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Synthesis and Characterization of Two New Energetic Polyamino and Nitro Pyridine Derivatives

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Abstract: A new azo-bridged pyridine derivative (*E*)-1,2-bis(2-chloro-3-nitropyridin-4-yl) diazene (**3**) and 2-chloro-4-amine-3,5-dinitropyridine (**2**) were synthesized through a direct nitration reaction using 2-chloro-4-aminopyridine (**1**) as a primary material, followed by a simple amination reaction to give (*E*)-1,2-bis(2-amino-3-nitro-pyridin-4-yl) diazene (**5**) and 2,4-diamino-3,5-dinitropyridine (**4**), with a total yield of 69% and 18%, respectively. Red colored crystals of compound **3** growing from CHCl₃ solvent at room temperature were used for X-ray diffraction analysis. The detonation performances of compounds **4** and **5** were calculated by Kamlet-Jacobs empirical equations. The results show that the crystal of compound **3** is monoclinic, space group *P2₁/N* with crystal parameters of *a*=9.965(2) Å, *b*=6.3190(13) Å, *c*=10.737(2) Å, *β*=93.75(3)°, *V*=674.6(2) Å³, *D_c*=1.689 g·cm⁻³, C₁₀H₄Cl₂N₆O₄, *M_r*=171.55, *F*(000)=344, *μ*(Mo K_α)=0.510 mm⁻¹, and *Z*=4. The detonation performance of compound **4** is similar to 2,4,6-trinitrotoluene (TNT), whereas the detonation performance of compound **5** is poor.

Key words: synthesis; crystal structure; pyridine derivatives; azo compounds; detonation performance**CLC number:** TJ55; O62**Document code:** A**DOI:** 10.11943/j.issn.1006-9941.2015.12.005

1 Introduction

Materials that can store and release large amounts of chemical energy on demand have a wide variety of applications. These materials must possess properties that allow them to be handled safely. Recently, the development of new energetic materials, focus on a class of so-called "high-nitrogen" compounds whose energy is derived from their very high positive heat of formation^[1-3]. Thus, superior energetic performances may also potentially be achieved by incorporation of azo-, azole-, azine-based building blocks^[4-7].

Many papers reveal that pyridine-based compounds have captured a major role in energetic material, and the potential uses of nitropyridine derivatives have been reported for the synthesis of novel insensitive explosives^[8-11]. These compounds take the inherent stability of the aromatic heterocyclic ring system and combine it with the insensitivity and stability associated with alternating amino and nitro groups.

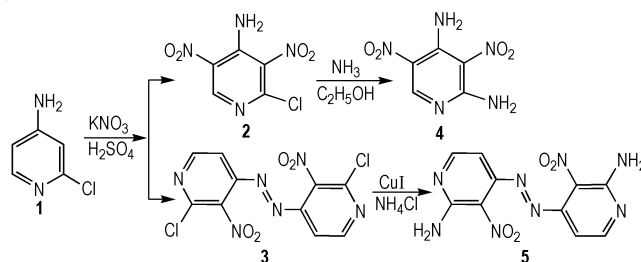
Pursuing our interests in extending the chemistry of energetic pyridines, and on combination azo-functionality with pyridine analogues, we initiated our work to develop azo-bridged pyridine derivatives by using 2-chloro-4-aminopyridine (**1**) as a primary material, and this is a new synthetic route to provide pyridine-based energetic materials bearing amino, nitro and azo groups.

2 Experimental

2.1 Materials and Instruments

The starting materials used in the present study were of AR grade. Column chromatographic purifications were performed on silica gel with 100-200 mesh. Melting point was measured on an X-4 melting point apparatus without correction. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) were recorded on a Bruker Advance Spectrometer (TMS as an internal standard). High-resolution mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analysis was carried out on a Perkin-Elmer instrument.

2.2 Synthetic Routes



Scheme 1

2.3 Synthesis of 2-Chloro-4-amine-3,5-dinitropyridine (**2**) and (*E*)-1,2-bis(2-chloro-3-nitro-pyridin-4-yl) diazene (**3**)

Compound **1** (3.20 g, 1, 25.00 mmol) was dissolved in 75 mL of concentrated sulfuric acid at room temperature, and potassium nitrate (10.10 g, 100.00 mmol) was added in portions with vigorous stirring. After the solution was clear, the reaction mixture was heated to 60 °C for 4 h and allowed to

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cool to room temperature. After pouring over ice, the mixture was filtered, washed with water to give a crude product. The light brown solid was dissolved in 50 mL ethyl acetate, and then filtered. The filtrate was dried over Na_2SO_4 and evaporated under reduced pressure to give light brown solid substance **2** of 3.27 g with yield 60%. m. p. 106–109 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ : 8.95 (t, 1H), 8.50 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ : 148.00, 144.70, 142.51, 133.43, 130.25; Anal. calcd for $\text{C}_5\text{H}_3\text{ClN}_4\text{O}_4$: C 27.48, H 1.38, N 25.64; found: C 27.53, H 1.45, N 25.53; MS (ESI) m/z : 216.91 : 218.89 = 3 : 1 (M–H). The filter cake was dissolved in 30 mL methanol, and then filtered to give red solid substance **3** of 0.98 g with yield 23%. m. p. 224–226 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 8.77 (d, $J=5.3$ Hz, 2H), 7.52 (d, $J=5.3$ Hz, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ : 151.11, 147.48, 142.83, 108.52; Anal. calcd for $\text{C}_{10}\text{H}_4\text{Cl}_2\text{N}_6\text{O}_4$: C 35.01, H 1.18, N 24.50; found: C 35.04, H 1.16, N 24.53.

2.4 Synthesis of 2,4-Diamine-3,5-dinitropyridine (4)

To a stirred solution of **2** (0.30 g, 1.38 mmol) in 25 mL of methanol was added dry ammonia for about 30 min at 0 °C, and another 3 h at room temperature. The precipitate was filtered, washed with water and dried to give gray solid substance **4** of 0.27 g with yield 98.6%. m. p. >270 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ : 9.47 (s, 1H), 9.33 (s, 1H), 9.10 (s, 1H), 9.03 (s, 1H), 8.91 (s, 1H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ : 157.34, 153.13, 147.40, 121.76, 113.24; Anal. calcd for $\text{C}_5\text{H}_5\text{N}_5\text{O}_4$: C 30.16, H 2.53, N 35.17; found C 30.12, H 2.55, N 35.23; MS (ESI) m/z : 197.99 (M–H).

2.5 Synthesis of (E)-1,2-bis(2-amino-3-nitro-pyridin-4-yl) diazene (5)

To a stirred solution of **3** (2.5 g, 7.31 mmol) in 10 mL of *N,N*-dimethylformamide (DMF) was added ammonium chloride (1.12 g, 20.94 mmol) in portions, and then a catalytic amount of cuprous iodide. The resulting mixture was then heated to 60 °C for 2.5 h, at which time complete consumption of the starting material was observed by thin layer chromatography. The reaction mixture was then poured over ice, and filtered, washed with water, and dried on air. The crude material was then purified via a silica gel column using EtOAc/PE as eluting solvent to give white solid substance **5** of 1.73 g with yield 78%. m. p. 154–156 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ : 8.96 (d, $J=5.25$ Hz, 2H), 8.61 (d, $J=5.25$ Hz, 2H), 7.89 (s, 1H), 7.42 (s, 1H); Anal. calcd for $\text{C}_{10}\text{H}_8\text{N}_8\text{O}_4$: C 39.48, H 2.65, N 36.83; found C 39.45, H 2.63, N 36.86.

Single crystals suitable for X-ray diffraction were obtained from slow evaporation of solvent CHCl_3 at room temperature.

2.6 Crystal Structure Determination

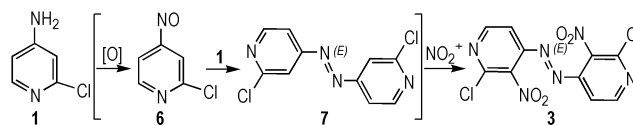
Red block single crystal of **3** (0.30 mm × 0.20 mm × 0.10 mm) was collected by a Nonius cad4 detector equipped with a graphite-monochromatic Mo K_α radiation ($\lambda=0.71073$ Å) using a $\omega/2\theta$ scan mode at 293(2) K. A total of 1306 reflections were collected in the range of $2.70^\circ \leq \theta \leq 25.39^\circ$, among which 1234 ($R_{\text{int}}=0.0355$) was independent and 962

was observed with $I > 2\sigma(I)$. The structure was solved by direct methods and expanded by difference Fourier techniques with SHELXL-97 program. All the non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were added according to the theoretical models. The full-matrix least-squares refinement gave $R_1=0.0528$, $wR_2=0.1419$ ($w=1/[\sigma^2(F_o^2)+(0.1000P)^2+0.1800P]$), where $P=(F_o^2+2F_c^2)/3$, $S=1.004$, $(\Delta\rho)_{\text{max}}=0.247$, $(\Delta\rho)_{\text{min}}=-0.350$ e/Å³, $(\Delta/\sigma)_{\text{max}}=0.000$ and $(\Delta/\sigma)_{\text{mean}}=0.000$.

3 Results and Discussion

3.1 Synthesis Description

When compound **1** was reacted with concentrated sulfuric acid and potassium nitrate at 60 °C, compound **2** (major) and azo compound (**3**, minor, not identified until X-ray quality crystals grow up) were isolated. Extending the reaction time or raising the reaction temperature did not change compound **3** into the major product. To verify the formation of compound **3**, it was shown that when compound **2** was isolated and then reacted with concentrated sulfuric acid and potassium nitrate at the same condition, and no new compound was found as the possible product. The result showed that nitration and diazo coupling reaction of compound **1** involved a parallel reaction, and once $-\text{NH}_2$ in the pyridine ring formed strong hydrogen bond with nitro groups at ortho positions, reactions couldn't occur even in harsh conditions. So it was likely that compound **1** underwent the oxidation and nitration processes successively to generate **3** (Scheme 2).



Scheme 2

Polyamino and nitro pyridines play an important role in energetic heterocyclic compounds which have been investigated as potential new insensitive explosives. When compound **2** reacted with ammonia in ethanol, compound **4** was obtained in a high yield smoothly. However, subsequent amination reaction of compound **3** with ammonia or ammonium chloride (NH_4Cl) failed, but succeeded with ammonium chloride and a catalytic amount of cuprous iodide to give compound **5** as a red solid. The result showed that the reaction might take place due to Cu-catalyzed C–N cross-coupling reaction mechanism, but not according to the more classical addition-elimination mechanism based on too many conjugated double bonds^[12].

3.2 Structural Description

The molecular structure and perspective view of the crystal packing in a unit cell of compound **3** are shown in Figs. 1 and 2, respectively. The selected bond lengths, bond angles and torsion angles are shown in Tables 1 and 2, respectively. Crystal data and structure refinement of compound **3** (CCDC: 956288) are shown in Table 3.

Compound **3** crystals in a *trans*-form, indicating that it may have lower energy than its *cis*-form. Cl–C(5) and C(4)–N(2)

bond of the nitro group are nearly coplanar with the pyridine ring and twisted out of the pyridine plane by 0.7° and -179.7° , respectively. However, the azo-bond of $N(3)-N(3A)$ is not coplanar with the pyridine ring, which twists out of it by -15.6° .

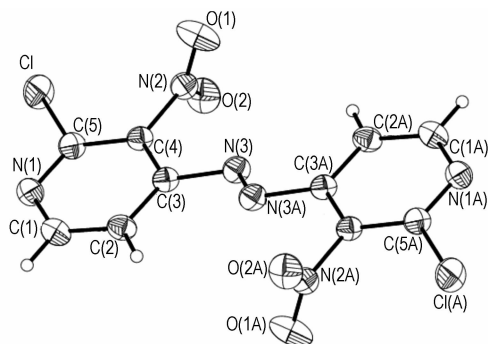


Fig. 1 Molecular structure of compound 3

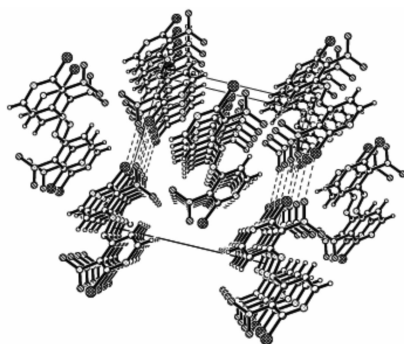


Fig. 2 Packing of the molecule 3 in the crystal lattice

Table 1 Selected bond lengths and bond angles for compound 3

bond	length/Å	bond	length/Å
Cl—C(5)	1.717(3)	N(1)—C(5)	1.318(4)
N(1)—C(1)	1.335(4)	N(3)—C(3)	1.433(4)
C(1)—C(2)	1.375(5)	O(2)—N(2)	1.214(3)
C(2)—C(3)	1.380(4)	N(2)—O(1)	1.208(3)
N(2)—C(4)	1.468(4)	C(3)—C(4)	1.387(4)
C(4)—C(5)	1.388(4)	N(3)—N(3A)	1.234(4)
bond	angle/(°)	bond	angle/(°)
C(5)—N(1)—Cl	116.9(3)	N(1)—C(1)—C(2)	124.4(3)
C(1)—C(2)—C(3)	118.5(3)	O(1)—N(2)—O(2)	124.8(3)
O(1)—N(2)—C(4)	117.3(3)	O(2)—N(2)—C(4)	117.9(3)
C(2)—C(3)—C(4)	117.5(3)	C(2)—C(3)—N(3)	126.0(2)
C(4)—C(3)—N(3)	116.5(2)	C(3)—C(4)—C(5)	119.6(3)
C(3)—C(4)—N(2)	119.6(2)	C(5)—C(4)—N(2)	120.7(2)
N(1)—C(5)—C(4)	122.9(3)	N(3)—C(3)—Cl	117.2(2)
C(4)—C(5)—Cl	119.8(2)		

3.3 Theoretical Studies

Theoretical calculations were carried out by the Gaussian 09 program suite^[13]. The geometry optimization of the molecular structure and frequency analyses were carried out by using the B3LYP functional with the 6-31G** basis set^[14]. The optimized structure was characterized to be true local energy

minima on the potential-energy surface without imaginary frequencies.

Table 2 Selected torsion angles for compound 3

bond	angle/(°)
C(5)—N(1)—C(1)—C(2)	0.8(5)
N(1)—C(1)—C(3)—C(4)	-1.3(5)
C(1)—C(2)—C(3)—C(4)	0.3(4)
C(1)—C(2)—C(3)—N(3)	-177.6(3)
N(3A)—N(3)—C(3)—C(2)	-15.6(5)
N(3A)—N(3)—C(3)—C(4)	166.4(3)
C(2)—C(3)—C(4)—C(5)	1.1(4)
N(3)—C(3)—C(4)—C(5)	179.2(2)
C(2)—C(3)—C(4)—N(2)	179.1(3)
N(3)—C(3)—C(4)—N(2)	-2.8(4)
O(1)—N(2)—C(4)—C(3)	-71.3(4)
O(2)—N(2)—C(4)—C(3)	109.8(3)
O(1)—N(2)—C(4)—C(5)	106.7(3)
O(2)—N(2)—C(4)—C(5)	-72.2(4)
C(1)—N(1)—C(5)—C(4)	0.7(4)
C(1)—N(1)—C(5)—Cl	-177.6(2)
C(3)—C(4)—C(5)—N(1)	-1.7(4)
N(2)—C(4)—C(5)—N(1)	-179.7(3)
C(3)—C(4)—C(5)—Cl	176.6(2)
N(2)—C(4)—C(5)—Cl	-1.5(4)

Table 3 Crystal data and structure refinement for compound 3

chemical formula	$C_{10}H_4Cl_2N_6O_4$
crystal system	monoclinic
space group	$P2_1/N$
size/mm ³	0.30×0.20×0.10
<i>a</i> /Å	9.965(2)
<i>b</i> /Å	6.3190(13)
<i>c</i> /Å	10.737(2)
β / (°)	93.75(3)
D_c /g·cm ⁻³	1.689
formula weight/g·mol ⁻¹	171.55
volume/Å ³	674.6(2)
<i>Z</i>	4
λ /Å	0.71073
<i>F</i> (000)	344
reflection collected/unique	1234/962
$R_1, wR_2(I > 2\sigma(I))$	0.0528, 0.1419
R_1, wR_2 (all data)	0.0686, 0.1559

Detonation velocity (D) and detonation pressure (p) are the most important targets of scaling the detonation characteristics of energetic materials. For CHNO type explosives, the Kamlet-Jacobs empirical equations^[15-16] was used to determine these parameters.

$$D = 1.01 (NM^{0.5}Q^{0.5})^{0.5} (1 + 1.30\rho_0) \quad (1)$$

$$p = 1.55\rho_0^2 NM^{0.5}Q^{0.5} \quad (2)$$

Where D is detonation velocity in $\text{km} \cdot \text{s}^{-1}$, p is detonation pressure in GPa, N is moles of gaseous detonation prod-

ucts per gram of explosives, M is the average molecular weights of gaseous products, Q is the energy of explosion in $\text{J} \cdot \text{g}^{-1}$ of explosive and ρ_0 is the crystal density in $\text{g} \cdot \text{cm}^{-3}$. N , M and Q are determined according to the largest exothermic principle, *i. e.*, for the CHNO explosives, all the N atom converts into N_2 , the O atom forms H_2O with H atom first and the remainder forms CO_2 with C atom. The remainder of C atom will exist in solid state if O atom does not satisfy full oxidation of C atom. The remainder of O atom will exist in O_2 if O atom is superfluous.

Table 4 Detonation performance of compounds **4** and **5** and comparison with TNT and RDX

compound	oxygen balance /%	volumn / $\text{cm}^3 \cdot \text{mol}^{-1}$	density / $\text{g} \cdot \text{cm}^{-3}$	detonation velocity / $\text{km} \cdot \text{s}^{-1}$	detonation pressure /GPa	energy of detonation / $\text{J} \cdot \text{g}^{-1}$
4	-68.33	112.97	1.76	7.27	23.13	1064.80
5	-105.24	176.37	1.72	6.16	16.11	760.35
TNT	-74.0	132.42	1.72	7.37	23.46	1374.60
RDX	0.00	124.92	1.78	8.88	34.75	1597.39

4 Conclusions

(1) The present investigation demonstrates the synthesis of two new energetic polyamino and nitro pyridine derivatives **5** and **4** with a total yield of 69% and 18%, respectively.

(2) Compound **3** is first synthesized and structurally determined by single crystal X-ray diffraction. It is monoclinic with space group $P2_1/N$.

(3) The detonation velocity and detonation pressure obtained by theoretical calculation are $7.27 \text{ km} \cdot \text{s}^{-1}$ and 23.13 GPa for compound **4** and $6.16 \text{ km} \cdot \text{s}^{-1}$ and 16.11 GPa for compound **5**.

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The calculated results in Table 4 indicate that compound **4** has a similar oxygen balance and detonation performance comparing to TNT^[17], but is worse than hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)^[18], and compound **5** is less competitive. However, as a new azo-bridged pyridine derivative, compound **5** has a high value of density, due to the introduction of the alternate amino and nitro group in the pyridine ring. Thus, the continuous work will focus on how to improve its derivatives' detonation performance through different synthetic routes.

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