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Energetic C-trinitromethyl-substituted pyrazoles: synthesis and characterization[†]

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A new family of *C*-trinitromethyl-substituted pyrazoles was designed and obtained in good yields by the reaction of N_2O_4 with the pyrazolecarbaldehyde oxime followed by further N-nitration and C-nitration. All of the new compounds were fully characterized by IR and NMR spectroscopy, elemental analysis and differential scanning calorimetry (DSC). Compounds **2** and **3** were further confirmed by X-ray crystallography. These pyrazole derivatives have good densities, positive enthalpies of formation and acceptable sensitivity values. Theoretical calculations carried out using Gaussian 03 and EXPLO5 program demonstrate good to excellent detonation velocities and pressures in the range of ADN and HMX. Compound **3** exhibiting a positive oxygen balance, high specific impulse and moderate thermal stability is a promising high energy density oxidizer.

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Introduction

The synthesis of novel energetic materials with improved performance and decreased sensitivity continues to be the ceaseless pursuit of researchers.¹ In recent years, polynitro-functionalized heterocycles have become an intense research area in the development of high performance energetic materials with not only excellent detonation properties, high densities and positive oxygen balances, but also good thermal stabilities and insensitivities to impact and friction.² The introduction of nitro groups *via* C- and N-functionalization tends to improve the densities and overall energetic performance of molecules. Therefore, design of polynitro-functionalized compounds is one of the most attractive tasks in the pursuit of ideal energetic materials, while seeking rational introduction methods of nitro groups plays a significant role in the synthesis of these important compounds.

Pyrazole ring has been frequently chosen as the fundamental component of energetic molecular structure for possessing large enthalpy of formation, high density and achieving positive oxygen balance easily.³ At the same time, the three catenated carbon atoms in pyrazole not only enhance thermal stability and impact insensitivity, but also endow the backbone with an opportunity for further functionalizations. In recent years, many nitropyrazole derivatives have been designed and synthesized as promising energetic materials (Fig. 1), such as 3,4-dinitropyrazole,⁴ 3,5-dinitropyrazole,⁴ 4-amino-3,5-dinitropyrazole,⁵ 3,4,5-trinitropyrazole⁶ and 3,4,5-trinitro-1-(nitromethyl)-1*H*-pyrazole.⁷ Moreover, significant work has been directed toward their preparation, theoretical calculations, thermal behavior, reactivity, and applications.

Among the nitro-based moieties, the trinitromethyl group has the highest oxygen content, and its introduction to a molecule is essentially equivalent to adding two nitro groups (since one of the nitro groups is necessary for the complete oxidation of the carbon atom in the methyl group). The incorporation of trinitromethyl groups into heterocycles is of interest to energetic materials industries for increasing the OB so as to improve the detonation performance. Typically, the wellknown preparation methods of trinitromethyl-substituted compounds involve condensation of the amino derivative with trinitroethanol and destructive nitration of a methylene active $RCH_2C(O)Me$, $RCH_2CH_2C(O)Me$, compound including RCH₂COOH, and so on.⁸ Trinitromethyl functionalized pyrazoles are expected to be excellent energetic materials with high densities and promising detonation properties. Recently, several pyrazole derivatives bearing trinitromethyl groups in

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Fig. 1 Examples of polynitropyrazole derivatives.



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Fig. 2 Representative pyrazole derivatives bearing trinitromethyl groups as oxygen-rich high performance energetic materials.

the N position have been synthesized as oxygen-rich high performance energetic materials (Fig. 2). For example, *N*-trinitroethylamino pyrazoles were synthesized by Shreeve *et al.* through Mannich reactions between N-amino nitropyrazoles and trinitroethanol.⁹ Later *N*-trinitromethyl nitropyrazoles were synthesized by destructive nitration of the corresponding *N*-acetonylpyrazoles.¹⁰ However, to the best of our knowledge, the preparation of *C*-trinitromethyl-substituted pyrazoles which may also hold considerable energetic properties has not yet been reported.

In our continuing search for new high-performance polynitro energetic materials, we are interested in developing novel trinitromethyl-substituted heterocyclic compounds. Herein, the *C*-trinitromethyl-substituted pyrazole was first synthesized by the reaction of N_2O_4 with 3-pyrazolecarbaldehyde oxime. Afterwards, 3-trinitromethylpyrazole was subsequently nitrated in N and C positions respectively by different nitration systems to increase energetic performance. Each of these compounds was fully characterized and their energetic properties were determined either empirically or theoretically.

Results and discussion

As was stated in the introduction, the introduction of trinitromethyl group in the C atom of pyrazole was first attempted through the reaction of N₂O₄ with 3-pyrazolecarbaldehyde oxime. The 3-pyrazolecarbaldehyde oxime was chosen in the consideration of the possible further nitration on other C atoms after the successful conversion of the formaldoxime into trinitromethyl group. The raw material 3-pyrazolecarbaldehyde oxime was readily synthesized by treatment of hydroxylamine hydrochloride with 3-pyrazolecarbaldehyde. Reaction of 3-pyrazolecarbaldehyde oxime with N₂O₄ resulted in two main products: the desired 3-trinitromethylpyrazole (1) and the unexpected 1-nitro-3-trinitromethylpyrazole (2). It was found that increasing the N2O4 concentration (within the range of 0.5-2.0 mL N₂O₄ per mmol 3-pyrazolecarbaldehyde oxime) increased the relative proportion of 2 in the product mixture. Pure compound 1 reacted with N2O4 in acetonitrile also afforded compound 2 in a moderate yield. These evidences proved that compound 1 was an intermediate in the formation of compound 2 and N2O4 was able to nitrate pyrazole in the N position which has not yet been reported in previous literatures as far as we know.

After the successful introduction of trinitromethyl into pyrazole ring, compound **1** was continuously subjected to nitration by fuming nitric acid and oleum to give 4-nitro-3trinitromethylpyrazole (3). It was found that reducing of reaction temperature from 80 °C to room temperature was favorable to improve yield to 68% with the reaction time of 2 hours. Additionally, the same treatment on 2 also led to giving 3, illustrating that the N-NO₂ was removed in the nitration process. Similar to compound 1, 3 was also attempted to react with N₂O₄, but the desired N-nitration did not happen (Scheme 1).

Single crystals of 2 and 3 suitable for single-crystal XRD were obtained by the slow evaporation of dichloromethane and petroleum ether solutions of these compounds at room temperature. The crystals were stable at room temperature and were found not to be hygroscopic. Their molecular structures are shown in Fig. 3–4.

Compound 2 crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell and has a calculated density of 1.886 g cm⁻³ at 153 K (Fig. 3). The C2–C3, C3–C4, C4–N5, C2–N4 and N4–N5 bond lengths are 1.409, 1.371, 1.357, 1.337 and 1.340 Å, respectively, which are in the normal range.¹¹ The bond length of N5–N6 is 1.442 Å, which corresponds to a N–N single bond. The bond lengths of C1–N1, C1–N2 and C1–N3 in the trinitromethyl group are 1.545, 1.528 and



Scheme 1 The synthesis route of 1, 2 and 3.



Fig. 3 Left: Molecular structure of 2; Right: packing diagram of 2.



Fig. 4 Left: Molecular structure of 3; Right: packing diagram of 3.

1.532 Å, respectively, all of which are longer than a standard C–N single bond (1.460 Å).¹² The nitro group bonded to the pyrazole is twisted out of the pyrazole plane based on the O7–N6–N5–C4 torsion angle (–7.121°) and O8–N6–N5–N4 torsion angle (–8.541°).

Dalton Transactions

Compound 3 crystallizes in a monoclinic crystal system with space group $P2_1/n$ and a density of 1.840 g cm⁻³ at 153 K (Fig. 4). The bond lengths and bond angles in the pyrazole ring of this compound are in the typical ranges. The C3-N5 bond length is 1.421 Å, which is shorter than the normal C-N single bond. Similar to 2, the C-N bond lengths in the trinitromethyl groups are longer than normal C-N single bonds. Compared to 2, the nitro group bonded to the pyrazole and the pyrazole ring are twisted relatively to each other more obviously with the O8-N5-C3-C2 torsion angle (13.00°) and O7-N5-C3-C4 torsion angle (12.69°), which is probably caused by the greater influence from the trinitromethyl group in the ortho-position. In the packing diagram of 3 there are five strong inter (between the activated 1-position protons and nitro groups, 2.09-2.82 Å) molecular hydrogen bonding interactions around each molecule.

The physicochemical and energetic properties of each of the compounds are summarized in Table 1.

In this work, the thermal stabilities of all compounds were determined by differential scanning calorimetry (DSC) measurements scanning at 5 °C min⁻¹ under dry, oxygen-free nitrogen over the temperature range from 25 to 500 °C. The melting points of these trinitromethyl pyrazoles 1–3 range from 59.9 °C (2) to 147.2 °C (3), while their decomposition temperatures are in the range from 104.1 °C (1) to 154.2 °C (3). Both 1 and 2 have lower melting points than TNT, while they hold low decomposition temperatures (1, 104.1 °C; 2, 113.0 °C), which can be attributed to the well-known instability of the trinitromethyl moiety at higher temperatures. Surprisingly, compound 3 has much better thermal stability compared to isomer 2 with a decomposition temperature of 154.2 °C, which is comparable to that of ADN (159 °C).

Density is one of the most important physical properties of energetic materials. The densities of all the compounds were measured using a gas pycnometer at 25 °C, and were found to be in the range of 1.64 (1) to 1.82 g cm^{-3} (2). It is generally

considered the bulky trinitromethyl group has a negative effect on crystal packing, so the trinitromethyl-substituted compounds are not inclined to obtain high densities. For example, compound **1** holds a lower density (1.64 g cm^{-3}) compared with other polynitro pyrazole derivatives with close oxygen balance such as **1**,3-dinitropyrazole and **3**,4-dinitropyrazole. Introduction of another nitro group into **1** resulted in the formation of **2** and **3**, accompanied with the increase of density, and obviously the nitro group in the N position has a significantly greater effect than in the C position.

The enthalpies of formation were computed based on the Gaussian 03 program package.¹³ All compounds exhibit positive enthalpies of formation in the range of 208.1-311.4 kI mol⁻¹, which are more positive than those of AP (-295.8kJ mol⁻¹), ADN (-149.8 kJ mol⁻¹) as well as RDX (92.6 kJ mol⁻¹) and HMX (116.1 kJ mol⁻¹). These high positive HOFs for all trinitromethyl pyrazoles derive from the high nitrogen content. Interestingly, compared to compound 1, 2 has a increase in HOF of 50.1 kJ mol⁻¹ while the HOF of isomer 3 decreases in a value of 53.2 kJ mol⁻¹. Using the calculated enthalpies of formation and the measured densities at ambient temperature, the detonation properties of all the compounds were determined using the EXPLO5 (v6.01) program.¹⁴ The calculated detonation velocities (D) and detonation pressures (P) fall in the range of 8249–8933 m s⁻¹ and 28.6–35.9 GPa, respectively, which are all significantly superior to those of ADN. Especially, compound 2 surpasses RDX overall in term of detonation properties.

Specific impulse (I_{sp}) is an extremely important parameter which determine the efficiency of a propellant. A propellant having a high specific impulse is more efficient as it produces more thrust per unit of propellant. The specific impulse values of synthesized compounds in this study were calculated under isobaric conditions at 7 MPa with an initial temperature of 3300 K by using EXPLO5 (v6.01). As can be seen from Table 1, 2 and 3 have much higher specific impulse values (2, 274 s; 3, 269 s) than AP (157 s) and ADN (202 s).

Oxygen balance (OB), which indicates the degree to which an explosive can be oxidized, is an important index for identifying the potential of energetic materials as explosives or oxidants. It can be described as the oxygen excess that a com-

Compd	$T_{\rm m}^{\ a}$	$T_d^{\ b}$	$ ho^{c}$	$\Delta_{\mathrm{f}} H_{\mathrm{M}}{}^{d}$	D^e	P^f	$I_{\rm sp}{}^g$	IS^h	FS^i	OB^j
1	70.6	104.1	1.64	261.3	8249	28.6	273	18	>360	3.69
2	59.9	113.0	$1.82/1.85^k$	311.4	8933	35.9	274	2.5	36	18.3
3	147.2	154.2	$1.75/1.80^k$	208.1	8598	32.2	269	3	80	18.3
RDX^{l}	204	230	1.80	92.6	8795	34.9	258	7.4	120	0
HMX^m	_	287	1.91	104.8	9320	39.6	_	7.4	120	0
AP^n	_	>200	1.95	-295.8	6368	15.8	157	15	>360	26
ADN^n	93	159	1.81	-149.8	7860	23.6	202	3-5	64-72	26

Table 1 Physicochemical and energetic properties of compounds 1, 2 and 3

^{*a*} Melting point (onset) [°C]. ^{*b*} Decomposition temperature (onset) [°C]. ^{*c*} Density measured by a gas pycnometer at 25 °C [g cm⁻³]. ^{*d*} Calculated enthalpy of formation [kJ mol⁻¹]. ^{*e*} Detonation velocity [m s⁻¹]. ^{*f*} Detonation pressure [GPa]. ^{*g*} Specific impulse [s]. ^{*h*} Impact sensitivity [J]. ^{*i*} Friction sensitivity [N]. ^{*j*} Oxygen balance assuming the formation of CO at combustion (for $C_aH_bO_cN_d$, OB = 1600(*c* - *a* - *b*/2)/MW, MW = molecular weight of compound.) [%]. ^{*k*} Crystal density at 298 K, recalculated from low-temperature X-ray densities, $\rho_{298 \text{ K}} = \rho_T/(1 + \alpha_v(298 - T_0))$, $\alpha_v = 1.5 \times 10^{-4}$, T_0 is the crystal testing temperature [g cm⁻³]. ^{*i*} Ref. 15. ^{*m*} Ref. 7.

pound needs to convert all carbon into carbon monooxide, all hydrogen into water and nitrogen into dinitrogen. Compound **1**, **2** and **3** all have positive OBs, exceeding that of RDX. Isomers **2** and **3** hold a high OB value of 18.3% which is comparable to the OBs of AP and ADN. Their combined nitrogen + oxygen contents of 81% are also significantly better compared to AP (65%). These results suggest that compound **3** is quite promising high energy density oxidizer with a high oxygen balance, a thermal stability comparable to ADN and a superior specific impulse compared with AP and ADN.

The sensitivities of these compounds towards impact (IS) and friction (FS) were determined by using a BAM drop hammer apparatus and BAM friction tester, respectively. Compound 1 (IS = 18 J, FS > 360 N) has impact and friction sensitivities similar to those of TNT. As a result of the introduction of a nitro group, 2 (IS = 2.5 J, FS = 36 N) and 3 (IS = 3 J, FS = 80 N) become more sensitive than 1 and RDX (IS = 7 J, FS = 120 N), which correspond to sensitive materials.

Conclusions

C-Trinitromethyl-substituted pyrazole derivatives including 3-trinitromethylpyrazole, 1-nitro-3-trinitromethylpyrazole and 4-nitro-3-trinitromethylpyrazole have been synthesized in moderate to excellent yields. All the compounds were fully characterized and their energetic properties were both measured and calculated. They possess excellent detonation properties in the range of 8249-8933 m s⁻¹ and 28.6-35.9 GPa, respectively, which are all significantly superior to those of ADN (7860 m s⁻¹, 23.6 GPa). The oxygen balances of compounds 2 and 3 are comparable to those of AP and ADN and their sensitivity values are in the range of primary explosives. In regard of the thermal stability, compound 1 and 2 hold low decomposition temperatures (1, 104.1 °C; 2, 113.0 °C) due to the instability of the trinitromethyl moiety, however, compound 3 has moderately high thermal stability ($T_d = 154 \text{ °C}$) comparable to that of ADN (T_d = 159 °C), which is attributed to the strong intermolecular hydrogen bonding interactions. Based on an ideal combination of detonation property, oxygen balance, specific impulse and thermal stability, compound 3 can serve as a promising candidate as a new high energy density oxidizer.

Experimental

Caution: Although none of the compounds described herein exploded or detonated in the course of this research, these energetic materials should be handled with extreme care using best safety practices (including the use of personal protective equipment such as leather gloves, face shield and ear plugs).

General

All starting materials were commercially available and were used as-received. IR spectra were obtained from KBr pellets using a Nicolet Magna IR 560 spectrophotometer (Madison, USA) over the range of 4000–400 cm⁻¹. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker ARX-400 instrument (Zurich, Switzerland). Chemical shifts are reported in ppm relative to tetramethylsilane. Elemental analyses (C, H and N) were performed using an Elementar Vario EL (Bremen, Germany). Liquid chromatography (LC)-MS electrospray ionization (ESI) data were acquired with an Agilent 6120 LC-MS spectrometer (Santa Clara, CA, USA). Crystal structures were determined on a Rigaku RAXIS IP diffractometer (Rigaku Corporation, Tokyo, Japan) with the SHELXTL crystallographic software package of molecular structure. The melting and decomposition points of the compounds were determined using a TA-DSC Q2000 differential scanning calorimeter (New Castle, DE, USA) at a scanning rate of 5 °C min⁻¹. Densities were measured at 25 °C using a Micromeritics Accupyc II 1340 gas pycnometer. The impact and friction sensitivity measurements were carried out with a BAM fall hammer apparatus (BFH-10) and a BAM friction apparatus (FSKM-10), respectively.

Theoretical studies

Calculations were performed using the Gaussian 03 suite of programs. The geometric optimization of the structures and frequency analyses employed the density functional theory (DFT) B3LYP method with the 6-311+G** basis set and singlepoint energies were calculated at the MP2/6-311+G** level. Each optimized structure was characterized to determine the true local energy minima on the potential energy surface without imaginary frequencies. The heats of formation (ΔH_f) of the neutral molecules were computed using the isodesmic reaction.17 The enthalpy of each isodesmic reaction was obtained by combining the MP2/6-311+G** energy difference for the reaction, the scaled zero point energies (B3LYP/ 6-311+G**) and other thermal factors (B3LYP/6-311+G**). Using these heats of formation and densities, detonation velocities and detonation pressures were calculated using the EXPLO5 v6.01 program according to the Kamlet–Jacobs equations.¹⁸

3-Trinitromethylpyrazole (1) and 1-nitro-3-trinitromethylpyrazole (2)

In a three-necked batch reactor equipped with a reflux condenser, 3-pyrazolecarbaldehyde oxime (0.56 g, 5 mmol) was dissolved in acetonitrile (20 mL) at room temperature. N₂O₄ (5 mL) was poured into a container in ice-water bath and then added dropwise into the reactor with vigorous stirring. The reaction mixture was subsequently heated to 60 °C and maintained at this temperature for 2 h. Then the mixture was cooled to room temperature and stirred vigorously to remove residual N₂O₄. The solvent was evaporated under vacuum and the residue was purified by column chromatography, using a Biotage Isolera One apparatus with a Flash Silica-CS column (25 g), eluting with *n*-hexane and dichloromethane. 0.42 g of pure product 1 as white solid (yield 38.25%) and 0.20 g of pure product 2 as white solid (14.96%) were isolated, respectively.

1: $R_{\rm f}$ = 0.3 (silica gel, 33% hexanes/dichloromethane); $m_{\rm p}$ = 70.6 °C; $T_{\rm d}$ = 104.1 °C; ¹H NMR (600 MHz, dmso): δ 8.12 (d,

 $J = 2.4 \text{ Hz}, 1\text{H}, 7.09 \text{ (d, } J = 2.4 \text{ Hz}, 1\text{H}); {}^{13}\text{C} \text{ NMR} (151 \text{ MHz}, dmso) \delta 134.54, 132.26, 110.64, 109.33 \text{ ppm; IR (KBr): 3170, 2960, 1604, 1593, 1361, 1300, 1219, 1056, 843, 802, 777 cm^{-1}; MS (ESI)$ *m*/*z*: 216 [M - 1]⁻, 171 [M - 46]⁻; elemental analysis for C₄H₃N₅O₆: calculated C 22.13, H 1.39, N 32.26%; measured C 22.05, H 1.32, N 32.33%.

2: $R_{\rm f}$ = 0.8 (silica gel, 33% hexanes/dichloromethane); $m_{\rm p}$ = 59.9 °C; $T_{\rm d}$ = 113.0 °C; ¹H NMR (600 MHz, dmso) δ 9.17 (d, J = 3.1 Hz, 1H), 7.53 (d, J = 3.1 Hz, 1H); ¹³C NMR (151 MHz, dmso) δ 134.93, 129.31, 118.95, 112.37 ppm; IR (KBr): 3144, 1655, 1619, 1596, 1301, 1259, 1135, 1048, 816, 802, 771 cm⁻¹; MS (ESI) m/z: 261 [M - 1]⁻, 216 [M - 46]⁻; elemental analysis for C₄H₂N₆O₈: calculated C 18.33, H 0.77, N 32.07%; measured C 18.26, H 1.01, N 32.15%.

3-Trinitromethyl-4-nitropyrazole (3)

3-Trinitromethylpyrazole (1) (1.09 g, 5 mmol) was added to a mixture of fuming HNO₃ (6 mL) and oleum (4 mL), with stirring and cooling in an ice bath. Then the reaction mixture was stirred at room temperature. After 2 hours, the reaction mixture was poured into cold water and extracted with ethyl acetate. The organic solution was dried over anhydrous MgSO₄. The solvent was evaporated under vacuum and the residue was purified by column chromatography on a Biotage Isolera One apparatus using a Flash Silica-CS column (25 g) and eluting with ethyl acetate and *n*-hexane. The product 3 was isolated with satisfactory purity as a white solid (0.89 g, 67.63%). $m_{\rm p}$ = 147.2 °C; $T_{\rm d}$ = 154.2 °C; ¹H NMR (600 MHz, dmso) δ 9.45 (s, 1H); ¹³C NMR (151 MHz, dmso) δ 134.59, 133.93, 130.37, 124.63 ppm; IR (KBr): 3253, 3142, 1610, 1588, 1547, 1520, 1494, 1379, 1301, 1280, 1221, 1083, 992, 802 cm⁻¹; MS (ESI) m/z: 261 [M - 1]⁻, 216 [M - 46]⁻; elemental analysis for C₄H₂N₆O₈: calculated C 18.33, H 0.77, N 32.07%; measured C 18.23, H 1.03, N 32.12%.

Conflicts of interest

There are no conflicts to declare.

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Paper

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