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Synthesis and Characterization of Pentanol-3-nitraza-5-azidonitrate

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Abstract: A novel energetic plasticizer containing —N—NO_2, —N_3 and —ONO_2 groups in molecular structure, pentanol-3-nitraza-5-azidonitrate (PNAN) (crude product) was designed and synthesized for the first time via reaction in dimethyl sulfoxide, using 1, 5-dinitrato-3-nitraza pentane (DINA) and sodium azide as raw materials The crude product was separated and purified bysilica gel column chromatography with the purity of 98.60%. The structure of PNAN was characterized by IR, ^{1}HNMR and elemental analyses. Some physicochemical properties of PNAN were obtained by the tests. Results show that the density is 1.46 g·cm^{-3}, decomposition temperature 172 ℃, glass transition temperature −41℃, viscosity 19.5 mPa·s, friction sensitivity 12% and impact sensitivity 56%.

Key words: pentanol-3-nitra-5-azidonitrate(PNAN); synthesis; characterization

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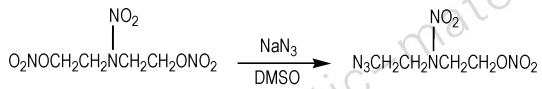
1 Introduction

The energetic azido compounds[1-2] including energetic azido plasticizers have received a great deal of attention as they impart additional energy to propellants and explosives[3-6]. It has been shown that the energetic azido plasticizers commonly applied, such as azide nitrate ester and 1,3-propanediol-2,2-bis(adzidomethyl) dinitrate (PDADN), can increase burning rate and energy of nitramine modified double base propellant [7-8], thought they have a critical shortcoming of high sensitivity to impact and shock, which implies that it is necessary to look for a new plasticizers with high performance and lower sensitivity. Fortunately, pentanol-3-nitraza-5-azidonitrate (PNAN) with nitramino (—N—NO_2), azido (—N_3) and nitrate ester group (—ONO_2) reported in this work is just such a plasticizer, which is synthesized for the first time via reaction in dimethyl sulfoxide, using 1, 5-dinitrato-3-nitraza pentane (DINA) and sodium azide as raw materials (Scheme 1), confirmed its structure and measured its physicochemical properties.



Scheme 1 The synthesis of PNAN

2 Experimental

2.1 Synthesis of PNAN

DINA (20 g, 0.083 mol) was slowly added to 40 mL of dimethyl sulfoxide at 50 ℃, and the solution was heated to 65 ℃ with good stirring. After DINA was completely dissolved in dimethyl sulfoxide solution, NaN_3 (6.5 g, 0.1 mol) was added in 2 h, then the mixture was held at 85 ℃ for 3 h. To generate the primary product, NaN_3 must be treated with an excess of DINA and also added in 2 h for several times. The optimum reaction conditions were as follows: the molar ratio of DINA to NaN_3 was 1∶0.8, reaction time 3 h, reaction temperature 85 ℃. After cooling an equal quantity of methylene chloride solvent was added and the entire organic portion was washed four times with water to remove dimethyl sulfoxide and inorganic salts. The methylene chloride solution was concentrated to give 18 g of light yellow oil. The products were detected by TLC (Thin Layer Chromatography). After dilution with acetone, the mixture was separated by column chromatography (SiO_2, petroleum ether∶EtOAc = 4∶1), then 7.14 g of colorless oil with a purity of 98.60% (HPLC) was obtained. The product was PNAN. Fig. 1 was the ^{1}H NMR spectra of PNAN. ^{1}H NMR ($CDCl_3$/TMS) δ: 3.659 (t, 2H, —CH_2N_3), 3.986 (t, 2H, —CH_2NNO_2), 4.195 (t, 2H, —CH_2NNO_2), 4.791 (t, 2H, —CH_2ONO_2); IR (KBr, ν/cm^{-1}): 2960, 1452, 1419, 882(—CH_2), 2108(—N_3), 1521(N—NO_2), 1226 (—ONO_2), 847(N—O); Anal. Calc (%) for $C_4N_6O_5H_8$: C 21.82, N 38.14, H 3.64; Found (%) C 21.85, N 37.70, H 3.64.

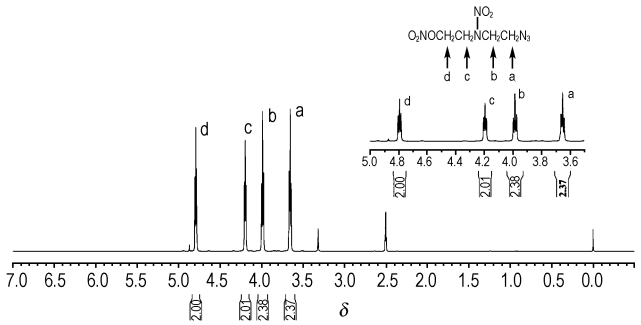


Fig. 1 ^{1}H NMR spectra of PNAN

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2.2 Properties of PNAN

Some physicochemical properties of PNAN obtained by the tests are all listed in Table 1, including the appearance, density, dissolubility, decomposition temperature, glass transition temperature, viscosity, friction sensitivity and impact sensitivity. In which, the decomposition temperature of 172 ℃ shows that PNAN has good heat-resistance ability. The friction sensitivity of 12% of PNAN is less than that of PDADN (80%[8]). The impact sensitivity of 56% of PNAN is less than that of PDADN (100%[8]), revealing that in comparison with PDADN, PNAN has better mechanical sensitivity.

Table 1 Properties of PNAN

properties	results	test condition
appearance	colorless oil	eyeballing
empirical formula	$C_4N_6O_5H_8$	—
density/g · cm^{-3}	1.46	density bottle method
dissolubility	soluble in methylene chloride, acetone, benzene, dimethyl sulfoxide,	experiment
oxygen balance/%	−43.6	—
decomposition temperature/℃	172	GJB772A−1997, method 502.1
glass transition temperature/℃	−41	dynamic thermomechanometry
viscosity/mPa · s	19.5	experiment
friction sensitivity/%	12	GJB772A−1997, method 602.1
impact sensitivity/%	56	GJB772A−1997, method 601.1

3 Results

Pentanol-3-nitraza-5-azidonitrate (PNAN) was synthesized for the first time with a density of 1.46 g · cm^{-3}, decomposition temperature of 172 ℃, glass transition temperature of −41 ℃, viscosity of 19.5 mPa · s, friction sensitivity of 12% and impact sensitivity of 56% , which is a colorless oil, soluble in methylene chloride, acetone, benzene and dimethyl sulfoxide, but insoluble in water and alcohol. It can be potentially used as an energetic plasticizer of solid propellants.

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3-硝基-5-叠氮基-3-氮杂戊醇硝酸酯的合成及表征

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摘 要: 用 *N*-硝基二乙醇胺二硝酸酯(DINA)和叠氮化钠为原料, 在二甲基亚砜中反应合成了一种分子中含—N—NO_2, —N_3, —ONO_2基团的新型含能增塑剂, 3-硝基-5-叠氮基-3-氮杂戊醇硝酸酯(PNAN)(粗品)。粗产品经硅胶柱色谱分离净化。所得纯产品的纯度为98.60%。纯产品的结构用 IR、^{1}H NMR 及元素分析表征。测试得到 PNAN 的密度为 1.46 g · cm^{-3}, 热分解温度为 172 ℃, 玻璃化转变温度为−41 ℃, 粘度为 19.5 mPa · s, 摩擦感度为 12%, 撞击感度为 56%。

关键词: 3-硝基-5-叠氮基-3-氮杂戊醇硝酸酯(PNAN); 合成; 表征

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