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Synthesis, Characterization and Theoretical Studies of Polynitro-bispyridines

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Abstract: A new compound *N*-(6-azido-3,5-dinitropyridin-2-yl)-2,6-diamine-3,5-dinitropyridine (**3**) was designed and synthesized via C—N cross-coupling reaction and azide substitution reaction, using 2-amine-6-chloro-3,5-dinitropyridine as a primary material with a total yield of 69%. Its structure was confirmed by ¹H NMR, ¹³C NMR, MS and elemental analysis. Theoretical calculations at DFT-B3LYP/6-31G** level were performed. Results show that the detonation performance of compound **3** are detonation velocity $D=7.89 \text{ km} \cdot \text{s}^{-1}$ and detonation pressure $p=28.37 \text{ GPa}$, revealing that its detonation performance is better than that of 2,4,6-trinitrotoluene (TNT).

Key words: energetic compound; polynitro-bispyridines; synthesis**CLC number:** TJ55; O62**Document code:** A**DOI:** 10.11943/j.issn.1006-9941.2015.05.018

1 Introduction

Nitrogen heterocyclic compounds are potential and promising candidates for high-energy density materials (HEDMs) owing to their higher heat of formation, density, and oxygen balance than their carbocyclic analogues. They have received a great amount of interest in recent years^[1-5].

Pyridine ring is a six-membered heterocycle, enabling incorporations of the nitro, amino, and azide functionality through substituted reactions over five positions. On the other hand, since a N atom contributes more to the density than a C atom, the presence of pyridine ring in a molecule is supposed to improve its density and correspondingly increase the detonation velocity and pressure^[6]. However, the difficulty of synthesizing some nitropyridines may be attributed to electron deficiency of pyridine ring, and thus making electrophilic aromatic substitution problematic. Up to now, the representative pyridine-based energetic materials contain only mono-pyridine structure, such as 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPYO), 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) and so on^[7].

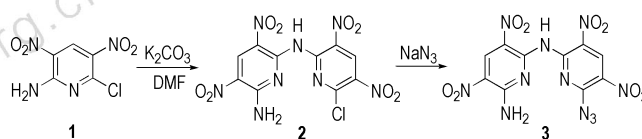
Based on the concept of increasing density and thermal stability by the use of alternating array of amino- and nitro-groups, novel and efficient synthesis of 2-amine-6-chloro-3,5-dinitropyridine (**1**)^[6], we would like to report the synthesis of *N*-(6-chloro-3,5-dinitropyridin-2-yl)-2,6-diamine-3,5-dinitropyridine (**2**) by C—N cross-coupling reaction, and subsequent azide substitution to give polynitro-bispyridines as new energetic materials, such as *N*-(6-azido-3,5-dinitropyridin-2-yl)-2,6-diamine-3,5-dinitropyridine (**3**).

2 Experimental

2.1 Materials and instruments

The starting materials **1** and 2-chloro-4-amine-3,5-dinitropyridine (**4**) were prepared according to literature^[8-9]. Other chemicals used in the present study were of AR grade and purchased from the trade without further purification. Melting point was measured on a X-4 melting point apparatus and was uncorrected. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) were recorded on a Bruker Avance Spectrometer. The coupling constants (J) were reported in hertz (Hz). High-resolution mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analyses were carried out on a Perkin-Elmer instrument.

2.2 Synthetic route



Scheme 1

2.3 Synthesis of 2

2.18 g (0.01 mol) **1** was dissolved in 20 mL *N,N*-dimethylformamide at room temperature, and then 1.50 g (0.15 mol) potassium bicarbonate was added with vigorous stirring. The mixture was kept for 4 h, at which time complete consumption of the starting material was observed by thin layer chromatography (TLC). The reaction mixture was then poured over ice, and filtered, washed with water, and dried on air. The crude material was purified via a silica gel column using EtOAc/PE as eluting solvent to give 1.70 g yellow solid, yield 85%, m. p.: 189–190 °C (dec.); ¹H NMR (DMSO-*d*₆, 500 MHz): δ : 13.67 (s, 1H), 10.18 (s, 1H), 9.26 (s, 1H), 9.25 (s, 1H), 9.11 (s, 1H); Anal (%), Calcd for

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$C_{10}H_5ClN_8O_8$ ($M_w=399.99$): C 29.98, H 1.26, N 27.97; found: C 29.89, H 1.29, N 27.91%; ESI-MS m/z : 398.81 $[M-H]^-$.

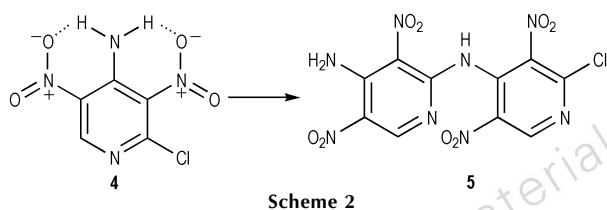
2.4 Synthesis of 3

To a stirred solution of **2** (2.00 g, 0.005 mol) in 50 mL acetone was added sodium azide (0.49 g, 0.0075 mol) portionwise. The resulting mixture was kept at room temperature for 30 min, at which time complete consumption of the starting material was observed by TLC. The reaction mixture was then evaporated under reduced pressure, washed with water, and dried on air. The crude product was then crystallized from EtOAc/PE to give 1.65 g deep yellow solid, yield 81%, m.p.: 165–167 °C(dec.); 1H NMR (DMSO- d_6 , 500 MHz): δ : 9.21 (s, 1H), 9.16 (s, 1H), 8.73 (s, 1H), 8.43 (s, 1H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ : 157.10, 153.59, 144.77, 135.99, 134.12, 131.83, 125.57, 120.75, 119.69, 115.29; Anal (%), Calcd for $C_{10}H_5N_{11}O_8$ ($M_w=407.03$): C, 29.50; H, 1.24; N, 37.84; found: C, 29.56; H, 1.19; N, 37.78%. ESI-MS m/z : 405.84 $[M-H]^-$.

3 Results and Discussion

3.1 Synthesis of 3

By investigation of the synthesis of polynitro-bispyridines, two polynitro derivatives of pyridine named **1** and **4** were attempted as starting materials, using a variety of bases, such as potassium carbonate, potassium bicarbonate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylamine (TEA). However, only **1** can be easily converted into **2** at room temperature. And for **4**, raising the reaction temperature, extending the reaction time, and changing different bases result in recovery of the starting material. This phenomenon proved that the intramolecular hydrogen bonds between amino and nitro groups in compound **4** hinder the formation of bispyridine **5** (Scheme 2).



Inspired by the structure of **2**, 6-diamino-3,5-dinitropyridine (ANPY), subsequent amination of **2** with ammonia was conducted, and after evaporation, washed with water, a yellow solid was obtained. However, its structure was hardly confirmed by NMR because of its insolubility in DMF, DMSO, and even CF_3COOH , which might be attributed to the formation of intramolecular and intermolecular hydrogen bonds which were associated with so many alternating amino and nitro groups, and thus weaken the solvent effect greatly.

Sodium azide is proved to be an efficient nucleophilic reagent, and the reaction with **2** in acetone, of course, proceeds very rapidly with initial nucleophilic displacement of chlorine by the azide ion to give the corresponding **3**. However, difficulties have been occurred in the synthesis of pyridofuroxans in the solvents of 10% ethanol aqueous solution (V/V) in the

presence of hydrochloric acid, acetic acid, toluene, DMF, and no desired product was detected, even at a higher temperature.

3.2 Theoretical Studies

Theoretical calculations were carried out by using the Gaussian 09 program suite^[10]. The geometry optimization of the molecular structure and frequency analyses were carried out by using the B3LYP functional with the 6-31G** basis set^[11–12]. The optimized structure was characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Detonation velocity (D) and detonation pressure (p) are the most important targets of scaling the detonation characteristics of energetic materials. For the explosives with CHNO elements, the Kamlet-Jacobs empirical equations^[13–14] (**1**) and (**2**) were used to determine these parameters.

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

$$p=15.58\rho_o^2 NM^{0.5}Q^{0.5} \quad (2)$$

Where D is detonation velocity in $km \cdot s^{-1}$, p is detonation pressure in GPa, N is the number of moles of gaseous detonation products per gram of explosive, M is the average molecular weight of gaseous products, Q is the chemical energy of the detonation reaction of explosive in $J \cdot g^{-1}$ and ρ_o is the crystal density in $g \cdot cm^{-3}$. Values of N , M and Q are determined according to the largest exothermic principle, i.e., for the explosives with CHNO elements, 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.

The calculated results indicate that compound **3** exhibits better detonation performance than TNT^[15], but it is worse than RDX^[16].

Table 1 Detonation performance of compound **3**, TNT and RDX

compound	OB ¹⁾ /%	V / $cm^3 \cdot mol^{-1}$	$\rho^{2)}$ / $g \cdot cm^{-3}$	$D^{3)}$ / $km \cdot s^{-1}$	$P^4)$ /GPa	$Q^5)$ / $J \cdot g^{-1}$
3	-57.00	215.77	1.89	7.89	28.37	1260.84
TNT ^[15]	-74.0	132.42	1.72	7.37	23.46	1374.60
RDX ^[16]	0.00	124.92	1.78	8.88	34.75	1597.39

Note: 1) oxygen balance; 2) density; 3) detonation velocity; 4) detonation pressure; 5) chemical energy of detonation.

4 Conclusions

The present investigation demonstrates the facile synthesis of new polynitro-bispyridine: **3** through C—N cross-coupling reaction and azide substitution with a total yield of 69%. Theoretical calculations show that the detonation properties of **3** ($D=7.89 km \cdot s^{-1}$, $p=28.37 GPa$) are satisfying.

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多硝基双吡啶的合成、表征和理论研究

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摘要:以 2-氨基-6-氯-3,5-二硝基吡啶为原料,经 C—N 偶联反应和叠氮化取代反应,设计/合成了一种新化合物 N-(6-叠氮基-3,5-二硝基吡啶-2-基)-2,6-二氨基-3,5-二硝基吡啶,总产率为 69%。用¹H NMR、¹³C NMR、质谱和元素分析鉴定了其结构,在 DFT-B3LYP/6-31G** 水平下预估该化合物的爆速为 7.89 km·s⁻¹,爆压为 28.37 GPa。表明,该化合物比 2,4,6-三硝基甲苯(TNT)有更好的爆轰性能。

关键词:含能化合物;多硝基双吡啶;合成;

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