文章编号：1006-9941(2017)12-1042-04

Synthesis and Properties of 4-Amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine

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Abstract: A novel thermally stable energetic material ,4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine(ABDP) was first synthesized via two-step reactions of nitration and condensation reaction using 4-amino-2,6-dichloropyridine as a raw material with a total yield of 36%, and its structure was characterized by nuclear magnetic resonance (NMR), mass spectrum (MS) and elemental analysis. Condensation reaction of 3-amino-1,2,4-triazole or 5-amino-1*H*-tetrazole and 4-amino-2,6-dichloro-3,5-dinitropyridine was investigated. Its thermal properties were studied by thermogravimetry(TG) and differential scanning calorimetry(DSC). Results show that similar nucleophilicity occurs at primary amine and secondary amine of 3-amino-1,2,4-triazole, but secondary amine in 5-amino-1*H*-tetrazole has higher nucleophilicity than that of primary amine. ABDP has a thermal decomposition peak at 323 ℃ accompanied with 94% mass loss. The detonation velocity and detonation pressure of 4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine are predicted by Rothstein´s method with the values of 8823 m·s^{-1} and 36.72 GPa, respectively.

Key words: synthesis; 4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine(ABDP); heat-resistant explosive; thermal analysis

CLC number: TJ55; O62 **Document code**: A **DOI**: 10.11943/j.issn.1006-9941.2017.12.012

1 Introduction

Polyamino and polynitro derivatives of pyridine are good examples of a general structure-property relationship among energetic ingredients, that the addition of amino-groups to a polynitropyridine increases the density and thermal stability and decreases the sensitivity compared to the corresponding *H*-atom-substituted nitropyridine. In general, the density increase outweighs the concomitant decrease in oxygen balance and heat of formation that accompanies the introduction of amino groups, resulting in better performance. Also, the decrease in oxygen balance and heat of formation, along with increased hydrogen bonding between the amino group and the nitro-groups, decreases sensitivity and increases thermal stability[1-2]. However, it is obvious that most energetic materials mentioned above have the disadvantage of detonation performance due to their low heat of formation and poor oxygen balance, especially detonation velocity (D) and detonation pressure (p). One approach to improve this insufficiency is to basically incorporate maximum possible percentage of nitrogen into energetic materials, because the introduction of nitrogen-rich energetic blocks into the nitropyridine determines some unique properties such as heat of formation, significant gas release in the form of environmentally benign nitrogen, and commonly include moieties such as five membered azoles[3-5].

Based on our continuous effort to synthesize insensitive high explosives, we have successfully synthesized several energetic four-substituted energetic pyridine derivatives such as 2-(5-amino-1*H*-tetrazol-2-yl)-4-amino-3,5-dinitropyridine and 6-(5-amino-1*H*-tetrazol-2-yl)-2-amino-3,5-dinitropyridine, whose detonation velocity are both 8.18 km·s^{-1} and detonation pressure are 30.7 GPa[4]. In the pursuit of new fully substituted energetic pyridine derivative, we have recently been focus on the synthesis and characterization of 4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine(ABDP), as well as the thermal performance was studied by thermogravimetry and differential scanning calorimetry.

Received Date: 2017-05-24; **Revised Date**: 2017-07-20

Project Supported: National Natural Science Foundation of China (21102125), Postdoctoral Science Foundation of Jiangsu Province of China (1601053B)

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2 Experimental

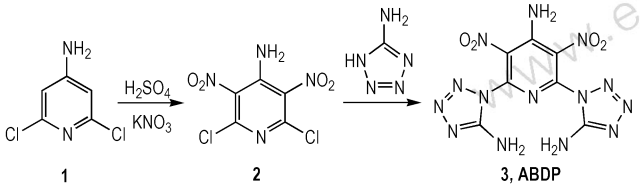
2.1 Materials and Instruments

All 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. ^{1}H NMR and ^{13}C NMR 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. Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis was conducted on a Q600SDT.

2.2 Synthetic Route

The synthetic route of ABDP is shown in Scheme 1.



Scheme 1 The synthetic route of ABDP

2.3 Synthesis of 2

4-Amino-2,6-dichloropyridine (1) (2.04 g, 12.59 mmol) was dissolved in 20 mL of concentrated sulfuric acid at room temperature, and potassium nitrate (3.40 g, 33.66 mmol) was added in portions with vigorous stirring. After the solution was clear, the reaction mixture was heated to 50 ℃ for 7 h and then cooled to room temperature. After pouring over ice, the solid was precipitated, filtered, washed with cold water, and then dried to give 4-amino-2,6-dichloro-3,5-dinitropyridine (**2**) as a yellow solid (1.91 g, 60%), m. p. 158–160 ℃. ^{1}H NMR (DMSO-d_6, 500 MHz): 8.25(s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): 142.39, 141.03, 132.00; Anal. Calcd. for $C_5H_2Cl_2N_4O_4$: C 23.74, H 0.80, N 22.14; found: C 23.65, H 1.02; N 22.19; MS (ESI) *m/z*: 250.82 : 252.83 : 254.82 =9 : 6 : 1 (M–H).

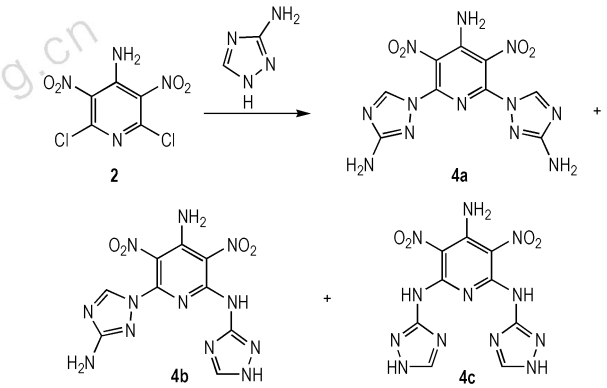
2.4 Synthesis Description

To a stirred solution of 5-amino-1*H*-tetrazole (0.85 g, 10 mmol) in 30 mL ethanol was added potassium bicarbonate (0.50 g, 5 mmol) and tetrabutylammonium bromide (0.16 g, 0.5 mmol) portionwise. The resulting mixture was kept at room temperature for 30 min, then 4-amino-2,6-dichloro-3,5-dinitropyridine(1.26 g, 5 mmol) was added. The reaction mixture was heated to 40 ℃ for 15 min and then cooled to room temperature. After pouring over ice, the solid was precipitated, filtered, washed with methanol and water for three times, and then dried to give a yellow solid 4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine (**3**, ABDP) (1.06 g, 61%);1H NMR (DMSO-d_6, 400 MHz): 12.01(s, 2H), 10.14(s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): 152.47, 150.82, 148.87, 112.19; Anal. Calcd. for $C_7H_6N_{14}O_4$: C 24.01, H 1.73, N 55.99; found: C 24.10, H 1.82, N 56.11; MS (ESI) *m/z*: 351.12(M+H).

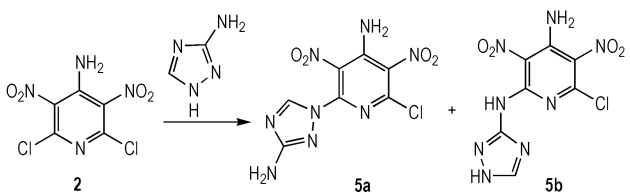
3 Results and Discussion

3.1 Synthesis of 3

By investigation of the successful synthesis of 2-(5-amino-2*H*-tetrazol-2-yl)-4-amino-3,5- dinitropyridine using 2-chloro-4-aminopyridine as starting material, fully substituted pyridine derivatives were designed by combining nitrogen rich compounds with orth- amino and nitro pyridines, so as to improve energetic properties but remaining insensitive performance. 4-nitroimidazole, nitroguanidine, 3-amino-1,2,4-triazole, 5-amino-1*H*-tetrazole were attempted to react with 4-amino-2,6-dichloro-3,5-dinitropyridine (**2**, ADDP) under appropriate conditions. However, the former two compounds failed to obtain the ideal products, mainly due to their weak nucleophilicity. When 3-amino-1,2,4-triazole was reacted with ADDP, three peaks were detected by liquid chromatograph/mass spectrometer (LC/MS), but only to find the same molecular mass (MS (ESI) *m/z*: 349.3 (M+H)) (Scheme 2). It is difficult to separate these three substances with regular column chromatography because of their poor solubility and polarity. Intermediates were also studied to find two products with the same molecular mass (MS (ESI) *m/z*: 301.2 (M+H)) (Scheme 3). This phenomenon maybe prove similar nucleophilicity for primary amine and secondary amine of 3-amino-1,2,4-triazole.



Scheme 2 Synthesis of 3-amino-1,2,4-triazole substituted pyridines



Scheme 3 Synthesis of 3-amino-1,2,4-triazole substituted pyridines

When reacted with 4-amino-2,6-dichloropyridine, 5-amino-1*H*-tetrazole was rapidly converted into 4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine (**3**, ABDP) at 40 ℃, and mass spectrum showed that its sole molecular mass was 350, ^{1}H NMR spectrum showed that two hydrogen signal in the amino group attaching to the pyridine ring was at 12.01 and one of the two amino groups attaching to the tetrazole ring was at 10.14, but the other was exchanged in the solution. The same pheonomenon occurs in the synthesis of 6-(5-amino-1*H*-tetrazol-2-yl)-2-amino-3, 5-dinitropyridine[6] whose structure is similar to that of ABDP.

3.2 Thermal Performance

The TG-DSC analysis was carried out at a heating rate of 5 ℃ · min^{-1} from 50 ℃ to 500 ℃ under N_2 atmosphere. The TG-DSC curves were showed in Fig. 1, which revealed that 4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine (**3**, ABDP) was thermally stable up to 315 ℃ and possessed a direct thermal decomposition process with a mass loss of 94%.

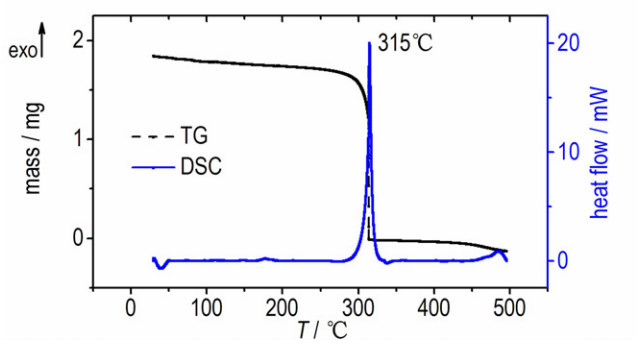


Fig. 1 TG-DSC curves of ABDP

3.3 Performance Studies

Detonation velocity (D), detonation pressure (p) and oxygen balance are calculated according to Rothstein's method[6-7]. For the ideal C, H, N, O type explosives, detonation velocity was predicted from the linear regression equation (1):

$$D=\frac{F-0.26}{0.55} \quad (1)$$

While the factor F is expressed as equation (2):

$$F=\left[100\times\frac{n(O)+n(N)\frac{n(H)}{2n(O)}+\frac{A}{3}-\frac{n(B)}{1.75}-\frac{n(C)}{2.5}-\frac{n(D)}{4}-\frac{n(E)}{5}}{M}\right]-G \quad (2)$$

Where G = 0.4 for liquid explosives, for solid explosives G=0; A=1 if the compound is aromatic, otherwise A=0 and where for one mole of the composition: n(O) = number of oxygen atoms, n(N) = number of nitrogen atoms, n(H) = number of hydrogen atoms, n(B) = number of oxygen atoms in excess of those already available to form CO_2 and H_2O, n(C) = number of oxygen atoms doubly bonded directly to carbon as in carbonyl $\diagdown C{=}O \diagup$, n(D) = number of oxygen atoms singly bonded directly to carbon as in a $\diagdown C{-}O{-}R \diagup$ linkage where R can equal —H, —NH_4, —C, etc. n(E) = number of nitrato groups existing either in a nitrate ester configuration or as nitric acid salt such as hydrazine mononitrate, M is molecular mass.

Detonation pressure was predicted according to the equation (3):

$$p=\frac{93.3D-456}{10} \quad (3)$$

Some detonation performance of ABDP are listed in Table 1, and compared with some known thermally stable energetic materials: hexanitrostibene(HNS), tetranitrodibenzo-1,3α,4,6α-tetrazapentalene(TACOT), 1,3,5-triamino-2,4,6-trinitropyridine (TATB), 2,6-bis(picrylamino)-3,5-dinitropyridine(PYX).

It was found that the oxygen balance of 4-amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine is calculated to be –59.4%, and this value is lower than that of PYX(–55.4%) and TATB(–55.8%), but higher than that of HNS(–67.5%) and TACOT(–77.9%). All thermally stable energetic materials mentioned in Table 1 exhibit a melting or decomposition temperature above 310 ℃. Furthermore, ABDP has a detonation velocity of 8823 m · s^{-1} and a detonation pressure of 36.72 GPa, which are significantly better than those of PYX, HNS, TACOT and TATB, revealing a better detonation performance as a novel potential thermally stable energetic material.

Table 1 Detonation performance of compounds ABDP, TACOT, TATB, HNS and PYX

compound	formula	molecular mass	OB / %	$T_{m.p.}$ / ℃	D / m · s^{-1}	p / GPa
ABDP	$C_7H_6O_4N_{14}$	350.21	–59.4	323	8823	36.72
HNS	$C_{14}H_6O_{12}N_6$	450.23	–67.5	316[2]	6830	18.12
TACOT	$C_{12}H_6O_8N_8$	390.22	–77.9	354[2]	6963	19.36
TATB	$C_6H_6O_6N_6$	258.13	–55.8	375[8]	7862	27.76
PYX	$C_{17}H_7O_{16}N_{11}$	621.30	–55.4	380[8]	7462	24.02

Note: OB is oxygen balance; $T_{m.p.}$ is melting point; D is detonation velocity; p is detonation pressure.

4 Conclusions

(1) 4-Amino-2,6-bis(5-amino-1*H*-tetrazol)-3,5-dinitropyridine was first synthesized via nitration and condensation using 4-amino-2,6-dichloropyridine as a raw material with a total yield of 36%. Its structure was characterized by nuclear magnetic resonance (NMR), mass spectrum (MS) and elemental analysis.

(2) ABDP exhibits some good detonation properties, such as high detonation pressure (36.72 GPa) and detonation velocity (8823 $m \cdot s^{-1}$).

(3) TG-DSC curves indicate that ABDP has a thermal decomposition peak at 323 ℃ accompanied with a mass loss of 97%.

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4-氨基-2,6-双(5-氨基-1*H*-四唑基)-3,5-二硝基吡啶的合成与性能

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摘　要: 以4-氨基-2,6-二氯吡啶为原料,经过硝化和缩合两步反应,合成出一种新型耐热炸药,4-氨基-2,6-双(5-氨基-1*H*-四唑基)-3,5-二硝基吡啶(ABDP),总收率为36%。采用核磁共振、质谱及元素分析对产物结构进行表征。分别研究了3-氨基-1,2,4-三氮唑和5-氨基四唑与4-氨基-2,6-二氯-3,5-二硝基吡啶的缩合反应,结果发现,3-氨基-1,2,4-三氮唑中伯胺和仲胺的亲核性相近,5-氨基四唑中仲胺的亲核性优于伯胺。用热重(TG)和差示扫描量热法(DSC)研究了ABDP的热分解性能,发现其在322 ℃有一个热分解峰,322 ℃时总热失重量为97%,采用Rothstein方法计算4-氨基-2,6-双(5-氨基-2*H*-四唑基)-3,5-二硝基吡啶的爆速为8823 $m \cdot s^{-1}$,爆压为36.72 GPa。

关键词: 合成; 4-氨基-2,6-双(5-氨基-1*H*-四唑基)-3,5-二硝基吡啶(ABDP); 耐热炸药; 热分析

中图分类号: TJ55; O62　　**文献标志码**: A　　**DOI**: 10.11943/j.issn.1006-9941.2017.12.012