason for its relative insensitivity. For the dinitromethyl substituted **15**, the electron density appears to be more evenly distributed over the molecular surface than in the case for the trinitromethyl substituted **10–14**. This would account for a lower impact sensitivity of **15** (20 J) compared to **11–14** (3–15 J).

Their densities were determined at room temperature by a gas pycnometer to be 1.853 (10) to 1.924 g cm⁻³ (11), which are higher than that of RDX (1.80 g cm^{-3}). Heats of formation were calculated using the Gaussian 09 (Revision A.02) suite of programs²⁴ with isodesmic reactions (ESI[†]). Compounds 10-15 have relatively high positive heats of formation (ΔH_f) falling between 386.55 (15) and 516.67 (10) kJ mol⁻¹, which exceed both RDX (86.3 kJ mol⁻¹) and HMX (116.1 kJ mol⁻¹). Using the calculated $\Delta H_{\rm f}$ values and the measured densities, the detonation parameters of 10-15 were calculated using the EXPLO5 V6.05.04 program.²⁵ Their detonation pressures (P) were predicted to be 29.0-36.3 GPa and the detonation velocities (D) is 8184-9082 m s⁻¹. Compounds 10, 12, 13, and 15 exhibited higher detonation properties compared to RDX (P = 33.6 GPa, D $= 8801 \text{ m s}^{-1}$).²⁰ In addition, the results calculated according to the Muravyev-Wozniak-Piercey method²⁶ show that compounds 10, 12, 13, and 15 have slightly higher metal acceleration abilities (1.03-1.04) than HMX (1.00).

Energetic materials with a zero or positive oxygen balance (OB) convert all C into CO_2 and all H into H_2O . It is desirable that the energy can be completely released upon explosion while producing a minimal amount of toxic gas, so they can be considered "greener" than those with negative OBs.²⁷ The OB values of **10–15** are all positive (+2.1% to +11.7%), indicating that they are potential high-energy oxidizers for solid propellants. Therefore, specific impulse (I_{sp}), the most significant measure of the efficiency of a propellant (in seconds), was also calculated by using EXPLO5 V6.05.04.²⁵ Compounds **10, 12, 13**, and **15** have specific impulses of 263.7–272.4 s, which are much



higher than those of AP (157 s), 19 ADN (202 s) 19 and HMX (258 s). 20

Introduction of a N-trinitromethyl moiety is an effective way to enhance the OB of an energetic material. This is seen with the N-trinitromethyl substituted nitropyrazoles 10 (+2.1%), 12 (+5.3%), and 13 (+5.0%) having higher OB than their analogues N-(3,5-dinitro-1*H*-pyrazol-4-yl)-*N*-methylnitramide (-27.6%),^{5b} 4-diazo-5-nitro-pyrazol-3-one $(-36.1\%),^{17}$ and LLM-116 (-32.4%).^{6b} In addition to the OB, their densities and heats of formation also increased to varying degrees (only the density of 13 decreased by 0.03 g cm^{-3}). In turn, their detonation velocities, detonation pressures, and metal acceleration abilities have all increased (Fig. 7). Taken together, these comparisons highlight the N-trinitromethyl strategy as an efficient functional modification to enhance OB and energy properties.

Conclusions

In conclusion, a series of N-trinitromethyl-substituted polynitro-pyrazoles were obtained by a simple and efficient synthesis, including N-acetomethylation followed by N-trinitromethylation. The novel compounds and their precursors were characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis, IR spectroscopy, and differential scanning calorimetry. The structures of 2, 6, 7, and 10-15 were confirmed by single-crystal X-ray diffraction. Compound 10 exhibits excellent energetic performance ($\rho = 1.853 \text{ g cm}^{-3}$; $\Delta H_{\rm f} = 516.67 \text{ kJ mol}^{-1}$; $D = 9082 \text{ m s}^{-1}$; P = 36.3 GPa), has a positive OB of +2.1%, and a promising specific impulse (272.4 s), making it an applicable high-energy dense oxidizer to replace AP in solid rocket propellants. The nitration of 7 with HNO₃/H₂SO₄ mixed acid generated in situ yielded the diazonium inner salt of polynitropyrazole 12, the higher density, higher performance, better oxygen balance and lower sensitivity of which relative to diazodinitrophenol (DDNP) make it a competitive candidate as a green primary explosive. Compound 13 is a secondary explosive with a high OB (+5.0%), comparable energy ($D = 9030 \text{ m s}^{-1}$; P = 35.6 GPa; $\eta = 1.03$) to HMX, and much lower sensitivity to external stimuli (IS = 12 J, FS = 240 N).

Experimental

Caution! All the nitro compounds are energetic materials. And they tend to explode unpredictably, under certain conditions. Caution should be exercised at all times during the handling of any of these compounds. Leather coat, ear protection, latex gloves, and face shield are strongly recommended for the experimental operation.

4-Chloro-3,5-dinitro-1*H*-pyrazole (1),^{12b} *N*-methyl-3,5-dinitro-1*H*-pyrazol-4-amine (2),^{5b} ammonium 4-amino-3,5-dinitropyrazole-1-ide (3),^{12b} 3,4,5-trinitro-1*H*-pyrazole (4),^{6c} 1-(4-amino-3,5-dinitro-1*H*-pyrazol-1-yl)propan-2-one (7),⁹ and 1-(3,4,5-trinitro-1*H*-pyrazol-1-yl)propan-2-one (9)²⁸ were synthesized according to the literature.

1-(4-(Methylamino)-3,5-dinitro-1*H*-pyrazol-1-yl)propan-2-one (5)

A solution of bromoacetone (2.88 g, 21 mmol, 1.765 mL) in acetone (3 mL) was added drop-wise to a solution of compound 2 (3.74 g, 20 mmol) and NaOH (0.8 g, 20 mmol) in water (10 mL). The resulting mixture was stirred at room temperature for 18 h and a precipitate was isolated, which was washed with ice-water (20 mL), dried in air, giving 5 as a brown solid (3.95 g, 81.3%). $T_{\rm m}$: 143 °C. ¹H NMR: δ 7.41, 7.40, 5.61, 2.98, 2.97, 2.26 ppm; ¹³C NMR: δ 200.36, 141.71, 132.58, 130.69, 33.17, 26.93 ppm. IR (ATR): $\tilde{\nu}$ 3352, 2940, 2360, 1729, 1608, 1518, 1486, 1435, 1415, 1382, 1366, 1331, 1306, 1208, 1178, 1119, 1035, 898, 830, 815, 790, 745, 658, 611, 581 cm⁻¹. Elemental analysis for C₇H₉N₅O₅ (243.179): calcd C 34.57, H 3.73, N 28.80%. Found: C 34.49, H 3.66, N 28.72%.

1-(4-Chloro-3,5-dinitro-1H-pyrazol-1-yl)propan-2-one (6)

a solution of bromoacetone (2.88 g, 21 mmol, 1.765 mL) in acetone (3 mL) was added drop-wise to a solution of compound 1 (3.85 g, 20 mmol) and NaOH (0.8 g, 20 mmol) in water (10 mL). The resulting mixture was stirred at room temperature for 18 h and a precipitate was isolated, which was washed with ice-water (20 mL), dried in air, giving **6** as a white solid (4.30 g, 86.5%). $T_{\rm m}$: 117 °C. ¹H NMR: δ 5.82, 2.32 ppm; ¹³C NMR: δ 199.63,

148.66, 142.53, 106.13, 64.15, 26.96 ppm. IR (ATR): $\tilde{\nu}$ 3585, 3015, 2938, 2359, 1737, 1557, 1538, 1501, 1448, 1408, 1361, 1317, 1205, 1174, 1144, 1071, 1045, 993, 895, 826, 813, 789, 744, 685, 647, 631, 549 cm⁻¹. Elemental analysis for $C_6H_5ClN_4O_5$ (248.579): calcd C 28.99, H 2.03, N 22.54%. Found: C 28.92, H 2.11, N 22.48%.

1-(5-Chloro-3,4-dinitro-1H-pyrazol-1-yl)propan-2-one (8)

Compound 4 (0.609 g, 3 mmol) was dissolved in DMF (3 mL), followed by the addition of sodium bicarbonate (0.252 g, 3 mmol) and potassium bromide (0.357 g, 3 mmol) in stirring. The reaction system was heated to 70 °C, then chloroacetone (0.333 g, 3.6 mmol, 0.287 mL) was added drop-wise, and the reaction was maintained at 70 °C for 2 h. After cooling to room temperature, the reaction was quenched in cold water and a precipitate was isolated, which was washed with ice-water (20 mL), dried in air, giving 8 as a white solid (0.223 g, 29.9%). $T_{\rm m}$: 131 °C. ¹H NMR: δ 5.61, 2.30 ppm; ¹³C NMR: δ 199.12, 147.12, 131.34, 123.29, 60.12, 27.00 ppm. IR (ATR): v 2999, 2954, 2184, 2173, 1993, 1965, 1731, 1538, 1506, 1428, 1400, 1361, 1336, 1310, 1200, 1174, 1071, 1061, 986, 900, 849, 833, 814, 795, 754, 698, 662, 648, 621, 587, 544 cm⁻¹. Elemental analysis for C₆H₅ClN₄O₅ (248.579): calcd C 28.99, H 2.03, N 22.54%. Found: C 29.06, H 2.09, N 22.49%.

N-(3,5-Dinitro-1-(trinitromethyl)-1H-pyrazol-4-yl)-Nmethylnitramide (10)

Compound 5 (0.365 g, 1.5 mmol) was added to an ice-cold 98% H_2SO_4 (2.4 mL) and the mixture was stirred at 0-5 °C for 30 min. Then 98% HNO₃ (2.6 mL) was added drop-wise into the mixture at 0 °C. After slowly warming to room temperature, the mixture was heated to 60 °C. The final reaction was stirred at 60 °C for 2 h. After pouring into ice-water with vigorous stirring, the final mixture was filtered, washed with ice-water and dried in air, giving **10** as a white solid (0.40 g, 70.0%). T_d : 139 °C. ¹H NMR: δ 3.81 ppm; ¹³C NMR: δ 206.56, 152.40, 142.14, 119.66, 41.22 ppm. IR (ATR): v 3566, 2934, 2360, 1646, 1633, 1610, 1559, 1478, 1454, 1434, 1397, 1365, 1329, 1289, 1261, 1242, 1150, 1087, 1062, 991, 945, 862, 837, 822, 794, 766, 752, 667, 592, 562 cm⁻¹. Elemental analysis for C₅H₃N₉O₁₂ (381.130): calcd C 15.76, H 0.79, N 33.08%. Found: C 15.82, H 0.81, N 33.11%.

4-Chloro-3,5-dinitro-1-(trinitromethyl)-1H-pyrazole (11)

Compound 6 (1.39 g, 5.6 mmol) was added to an ice-cold 98% H_2SO_4 (6.0 mL) and the mixture was stirred at 0–5 °C for 30 min. Then 98% HNO₃ (6.5 mL) was added drop-wise into the mixture at 0 °C. After slowly warming to room temperature, the mixture was heated to 60 °C. The final reaction was stirred at 60 °C for 5 h. After pouring into ice-water with vigorous stirring, the final mixture was filtered, washed with ice-water and dried in air, giving **11** as a white solid (1.25 g, 65.4%). *T*_m: 72 °C; *T*_d: 136 °C. ¹³C NMR: δ 206.91, 154.58, 144.41, 115.41 ppm. IR (ATR): $\tilde{\nu}$ 3586, 2935, 2360, 1737, 1646, 1627, 1606, 1575, 1533, 1428, 1390, 1314, 1257, 1167, 1090, 988, 857, 830, 816, 792, 762, 745, 724, 629, 576 cm⁻¹. Elemental analysis for $C_4 ClN_7 O_{10}$ (341.533): calcd C 14.07, N 28.71%. Found: C 14.16, N 28.78%.

4-Diazo-5-nitro-2-(trinitromethyl)-2,4-dihydro-3H-pyrazol-3one (12)

Compound 7 (0.343 g, 1.5 mmol) was added to an ice-cold 98% H_2SO_4 (2.4 mL) and the mixture was stirred at 0-5 °C for 30 min. Then 98% HNO₃ (2.6 mL) was added drop-wise into the mixture at 0 °C. After slowly warming to room temperature, the mixture was heated to 60 °C. The final reaction was stirred at 60 °C for 3 h. After pouring into ice-water with vigorous stirring, the final mixture was filtered, washed with ice-water and dried in air, giving **12** as a white solid (0.316 g, 69.3%). T_d : 128 °C. ¹³C NMR: δ 158.75, 155.20, 150.62, 123.47 ppm. IR (ATR): ν̃ 3501, 2934, 2359, 2197, 1751, 1634, 1596, 1542, 1482, 1446, 1389, 1357, 1319, 1262, 1193, 1156, 1061, 1023, 995, 860, 837, 822, 792, 763, 725, 696, 674, 638, 606, 567 cm⁻¹. Elemental analysis for C₄N₈O₉ (304.091): calcd C 15.80, N 36.85%. Found: C 15.73, N 36.82%.

3,5-Dinitro-1-(trinitromethyl)-1H-pyrazol-4-amine (13)

Compound 7 (0.343 g, 1.5 mmol) was added to an ice-cold 98% H_2SO_4 (2.4 mL) and the mixture was stirred at 0–5 °C for 30 min. Then 98% HNO₃ (2.6 mL) was added drop-wise into the mixture at 0 °C. After slowly warming to room temperature within 2 h, the final reaction was stirred at room temperature for 6 h. After pouring into ice-water with vigorous stirring, the insoluble impurities were filtered off, and the filtrate was left to stand for 12 h, and a large amount of precipitates were formed. Washed with ice-water and dried in air, giving 13 as a pale solid (0.217 g, 44.9%). T_d : 143 °C. ¹H NMR: δ 8.07 ppm; ¹³C NMR: δ 206.41, 148.76, 133.18, 130.74 ppm. IR (ATR): $\tilde{\nu}$ 3675, 3484, 3361, 2987, 2901, 2199, 1756, 1659, 1633, 1618, 1599, 1578, 1539, 1469, 1388, 1310, 1265, 1224, 1066, 1052, 975, 863, 838, 820, 794, 758, 738, 691, 655, 639, 597 cm⁻¹. Elemental analysis for C₄H₂N₈O₁₀ (322.106): calcd C 14.92, H 0.63, N 34.79%. Found: C 14.99, H 0.66, N 34.85%.

5-Chloro-3,4-dinitro-1-(trinitromethyl)-1H-pyrazole (14)

Compound 8 (1.39 g, 5.6 mmol) was added to an ice-cold 98% H_2SO_4 (6.0 mL) and the mixture was stirred at 0-5 °C for 30 min. Then 98% HNO₃ (6.5 mL) was added drop-wise into the mixture at 0 °C. After slowly warming to room temperature, the mixture was heated to 60 °C. The final reaction was stirred at 60 °C for 3 h. After pouring into ice-water with vigorous stirring, the final mixture was filtered, washed with ice-water and dried in air, giving 14 as a white solid (1.07 g, 56.1%). T_m: 69 °C; T_d: 145 °C. ¹³C NMR: δ 206.25, 151.88, 136.72, 124.90 ppm. IR (ATR): ν̃ 2887, 1966, 1621, 1606, 1563, 1537, 1487, 1456, 1361, 1328, 1265, 1140, 1084, 981, 965, 863, 834, 812, 791, 764, 701, 662, 634, 623, 599, 571, 565, 551 cm⁻¹. Elemental analysis for $C_4 ClN_7 O_{10}$ (341.533): calcd C 14.07, N 28.71%. Found: C 14.12, N 28.76%.

1-(Dinitromethylene)-3,4-dinitro-5-oxo-4,5-dihydro-1Hpyrazol-1-ium-4-ide (15)

Compound 9 (0.389 g, 1.5 mmol) was added to an ice-cold 98% H_2SO_4 (2.4 mL) and the mixture was stirred at 0-5 °C for 30 min. Then 98% HNO₃ (2.6 mL) was added drop-wise into the mixture at 0 °C. After slowly warming to room temperature within 2 h, the final reaction was stirred at room temperature for 6 h. After pouring into ice-water with vigorous stirring, the solution was left to stand for 12 h, a small amount of precipitates were formed. Washed with ice-water and dried in air, giving **15** as a white solid (0.154 g, 37.2%). $T_{\rm d}$: 179 °C. ¹³C NMR: δ 200.33, 140.25, 131.54, 130.15 ppm. IR (ATR): $\tilde{\nu}$ 1635, 1511, 1372, 1318, 1279, 1122, 1044, 824, 756, 559 cm⁻¹. Elemental analysis for C₄N₆O₉ (276.077): calcd C 17.40, N 30.44%. Found: C 17.33, N 30.51%.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe and A. Subhananda Rao, *J. Hazard. Mater.*, 2009, 161, 589–607; (b) D. G. Piercey, D. E. Chavez, B. L. Scott, G. H. Imler and D. A. Parrish, *Angew. Chem., Int. Ed.*, 2016, 55, 15315–15318.
- 2 (a) T. M. Klapötke, C. Petermayer, D. G. Piercey and J. Stierstorfer, J. Am. Chem. Soc., 2012, 134, 20827–20836;
 (b) P. Yin, Q. Zhang and J. M. Shreeve, Acc. Chem. Res., 2016, 49, 4–16; (c) W. Zhang, J. Zhang, M. Deng, X. Qi, F. Nie and Q. Zhang, Nat. Commun., 2017, 8, 181; (d) P. Yin, J. Zhang, G. H. Imler, D. A. Parrish and J. M. Shreeve, Angew. Chem., Int. Ed., 2017, 56, 8834–8838.
- 3 (*a*) H. Gao and J. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377–7436; (*b*) A. A. Dippold and T. M. Klapötke, *J. Am. Chem. Soc.*, 2013, **135**, 9931–9938.
- 4 (a) Y. Qu and S. P. Babailov, *J. Mater. Chem. A*, 2018, **6**, 1915–1940; (b) Y. Zhang, Y. Li, J. Hu, Z. Ge, C. Sun and S. Pang, *Dalton Trans.*, 2019, **48**, 1524–1529.
- 5 (a) S. Zhang, Z. Gao, D. Lan, Q. Jia, N. Liu, J. Zhang and K. Kou, *Molecules*, 2020, 25, 3475; (b) C. He, J. Zhang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2013, 1, 2863–2868; (c) M. Deng, Y. Feng, W. Zhang, X. Qi and Q. Zhang, *Nat. Commun.*, 2019, 10, 1339; (d) H. Huang, Y. Shi, H. Li, H. Li, A. Pang and J. Yang, *Org. Lett.*, 2020, 22, 5866–5869.
- 6 (a) S. Ek and N. V. Latypov, J. Heterocycl. Chem., 2014, 51, 1621–1627; (b) M. Zhang, P. F. Pagoria, G. H. Imler and D. Parrish, J. Heterocycl. Chem., 2019, 56, 781–787; (c) G. Hervé, C. Roussel and H. Graindorge, Angew. Chem., Int. Ed., 2010, 49, 3177–3181; (d) Y. Li, Y. Shu, B. Wang, S. Zhang and L. Zhai, RSC Adv., 2016, 6, 84760–84768; (e) W. Zhang, H. Xia, R. Yu, J. Zhang, K. Wang and Q. Zhang, Propellants, Explos., Pyrotech., 2020, 45, 546–553; (f) P. Yin,

- J. Zhang, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2016, 55, 12895–12897.
- 7 (a) Y. Feng, J. Wang and Z. Li, Cryst. Growth Des., 2021, 21, 4725-4731; (b) Y. Zhang, Y. Huang, D. A. Parrish and J. M. Shreeve, J. Mater. Chem., 2011, 21, 6891-6897; (c) M. F. Bölter, A. Harter, T. M. Klapötke and J. Stierstorfer, ChemPlusChem, 2018, 83, 804-811.
- 8 (a) P. Yin, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *Chem.-Asian J.*, 2017, 12, 378–384; (b) P. Yin, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2016, 55, 14409–14411.
- 9 B. Guo, X. Zhang, X. Lin, H. Huang and J. Yang, *New J. Chem.*, 2021, **45**, 20426–20431.
- 10 (a) W. Zhang, Y. Yang, Y. Wang, T. Fei, Y. Wang, C. Sun and S. Pang, *Chem. Eng. J.*, 2023, 451, 138609; (b) I. L. Dalinger, I. A. Vatsadze, T. K. Shkineva, A. V. Kormanov, M. I. Struchkova, K. Yu. Suponitsky, A. A. Bragin, K. A. Monogarov, V. P. Sinditskii and A. B. Sheremetev, *Chem.-Asian J.*, 2015, 10, 1987–1996.
- 11 D. Kumar, G. H. Imler, D. A. Parrish and J. M. Shreeve, J. Mater. Chem. A, 2017, 5, 10437–10441.
- 12 (a) J. Zhang, C. He, D. A. Parrish and J. M. Shreeve, *Chem.-Eur. J.*, 2013, **19**, 8929–8936; (b) D. Fischer, J. L. Gottfried, T. M. Klapötke, K. Karaghiosoff, J. Stierstorfer and T. G. Witkowski, *Angew. Chem., Int. Ed.*, 2016, **55**, 16132– 16135; (c) P. Yin, J. Zhang, D. A. Parrish and J. M. Shreeve, *Chem.-Eur. J.*, 2014, **20**, 16529–16536.
- 13 (a) I. L. Dalinger, I. A. Vatsadze, T. K. Shkineva, G. P. Popova, S. A. Shevelev and Y. V. Nelyubina, *J. Heterocycl. Chem.*, 2013, 50, 911–924; (b) P. Yin, C. He and J. M. Shreeve, *J. Mater. Chem. A*, 2016, 4, 1514–1519.
- 14 (a) P. Yin, J. Zhang, C. He, D. A. Parrish and J. M. Shreeve, J. Mater. Chem. A, 2014, 2, 3200–3208; (b) G. Li, H. Huang, J. Yang, C. Yan, W. Li and H. Duan, Polyhedron, 2021, 199, 115098; (c) P. Yin, D. A. Parrish and J. M. Shreeve, Chem.– Eur. J., 2014, 20, 6707–6712.
- 15 Y. Zhang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem.*, 2012, 22, 12659–12665.
- 16 Y. Xu, C. Shen, Q. Lin, P. Wang, C. Jiang and M. Lu, *J. Mater. Chem. A*, 2016, 4, 17791–17800.
- 17 Y. Du, J. Zhang, P. Peng, H. Su, S. Li and S. Pang, New J. Chem., 2017, **41**, 9244–9249.
- 18 M. A. Spackman and D. Jayatilaka, *CrystEngComm*, 2009, 11, 19–32.
- 19 Q. Yu, F. Li, P. Yin, S. Pang, R. J. Staples and J. M. Shreeve, *J. Mater. Chem. A*, 2021, **9**, 24903–24908.
- 20 N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey and J. Stierstorfer, *J. Mater. Chem.*, 2012, **22**, 20418–20422.
- 21 T. Lu and F. Chen, J. Comput. Chem., 2012, 33, 580-592.
- 22 A. Hammerl, T. M. Klapötke, H. Nöth and M. Warchhold, *Propellants, Explos., Pyrotech.*, 2003, **28**, 165–173.
- 23 (a) J. S. Murray, M. C. Concha and P. Politzer, *Mol. Phys.*, 2009, 107, 89–97; (b) P. Politzer, J. S. Murray, J. M. Seminario, P. Lane, M. E. Grice and M. C. Concha, *THEOCHEM*, 2001, 573, 1–10.
- 24 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,

B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato,
X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng,
J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota,
R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda,
O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd,
E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi,
J. Normand, K. Raghavachari, A. Rendell, J. C. Burant,
S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam,
M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo,
J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev,
A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,

P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford, CT, 2009.

- 25 M. Sućeska, *EXPLO5 V6.05.04*, Brodarski Institute, Zagreb, Croatia, 2020.
- 26 N. V. Muravyev, D. R. Wozniak and D. G. Piercey, *J. Mater. Chem. A*, 2022, **10**, 11054–11073.
- 27 C. He and J. M. Shreeve, Angew. Chem., Int. Ed., 2016, 55, 772–775.
- 28 S. Zhang, F. Wang, X. Li, K. Yu, X. Qiu, C. Zhu and Z. Zhou, *Chinese invention Pat.*, CN114149372A, 2021.