Synthesis and Properties of Energetic Hydrazinium 5-Nitro-3-dinitromethyl-2H-pyrazole by Unexpected Isomerization of N-Nitropyrazole

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ABSTRACT: A new energetic salt, hydrazinium 5-nitro-3-dinitromethyl-2H-pyrazole, was synthesized using 1-nitro-3-trinitromethylpyrazole and hydrazine as raw materials and fully characterized by IR and NMR spectroscopy, elemental analysis, and X-ray crystallography. The isomerization of N-nitropyrazole in the reaction condition was first reported and the possible mechanism was explained by the density functional theory method. The salt has good density, high positive enthalpy of formation, high density, and achieving positive oxygen balance (OB) easily. Meanwhile, the nitro-based moieties including nitro, nitramino, dinitromethyl, and trinitromethyl represent the most common energetic functional groups. Given the established instability of trinitromethyl groups attached to imidazoles, triazoles, and tetrazoles into the corresponding dinitromethylide salts by the treatment with hydrazine and hydroxylamine have been reported. Based on these successful examples, 1-nitro-3-trinitromethylpyrazole was subject to attempted analogical conversion. On the other hand, C-nitropyrazoles are more stable than N-nitropyrazoles due to the higher bond dissociation energy of C=NO2 in the former. Conventionally, the isomerization of N-nitropyrazole to C-nitropyrazole occurs by thermal rearrangement in high boiling solvents (chlorobenzene, anisole, xylene, mesitylene, n-decane, N-methylformamide, propylene glycol, benzonitrile, etc.) at high temperatures (120–190 °C) for a long time (3–7 h). Given these backgrounds, 1-nitro-3-trinitromethylpyrazole exhibits not only the highest density and detonation performance but also a poor thermal stability and the highest sensitivity to impact and friction, which is the result of the combined effect of trinitromethyl and nitramine groups. Given the established instability of trinitromethyl group at high temperature, the dinitromethyl with a coplanar geometric structure is expected to give rise to a better stability as well as a lower sensitivity. Interestingly, the denitration reactions of trinitromethyl groups attached to imidazoles, triazoles, and tetrazoles into the corresponding dinitromethylide salts by the treatment with hydrazine and hydroxylamine have been reported.

INTRODUCTION

The design and synthesis of novel energetic materials with high density, high energy, and acceptable sensitivity to heat, friction (FS), and impact (IS) are useful for a variety of explosive and propellant formulations remain a challenge. In recent years, five-membered N-heterocyclic compounds (azoles) have been frequently chosen as skeletons of energetic molecules for possessing large enthalpy of formation, high density, and achieving positive oxygen balance (OB) easily. Meanwhile, the nitro-based moieties including nitro, nitramino, dinitromethyl, and trinitromethyl represent the most common energetic functional groups, which can contribute markedly to the overall performance of energetic compounds. Therefore, polynitro-functionalized azoles have emerged as extremely attractive and competitive candidates for the next generation of advanced energetic materials.

In the past few decades, a lot of effort has been dedicated to the design and synthesis of polynitropyrazoles, and a number of polynitropyrazoles are identified as promising candidates for the development of new energetic materials, such as 3,4,5-trinitropyrazole, 3,4,5-trinitro-1-(nitromethyl)-1H-pyrazole, 3,4-dinitro-N-(2,2,2-trinitroethyl)-1H-pyrazol-1-amine, and 3,5-dinitro-1-(trinitromethyl)pyrazole (Figure 1). Previously, we have reported the synthesis of C-trinitromethyl-substituted pyrazoles by the reaction of N2O4 with pyrazolecarbaldehyde oxime. Among them, 1-nitro-3-trinitromethylpyrazole exhibits not only the highest density and detonation performance but also a poor thermal stability and the highest sensitivity to impact and friction, which is the result of the combined effect of trinitromethyl and nitramine groups. Given the established instability of trinitromethyl group at high temperature, the dinitromethyl with a coplanar geometric structure is expected to give rise to a better stability as well as a lower sensitivity. Interestingly, the denitration reactions of trinitromethyl groups attached to imidazoles, triazoles, and tetrazoles into the corresponding dinitromethylide salts by the treatment with hydrazine and hydroxylamine have been reported.

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projected to undergo denitration and isomerization to gain a better stability and lower sensitivity; meanwhile, too much of a detonation performance penalty should also be avoided.

In our continuing efforts to prepare new high-performance polynitro compounds, we now report the design and synthesis of a new dinitromethylpyrazole salt using 1-nitro-3-trinitromethylpyrazole and hydrazine as raw materials, in which denitration and isomerization reactions occur simultaneously. The new compound, hydrazinium 5-nitro-3-dinitromethyl-2H-pyrazole, was fully characterized and the possible reaction mechanism was also explained by the density functional theory (DFT) method. Finally, its physicochemical and energetic properties were determined either empirically or theoretically, highlighting the salt as a promising alternative explosive.

**RESULTS AND DISCUSSION**

**Synthesis.** In the synthesis pathway of our target compound 3 (Scheme 1), the intermediate, 1-nitro-3-trinitromethylpyrazole (2), was obtained through our previous procedures, in which 3-pyrazolecarbaldehyde was chosen as the starting material. Then, compound 2 was treated with hydrazine at room temperature to obtain its dinitromethylide salt based on the previous analogical reactions in other azoles. In addition to the successful denitration of the trinitromethyl group, the N−NO2 group was also observed to migrate to C(5) atom, resulting in the generation of an unexpected product, hydrazinium 5-nitro-3-dinitromethyl-2H-pyrazole.

To the best of our knowledge, this is the first report of the isomerization of N-nitropyrazole in this manner, which distinctly differs from the conventional thermal rearrangement method. This discovery may provide a convenient chemistry procedure for the synthesis of C-nitropyrazole derivatives, overcoming the limitations and drawbacks of the current method such as tedious work-up, use of obnoxious solvents, rearrangements at higher temperature, and safety problems.

**Isomerization Mechanism.** To deeply understand the possible isomerization mechanism, we performed a theoretical investigation using Gaussian 16 program package on the four designed reaction pathways that involve two different reactants, 1-nitro-3-trinitromethylpyrazole and 1-nitro-3-dinitromethylpyrazole anion, to effect the removal of nitronium ion. Each reactant has two kinds of reaction pathways. In the first kind of pathway, the proton migrates first and subsequently the (N-)NO2 group shifts to the adjacent carbon atom. More specifically, the proton on the C(5) atom migrates first to the nearest oxygen atom in the nitramino group and then the (N-)NO2 bond rotates, causing a proton to shift to N(2), and finally the (N-)NO2 group shifts to the adjacent C(S) atom. In the second kind of pathway, the migration sequence is opposite. The (N-)NO2 bond shifts to the C(S) atom initially and then the proton transfers to N(2) by the way of N(1).

The reaction pathways A and B belong to the first migration method, which start from 1-nitro-3-trinitromethylpyrazole and

![Figure 1. Examples of energetic polynitropyrazole compounds.](image1)

![Scheme 1. Synthesis Route of Compound 3](image2)

![Figure 2. Potential energy surface of isomerization in the first migration manner from 1-nitro-3-trinitromethylpyrazole. The free energies at 298 K relative to 1-nitro-3-trinitromethylpyrazole in kJ mol−1, the imaginary frequencies in cm−1, and the key bond lengths in Å (reaction pathway A).](image3)
1-nitro-3-dinitromethylpyrazole anion, respectively (Figures 2 and 3). They are thermodynamically favorable and release free energies of 68.9 and 132.8 kJ mol$^{-1}$, respectively. They are very difficult to realize because the effective barriers from reactants to the transition states with the highest free energies are 432.5 and 444.1 kJ mol$^{-1}$, respectively. Therefore, the first migration manner with extremely high activation energy barriers is not feasible in the view of dynamics.

The reaction pathway C starting from 1-nitro-3-trinitromethylpyrazole is shown in Figure 4, in which the (N-)NO$_2$ group shifts before the migration of the proton. The intermediate 5-nitro-3-trinitromethyl-1H-pyrazole unreasonably possesses a lower free energy (−76.2 kJ mol$^{-1}$) than that of the product 5-
nitro-3-trinitromethyl-2H-pyrazole (−68.9 kJ mol\(^{-1}\)). In addition, the effective energy barrier is 180.3 kJ mol\(^{-1}\). When the reaction pathway D (Figure 5) starts from 1-nitro-3-dinitromethylpyrazole anion, the intermediate 5-nitro-3-dinitromethyl-1H-pyrazole anion has a higher free energy (−69.0 kJ mol\(^{-1}\)) than that of the product 5-nitro-3-dinitromethyl-2H-pyrazole anion (−132.8 kJ mol\(^{-1}\)). It reveals that 5-nitro-3-dinitromethyl-2H-pyrazole anion is thermodynamically favorable. Besides, it only crosses an effective barrier of 155.2 kJ mol\(^{-1}\) which is the lowest among the four reaction pathways. Above all, the reaction pathway D is the most possible reaction pathway, namely, the denitration reaction occurs before the isomerization and then the (N-)NO\(_2\) group shifts before the migration of the proton for the formation of compound 3.

**Crystal Structure.** The single crystal of 3 suitable for single-crystal X-ray diffraction was obtained by the slow evaporation of a MeOH solution at room temperature. The crystal was stable at room temperature and was found not to be hygroscopic. The results concerning crystallographic data collection and structure refinements are summarized in Table 1. The molecular structure is shown in Figure 6.

Compound 3 crystallizes in the triclinic space group \(\text{P}\bar{1}\) with two molecules per unit cell and has a calculated density of 1.874 g cm\(^{-3}\) at 153 K. The crystal structure of 3 consists of one hydrazine cation and one 5-nitro-3-dinitromethyl-2H-pyrazole anion. Of note, the proton is bonded to N3 rather than N4 atom of the pyrazole ring as supported by the X-ray molecular structure. The C1–C2, C2–C3, C3–N3, N3–N4, and C1–N4 bond lengths are 1.391, 1.398, 1.368, 1.345, and 1.337 Å, respectively, which are in the normal range.\(^{28}\) The C1–N5 bond length is 1.436 Å, which is slightly shorter than a standard C–N single bond (1.460 Å).\(^{29}\) In addition, the C4–N1 and C4–N2 bond lengths of the dinitromethyl group are 1.396 and 1.403 Å, respectively, and thus are both much shorter than those of the normal C–N single bonds and the analogous bonds in its parent compound 2 whose average

![Figure 6](image-url)
value is 1.535 Å. This can be explained by the change in the electron density distribution after the removal of a nitro substituent of the trinitromethyl group. The remaining atoms of the dinitromethyl group are inclined to form a plane with the torsion angles O4–N2–C4–N1 = −6.268° and O2–N1–C4–N2 = −0.113°. Meanwhile, the dinitromethyl group also lies in the plane of the pyrazole ring (N2–C4–C3–N3 = 1.02° and C2–C3–C4–N1 = 4.76°), illustrating that the S-nitro-3-dinitromethyl-2H-pyrazole anion is a coplanar structure.

Physicochemical and Energetic Properties. The physicochemical and energetic properties of compound 3 are summarized in Table 2.

In this work, the differential scanning calorimetry (DSC) and thermogravimetry (TG) technologies were employed to determine the thermal stability of the salt 3. The tests were performed by the samples of 0.5 mg in covered Al containers scanning at 5 °C min⁻¹ under dry, oxygen-free nitrogen over the temperature range from 25 to 500 °C. As shown from the DSC curve of 3 (Supporting Information Figure S3), there is only one exothermic process with an onset temperature of 128.5 °C and a peak temperature of 180.2 °C, which corresponds to the thermal decomposition of 3. Compared with its parent compound 2, 3 displays a better thermal stability owing to the conversion of the unstable trinitromethyl group into dinitromethylide salt.

Oxygen balance (OB), which indicates the degree to which an explosive can be oxidized, has an important and direct effect on the sensitivity, strength, and brisance of an explosive. On the basic carbon monoxide (CO), compound 3 exhibits a negative OB value of −9.64%, which is higher than that of TNT (−24.7%) but inferior to those of RDX and HMX (0%).

Heat of formation (HOF) is one of the important characteristics of energetic salts, which is directly related to the number of nitrogen–nitrogen bond in an ionic species. The calculations of HOF were performed by the isodesmic reaction using Gaussian 16 suite of programs. The HOF of compound 3 was estimated to be 194.8 kJ mol⁻¹, which was more positive than those of RDX (92.6 kJ mol⁻¹) and HMX (116.1 kJ mol⁻¹). The high positive HOF mainly derives from the high nitrogen content.

Density is an important parameter in evaluating the performance of energetic compounds. According to the Kamlet–Jacobs equation, the detonation pressure (P) depends on the square of the density, and the detonation velocity (D) is proportional to the density. The density of compound 3 was measured using a gas pycnometer at room temperature, and its density was 1.80 g cm⁻³, which is quite close to that of RDX (1.81 g cm⁻³). Moreover, the density falls within the acceptable range for new high-performance energetic materials (1.8–2.0 g cm⁻³).

With the calculated value of HOF and the experimental value of density at ambient temperature, the detonation pressure (P) and detonation velocity (D) of energetic salt 3 were calculated using EXPLO5 program (version 6.01). The calculated detonation pressure and velocity are 33.8 GPa and 8790 m s⁻¹, respectively, which are remarkably superior to those of TNT (21.3 GPa, 7300 m s⁻¹) and very similar to those of RDX (34.9 GPa, 8795 m s⁻¹).

The sensitivities of compound 3 toward impact (IS) and friction (FS) were determined using a BAM drop hammer apparatus and a BAM friction tester, respectively. Compared with compound 2, compound 3 exhibits significantly lower sensitivities toward impact and friction. Compound 3 has an impact sensitivity (7 J) comparable to that of HMX, while its friction sensitivity (192 N) is lower than those of HMX and RDX.

### CONCLUSIONS

A new energetic salt, hydrazinium 5-nitro-3-dinitromethyl-2H-pyrazole, has been synthesized by the reaction of 1-nitro-3-trinitromethylpyrazole with hydrazine. The new compound was fully characterized and the isomerization mechanism of N-nitropyrazole in the process was also explained by the density functional theory (DFT) method. The discovery may contribute significantly to the development of rational synthesis methods of C-nitropyrazoles as well as other polynitro-substituted azoles. Subsequently, the physicochemical and energetic properties of the energetic salt were both measured and calculated theoretically. The enthalpy of formation of the salt was calculated using Gaussian 16 programs with a result of 194.8 kJ mol⁻¹, which was significantly superior to those of RDX and HMX. The salt possesses excellent detonation properties (D = 8790 m s⁻¹, P = 33.8 GPa), which are comparable to those of RDX. In the terms of stability toward thermal, impact, and friction, the energetic salt displays a better thermal stability and a lower sensitivity than its parent compound 2 on account of the formations of dinitromethylide salt and C–NO₂ group. Based on an overall energetic evaluation, compound 3 can serve as a promising alternative explosive.

### EXPERIMENTAL SECTION

**General 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

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**Table 2. Physicochemical and Energetic Properties of Compound 3**

| compd | \( T_m \) \( ^° \text{C} \) | \( T_d \) | \( \rho' \) | \( \Delta H_{f298} \) | \( D' \) | \( P' \) | \( IS' \) | \( FS' \) | \( OB' \) |
|-------|----------------|---------|-------|----------------|---------|------|-------|------|------|
| 2     | 59.9           | 113.0   | 1.82/1.85 | 311.4         | 8933    | 35.9 | 2.5   | 36   | 18.3 |
| 3     | 128.5          | 1.80/1.84 | 194.8 | 8790         | 33.8    | 7    | 192   | -9.64 |
| TNT   | 81             | 295     | 1.65  | -59.4        | 7300    | 21.3 | 15    | >353 | -24.7 |
| RDX   | 204            | 230     | 1.81  | 92.6         | 8795    | 34.9 | 2.5   | 120  | 0    |
| HMX   | 275            | 279     | 1.94  | 116.1        | 9220    | 41.5 | 120   | 0    | 0    |

**Note:** *Melting point (onset) (°C). *Decomposition temperature (onset) (°C). *Density measured by a gas pycnometer at 25 °C (g cm⁻³). *Calculated enthalpy of formation (kJ mol⁻¹). *Detonation pressure (GPa). *Impact sensitivity (J). *Friction sensitivity (N). *Oxygen balance assuming the formation of carbon monoxide (CO) at combustion (for \( \text{C}_2\text{H}_6\text{O}_6 \text{N}_8 \text{O}_8 \) \( \text{OB} = 1600 (c - a - b/2) / \text{MW}, \text{MW} = \text{molecular weight of compound} \) (%). *Crystal density at 298 K, recalculated from low-temperature X-ray densities, \( \rho_{928} = \rho_{298} / (1 + \alpha(298 - T_0)) \), \( \alpha = 1.5 \times 10^{-4}, T_0 \) is the crystal testing temperature (g cm⁻³).*
personal protective equipment such as leather gloves, face shield, and ear plugs).

Materials and Measurements. All starting materials were commercially available and used as received. IR spectra were obtained from KBr pellets using a Nicolet Magna IR 560 spectrophotometer (Madison) over the range of 4000–400 cm$^{-1}$. $^1$H NMR and $^{13}$C 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). 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 compound were determined using a TA–DSC Q2000 differential scanning calorimeter (New Castle, DE). 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.

Computational Methods. The quantum chemistry calculations were performed using Gaussian 16 suite of programs.$^{27}$ The electronic structures were calculated by the B3LYP$^{15,36}$ (a hybrid density functional method) and MP2$^{37}$ (the second-order Møller–Plesset perturbation theory) methods. The two basis sets, 6-31G* and 6-311+G**, were combined with these methods. The reactants, intermediates, and products locate at the local minimum points of the potential energy surface without any imaginary frequency. The transition states locate at the first-order saddle points of the potential energy surface with only one imaginary frequency. The potential energy surfaces of the isomerization mechanism were calculated at the B3LYP/6-31G* level. For the calculation of the enthalpy of formation, the geometric optimization of the structures and frequency analyses employed the B3LYP/6-311+G** level and single point energies were calculated at the MP2/6-311+G** level. 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 the enthalpy of formation and density, detonation performances were calculated using EXPLO5 v6.01 program$^{34}$ according to the Kamlet–Jacobs equations.$^{31–33}$

Synthesis of 1-Nitro-3-trinitromethylpyrazole (2). The starting material 1-nitro-3-trinitromethylpyrazole (2) was synthesized based on the literature.$^1$

Synthesis of Hydrazinium 5-Nitro-3-dinitromethyl-2H-pyrazole (3). An 80% solution of hydrazine hydrate (3 mmol) in methanol (5 mL). The resulting mixture was stirred at room temperature for 4 h. Then, the solvent was evaporated under vacuum, and the residue was recrystallized from methanol to give the light-yellow target product (153 mg, 61.9%). $^1$H NMR (600 MHz, DMSO) $\delta$ 13.71 (s, 1H), 8.58 (s, 4H), 7.09 (s, 1H); $^{13}$C NMR (151 MHz, DMSO) $\delta$ 155.58 (s), 137.10 (s), 109.83 (s), 102.05 (s); IR (KBr): 3238, 3194, 1594, 1543, 1487, 1463, 1334, 1282, 1223, 1185, 1110, 1002, 952, 836, 759 cm$^{-1}$; elemental analysis for C$_4$H$_7$N$_7$O$_6$: calculated C 19.28, H 1.27, N 39.47%; measured C 19.33, H 2.72, N 39.47%.
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