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Synthesis of 6-Dinitroethylene-4,5,8-trinitro-5,6,7,8- tetrahydro-4*H*-imidazo[4,5-e] furazano[3,4-b]piperazine

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Abstract: A novel energetic compound, 6-dinitroethylene-4,5,8-trinitro -5,6,7,8- tetrahydro -4*H*- imidazo [4,5-e] furazano [3,4-b] piperazine (PNEIFP), was designed and synthesized from glyoxal and FOX-7 by two cyclizations and nitration. In addition, some properties of PNEIFP were calculated by Gaussian 09 program and VLW formula. The results show that its density is 2.02 g·cm^{-3}, and the detonation velocity is 9681.0 m·s^{-1}, and the enthalpy of formation is 724.1 kJ·mol^{-1}. PNEIFP easily decomposes at room temperature.

Key words: organic chemistry; synthesis; 6-dinitroethylene-4,5,8-trinitro -5,6,7,8-tetrahydro-4*H*- imidazo [4,5-e] furazano[3,4-b]piperazine; performance

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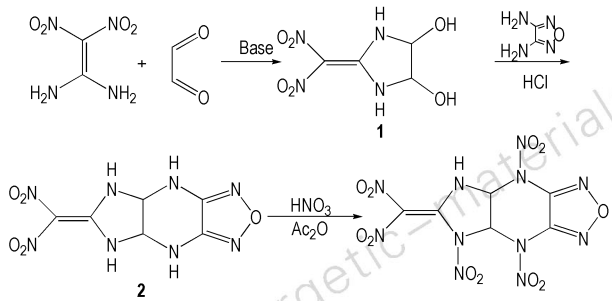
1 Introduction

In the last decades, the furazan fused ring compounds have attracted more attention owing to their high density, high specific volume and high nitrogen content[1-5]. A novel energetic compound based on furazan and piperazine fused ring, 6-dinitroethylene-4,5,8-trinitro-5,6,7,8-tetrahydro-4*H*- imidazo [4,5-e] furazano[3,4-b]piperazine (PNEIFP), was firstly designed and its physico-chemical performances were calculated by Gaussian 09 program[6] and VLW method[7] (density 2.02 g·cm^{-3}, enthalpy of formation +724.1 kJ·mol^{-1}(298 K) and detonation velocity 9681.0 m·s^{-1}). Using glyoxal and 1,1-diamino-2,2-dinitroethylene (FOX-7) as starting materials, PNEIFP was synthesized for the first time via the reactions of two cyclizations and nitration with a total yield of 5.2% (Scheme 1), PNEIFP and its intermediates were characterized by NMR, IR, MS and EA etc. However, it is found that PNEIFP shows a bad stability, easily decomposes at room temperature.



Scheme 1 Synthetic route of PNEIFP

2 Experimental

2.1 Synthesis of 4,5-dihydroxy-2-dinitroethyleneimidazo(1)

Glyoxal (40% in water, 7.5 g, 0.05 mol), 10 mL water were mixed and stirred at room temperature. To this mixture, Na_2CO_3 (0.15 g, 1.4 mmol) was added, and then FOX-7 (7.4 g, 0.05 mol) was added in batches after Na_2CO_3 dissolved, the mixture was stirred for another 4 h. The yellow precipitate was filtered to obtain 8.3 g solid with a yield of 80.6% and a purity of 99.0% (HPLC). IR (KBr, ν/cm^{-1}): 3483, 3429(—OH), 3307(—NH), 1602(—C═N), 1562, 1352(—NO_2), 1048(—C—O); ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 4.978 (s, 2H, OH), 6.729(s, 2H, CH),9.660(s, 2H, NH); ^{13}C NMR (DMSO-d_6, 500 MHz), δ: 85.95 (CH), 129.27 (C(NO_2)$_2$), 152.92 (C═C); Anal. calcd for $C_4H_6O_6N_4$:C 23.31, H 2.93, N 27.18; found C 22.79, H 2.91, N 26.91.

2.2 Synthesis of 6- dinitroethylene -5,6,7,8-tetrahydro-4*H*-imidazo[4,5-e] furazano[3,4-b]piperazine (2)

1 (2.06 g, 0.01 mol), 10 mL distilled water were transferred into a three-necked round-bottomed flask with a mechanical stirrer, then 37% hydrochloric acid (7 mL, 0.08 mol) was added dropwise. After being warmed to 70 ℃ and **1** dissolved completely, 3,4-diaminofurazan (1.0 g, 0.01 mol) was added in batches and the mixture was stirred for another 2 h at this temperature. The solution was cooled to 10 ℃, then, the deep red precipitate was filtered to obtain 1.0 g solid with a yield of 37.0% and a purity of 98.5% (HPLC). IR (KBr, ν/cm^{-1}): 3323 (—NH), 1543, 1320 (—NO_2), 1615, 1520, 1098 (furazan); ^{1}H NMR (DMSO-d_6, 500 Hz) δ: 5.631 (2H, s, CH),7.738(2H, s, NH-piperazine), 9.489(2H, s, NH-imidazolidin); ^{13}C NMR (DMSO-d_6, 125 Hz) δ: 64.578 (CH), 129.306 (C(NO_2)$_2$), 145.645 (C-furazan), 152.356 (C═C); Anal. calcd for $C_6H_6O_5N_8$: C 26.67, H 2.22, N 41.48;found C 26.68, H 2.52, N 40.26.

2.3 Synthesis of 6- dinitroethylene -4,5,8 –trinitro -5,6,7,8- tetrahydro- 4*H*-imidazo[4,5-e] furazano [3,4-b]piperazine (PNEIFP)

2 (0.38 g, 1.4 mmol) and 5 mL 100% nitric acid were added in a three-necked round-bottomed flask with a stirrer. The reaction mixture was cooled to –5 ℃, and then acetic anhydride was added dropwise. After acetic anhydride was added

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completely, it was stirred for another 5 h at 0 ~5℃. The final mixture was put into ice water, and then the yellow precipitate was filtered to obtain 0.1 g solid with a yield of 17.5% and purity of 98.7%. IR (KBr, ν/cm^{-1}): 3381(—NH), 1619,1384 (—NO_2), 1756, 1471,1033 (furazan); ^{1}H NMR (Acetone, 500 Hz)δ: 6.868 (s, CH), 8.375 (s,CH), 9.593(s, NH-imidazolidin); ^{13}C NMR(DMSO-d_6, 125 Hz)δ: 64.763(CH), 70.572 (CH), 140.959 (C(NO_2)$_2$), 142.844 (2C, C-furazan), 148.256 (C═C); Anal. calcd for $C_6H_3O_{11}N_{11}$: C 17.86, H 0.741, N 38.02;found C 17.78, H 1.28, N 34.48.

2 Property

Physico-chemical properties, such as density and enthalpy of formation were calculated by Gaussian 09 program[6], its detonation velocity and detonation pressure were calculated by VLW method[7]. The data of performances for PNEIFP were showed in the Table1.

Table 1 Performances of PNEIFP

properties	appearance	dissolubility	decomposition temperature/℃	density /g·cm^{-3}	detonation velocity/m·s^{-1}	detonation pressure/GPa	enthalpy of formation/kJ·mol^{-1}	explosion heat /J·g^{-1}
results	yellow solid	soluble in acetone and DMSO	20	2.02	9681.0	44.45	724.10	7303.0
condition	Eyeballing (tested)	experimental method (tested)	TLC analysis (tested)	Gaussian 09 program(caculated)	VLW method (caculated)	VLW method (caculated)	Gaussian 09 program(caculated)	K-J formula (caculated)

Note: DMSO is dimethyl sulfoxide.

A new furazan fused ring energetic compound, 6-dinitroethylene-4,5,8-trinitro -5,6,7,8- tetrahydro -4*H*- imidazo [4,5-e] furazano [3,4-b]piperazine (PNEIFP), was synthesized for the first. In addition, some properties of PNEIFP were obtained by calculation or test. The calculated results show that the density, enthalpy of formation, detonation velocity, and detonation pressure of PNEIFP are 2.02 g·cm^{-3}, 724.1 kJ·mol^{-1}, 9681.0 m·s^{-1} and 44.45 GPa, respectively. The above fact showed that PNEIFP exhibits good explosive performance. It is a pity that PNEIFP easily decomposes at room temperature.

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6-偕二硝基乙烯基-4,5,8-三硝基-5,6,7,8-四氢化-4*H*-咪唑烷并[4,5-e]呋咱并[3,4-b]哌嗪的合成

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摘 要: 以 FOX-7 和乙二醛为原料,经过两步缩合环化反应和硝化反应,首次设计并合成出了一种新型的呋咱稠环硝胺化合物6-偕二硝基乙烯基-4,5,8-三硝基-5,6,7,8-四氢化-4*H*-咪唑烷并[4,5-e]呋咱并[3,4-b]哌嗪(PNEIFP)。采用 Gaussian 09 程序和 VLW 方程计算 PNEIFP 的密度、生成焓和爆速分别为 2.02 g·cm^{-3}、724.1 kJ·mol^{-1}和 9681.0 m·s^{-1}。利用 TLC 跟踪实验的方法,确定 PNEIFP 室温下易分解。

关键词: 有机化学; 合成; 6-偕二硝基乙烯基-4,5,8-三硝基-5,6,7,8-四氢化-4*H*-咪唑烷并[4,5-e]呋咱并[3,4-b]哌嗪; 性能

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