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Synthesis of 1,1′-Azobis(3,5-dinitropyrazole)

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Abstract: A nitrogen-rich, polynitro energetic compound with an *N*,*N*-azo linkage, 1,1′-azobis(3,5-dinitropyrazole)(ABDNP), was synthesized using 3,5-dinitropyrazole(DNP) as starting material via neutralization, *N*-amination and oxidative coupling reaction etc, and its structure was characterized by IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. The effect of oxidizing agents on the coupling reaction were investigated. Results show that tert-butyl hypochlorite(*t*-BuOCl) is a better oxidizing agent with yield of ABDNP up to 43.5%. The physical-chemical and detonation performance of ABDNP were calculated by Gaussian 09 and VLW equation with density 1.94 g·cm^{-3}, detonation velocity 9309.0 m·s^{-1} and detonation pressure 42.2 GPa, better than those of RDX.

Key words: 1,1′-azobis(3,5-dinitropyrazole)(ABDNP); oxidative coupling reaction; synthesis; performance

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1 Introduction

New strategies in energetic materials research focus on nitrogen-rich/high positive heat of formation compounds[1-2]. Nitrogen-rich compounds have therefore received increasing attention as promising candidates for high energy-density materials(HEDM) which may be used as propellants, explosives or especially as gas generators[3-5], and the generation of nitrogen gas as an end product of nitrogen-rich compounds is highly favored for the enhancement of energy and avoiding environmental pollution[6-8]. Nitrogen-rich compounds based on C/N heteroaromatic rings with high nitrogen content like triazole, tetrazole, triazine and tetrazine are at the forefront of high energy research. Recently, the combination of an azo group with nitrogen-rich heteroaromatic rings has been extensively studied because the azo linkage not only desensitizes but also dramatically increases the heat of formation , such as 3,3′-azobis(1,2,4-triazole)[9], 5,5′-dinitro-3,3′-azo-1H-1,2,4-triazole[10], 3,3′-azobis-(6-amino-1,2,4,5-tetrazine)[11] and 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine[12], where the two heteroaromatic rings are connected by a C—N＝N—C linkage. However, if the azo group is attached to the nitrogen of the heteroaromatic rings to create a rather long chain of catenated nitrogens (N—N＝N—N linkage), such a polynitrogen structure can result in unique properties and features of these energetic compounds, such as 4,4′-azo-1,2,4-triazole[9], 1,1′-azobis-1,2,3-triazole[13], 1,1′-azobis(tetrazole)[1], 2,2′-azobis(5-nitrotetrazole)[14] and 1,1′-azobis(5-methyltetrazole)[15]. Unfortunately, some of the above compounds don't own excellent detonating performance or thermal unstable.

In this paper, a nitrogen-rich energetic material, 1,1′-azobis(3,5-dinitropyrazole)(ABDNP), which contain the NO_2, N—N＝N—N and pyrazole ring, was synthesized using 3,5-dinitropyrazole(DNP) as starting material(Scheme 1). The property of ABDNP was estimated by a B3LYP method on 6-31G(d,p) basis set of Gaussian 09[16] procedure.

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2 Experimental

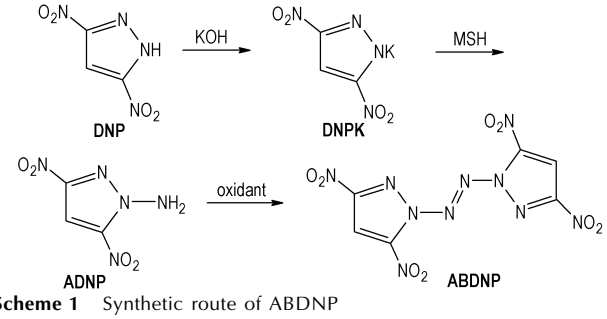
2.1 General methods and materials

Melting points were determined using an open capillary tube. Infrared(IR) spectra were recorded on a Nicolet NEXUS 870 Infrared spectrometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 500 NMR spectrometer with TMS as the internal standard. Mass spectra were acquired using a GCMS-QP 2010 Micromass UK spectrometer. Elemental analyses were performed on a VARI-EI-3 elemental an alyzer.

DNP and *O*-mesitylenesulfonylhydroxylamine (MSH) were self-synthesized. Ethanol, potassium hydroxide, acetonitrile and isopropyl were of AR grade, purchased from Chengdu Kelong Chemical Reagents Factory.

2.2 Synthetic route

ABDNP was synthesized using DNP and MSH as starting materials. The synthetic route was as follow (Scheme 1).



Scheme 1 Synthetic route of ABDNP

2.3 Synthesis of ABDNP

2.3.1 Synthesis of 1-amino-3,5-dinitropyrazole(ADNP)

2.0 g(0.13 mol) of DNP was dissolved in 15.0 mL etha-

nolat room temperature, then 14.2 g 5% potassium hydroxide (0.13 mol) was added dropwise at 5–10 ℃. After two hours at room temperature, the precipitate was filtered off, washed with ethanol and ice-water, and dried to give 2.25 g yellow solid 3,5-dinitropyrazole potassium salt(DNPK) with a yield of 90.7%. ^{1}H NMR(D_2O-d_2, 500 MHz),δ:7.399(s, 1H, —CH); ^{13}C NMR(D_2O-d_2, 125 MHz),δ: 99.24, 156.18; IR (KBr, ν/cm^{-1}): 3157 (—CH), 1539, 1378, 1351 (—NO_2), 1270, 835, 755 (Pyrazole). Anal. Calcd for $C_3HN_4O_4K$(%): C 18.37, H 0.51, N 28.56; found(%) C 18.40, H 0.49, N 28.54.

0.5 g(2.55 mmol) of DNPK was dissolved in 15.0 mL anhydrous acetonitrileat room temperature. Then a solution of 0.77 g(3.57 mmol) of MSH in 2.5 mL anhydrous acetonitrile was added dropwise to the above reaction mixture at 0–3 ℃. After 20 h at room temperature, the precipitate was filtered off, the filtrate was concentrated in vacuo to give yellow oil compound. Recrystallization with water to obtain 0.37 g buff solid ADNP with a yield of 84.1%, m. p.: 111.5–112.1 ℃. ^{1}H NMR(DMSO-d_6, 500 MHz),δ: 7.105(s, H, —CH), 8.006(s, 2H, —NH_2); ^{13}C NMR(DMSO-d_6, 125 MHz), δ: 101.69, 140.07, 147.66; IR(KBr, ν/cm^{-1}): 3355, 3287 (—NH_2), 3154 (—CH), 1508, 1381, 1356 (—NO_2), 1556, 845, 741 (Pyrazole). Anal. Calcd for $C_3H_3N_5O_4$ (%): C 20.82, H 1.75, N 40.46; found(%) C 20.80, H 1.78, N 40.50.

2.3.2 Synthesis of ABDNP

0.1 g(0.58 mmol) of ADNP was dissolved in 10.0 mL acetonitrileat room temperature, cooled to 0-5℃, with stirring under nitrogen, and treated with 0.082 g(0.75 mmol) of *t*-butyl hypochlorite over 3 minutes. The resulting solution was stirred at 20–25 ℃ for another 2 hours, concentrated in vacuo, and triturated with 2.0 mL isopropyl alcohol. The precipitate was filtered off, washed with isopropyl alcohol and ice-water, and dried to give 43.0 mg yellow solid ABDNP with a yield of 43.5%. ^{1}H NMR(DMSO-d_6, 500 MHz),δ: 8.625 (s, 2H, 2-CH); ^{13}C NMR(DMSO-d_6, 125 MHz), δ: 106.03, 146.09, 153.39; IR(KBr,ν/cm^{-1}): 3154, 3135 (—CH), 1530, 1390, 1331(—NO_2), 1215, 1136, 1027 (pyrazole ring); Anal. Calcd for $C_6H_2N_{10}O_8$(%): C 21.06, H 0.59, N 40.94; found(%) C 21.08, H 0.57, N 40.92. ESI-MS(m/z): 377[M+^{35}Cl]$^-$、379[M+^{37}Cl]$^-$.

3 Results and discussion

3.1 Synthesis

3.1.1 Synthesis of MSH

MSH is unfortunately not stable in storage so before each reaction it was prepared from ethyl *O*-2,4,6-trimethylsulphonylacetohydroximate by hydrolysis with 70% perchloric acid. After hydrolysis it was poured into ice-water, extracted with dichloromethane, and the dichloromethane solution was dried over sodium sulfate, the dichloromethane was concentrated in vacuo to give white solid compound MSH.

3.1.2 Synthesis of ABDNP

To obtain ABDNP, we treated ADNP with different oxidizing agents as azo coupling reagent by following the synthetic procedures used for the generation of reported compounds[1,9,13-15]. A host of different oxidants, which were successfully used to prepare compounds, containing the C—N = N—C structure from energetic compounds with the C—NH_2 group, were selected. Unfortunately, no formation of compound ABDNP was observed by following use of oxidants except tert-butyl hypochlorite(*t*-BuOCl), sodium dichloroisocyanurate(SDCI) and trichloroisocyanuricacid(TCICA) in Table 1.

Table 1 Oxidative coupling reaction of ADNP with different oxidants

oxidant	solvent	mol ratio[1)]	*T*/℃	*t*/h	yield/%
t-BuOCl	CH_3CN	1∶1.25	r.t.[2)]	1	43.5
SDIC	CH_3CN	1∶1.1	0	1	33.6
TCICA	CH_3CN	1∶1.1	0	1	38.1
$KMnO_4$/NaOH	None	1∶1	55	7	0
$KMnO_4$/HCl	None	1∶1	55	7	0
10% NaClO	None	1∶1	r.t.	3	0
H_2O_2	CH_3CN	1∶1	r.t.	7	0

Note: 1) mol ratio of 1-amino-3,5-dinitropyrazole to oxidant, 2) room temperature.

3.2 Property of ABDNP

The structure of ABDNP was optimized by Gaussian 09[16] in order to obtain their stable geometric configuration, and their density and heat of formation were computed. The detonation parameters were obtained by VLW equation[17] using density and heat of formation as basic data. The performance of ABDNP and 1,3,5-trinitro-1,3,5-triazinane (RDX)[18] were shown in Table 2.

Table 2 Properties of ABDNP and RDX

performances	ABDNP	RDX
appearance	yellow solid	white crystal
density/g·cm^{-3}	1.94	1.82
nitrogen content/%	40.94	37.84
melting point/℃	–	203.3
decomposition peak temperature/℃	239.6	244.6
detonation velocity/m·s^{-1}	9309.0	8386
detonation pressure/GPa	42.2	33.7
heat of formation/kJ·mol^{-1}	992.1	89.28
CCDC number	1015098	–

4 Conclusions

A nitrogen-rich, polynitro energetic compound with an *N*,*N*-azo linkage, 1,1′-azobis(3,5- dinitropyrazole)(ABDNP), can be obtained by three different coupling reagents from 1-amino-3,5-dinitropyrazole(ADNP) with yield of 43.5%.

ABDNP has better detonation performances than RDX. Especially, ABDNP has higher positive heat of formation, which is 992.1 kJ·mol^{-1} than 89.28 kJ·mol^{-1} of RDX. The thermal decomposition temperature of ABDNP is 239.6 ℃, indicating that ABDNP has preferable thermal stability.

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1,1′-偶氮双(3,5-二硝基吡唑)的合成

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摘 要: 以3,5-二硝基吡唑(DNP)为原料,经中和、N-胺化、氧化偶联等反应合成了一种含 *N*,*N*-偶氮结构的富氮、多硝基含能化合物——1,1′-偶氮双(3,5-二硝基吡唑)(ABDNP),采用红外、核磁(^{1}H NMR, ^{13}C NMR)、质谱及元素分析表征了该化合物的结构;考察了不同氧化剂体系对偶联反应的影响;并计算了化合物 ABDNP 的物化及爆轰性能。结果表明,使用次氯酸叔丁酯作为氧化剂最好,ABDNP 收率为 43.5%;其密度为 1.94 g·cm^{-3}, 爆速为 9309.0 m·s^{-1},爆压为 42.2 GPa,优于 RDX。

关键词: 1,1′-偶氮双(3,5-二硝基吡唑)(ABDNP); 氧化偶联反应; 合成; 性能
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