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Synthesis of 6-Nitroimino-4,8-dinitro-5,6,7,8-tetrahydro-4*H*-imidazo[4,5-e]furazano[3,4-b]pyrazine

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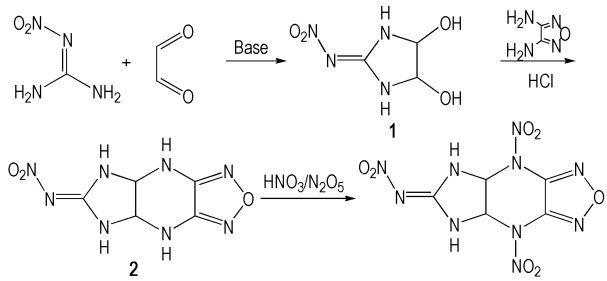
1 Introduction

In the last decades, the furazan fused ring compounds have been paid much more attention owing to their characteristics, such as high density, high specific volume and high nitrogen content[1-3]. A novel energetic compound based on furazan fused ring, 6-nitroimino-4,8-dinitro-5,6,7,8- tetrahydro-4*H*- imidazo [4,5-e] furazano [3,4-b] pyrazine (NIFDNP), was firstly designed and its properties of physicochemical and detonation were calculated by Gaussian 09 program[4] and VLW method[5]. Using glyoxal and nitroguanidine as starting materials, NIFDNP was synthesized for the first time via the reactions of twice cyclizations and nitrification with a total yield of 14.3% (Scheme 1), NIFDNP and its intermediates were characterized by the means of NMR, IR, MS and EA etc. Furthermore, its melting point was tested by melting point apparatus.



Scheme 1 The synthetic route of NIFDNP

2 Experimental

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

Glyoxal (40% in water, 27.9 g, 0.2 mol), 13 mL water were mixed and stirred at room temperature. To this mixture, Na_2CO_3 (0.48 g, 0.0045 mol) was added, and then nitroguanidine (20.8 g, 0.2 mol) was added in batches after Na_2CO_3 dissolved completely, the mixture was stirred for another 4 h. The pink precipitate was filtered to obtain 26.2 g solid with a yield of 80.9% and a purity of 99.9% (HPLC). IR (KBr, cm^{-1}) υ: 3375, 3323 (—OH), 3220, 3130 (—NH), 1602 (—C═N), 1560, 1339 ($—NO_2$), 1361 (—CH),1045 (—C—O); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 160.95 (C═N—NO_2), 85.38(CH); Anal. calcd for $C_3H_6O_4N_4$: C 22.23, H 3.73, N 34.56; found C 22.03, H 6.68, N 34.17.

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

1(8.1 g, 0.05 mol), 50 mL distilled water were transferred into a three-necked round-bottomed flask with a mechanical stirrer, then 37% hydrochloric acid (35 mL, 0.4 mol) was added dropwise. After warmed to 60 ℃, 1 was dissolved completely, 3,4-diaminofurazano (5.0 g, 0.05 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 orange precipitate was filtered to obtain 9.0 g solid with a yield of 64.5% and a purity of 99.2% (HPLC). IR (KBr, cm^{-1}) υ: 3350, 3221 (—NH), 1639 (—C═N), 1396 (—CH), 1584, 1396 ($—NO_2$) 1621, 1548, 1085 (furazan); ^1H NMR(DMSO-d_6, 500 MHz) δ: 5.438 (2H, s, CH),7.868 (2H, s, NH-ipiperazine), 9.128 (2H, s, NH-imidazolidin); Anal. calcd for $C_5H_6O_3N_8$: C 26.55, H 2.67, N 49.55; found C 26.45, H 2.68, N 49.93.

2.3 Synthesis of 6-nitroimino-4,8-dinitro-5,6,7,8-tetrahydro-4*H*- imidazo[4,5-e] furazano [3,4-b] pyrazine (NIFDNP)

A solution of N_2O_5 (1.8 g, 0.017 mol) in 6 mL 100% nitric acid was placed in a 50 mL three-necked round-bottomed flask with a magnetic stirrer. This was cooled to −5℃ and stirred while 2 (0.4 g, 0.0018 mol) was added in small portion over 5 min. The mixture was allowed to 0 −5 ℃ over 5 h. Then the reaction mixture was poured into methylene chloride (60 mL) and cooled to −10 ℃ over 12 h. The white precipitate was filtered to obtain 0.2 g solid with a yield of and 27.4% and a purity of 98.9 % (HPLC). IR (KBr, cm^{-1}) υ: 3432, 3281 (—NH), 1617, 1590, 1356 (furazan), 1400 (—CH), 1532, 1334, 1356 ($—NO_2$); ^{13}C NMR(Acetone-d_6, 125 MHz) δ: 160.95(C═N—NO_2), 141.86 (CH), 70.02 (C-furazan); Anal. calcd for $C_5H_4O_7N_{10}$: C 18.99, H 1.27, N 44.30;found C 18.56, H 1.44, N 44.20; MS(EI) m/z: 315 (M-1).

2.4 The physicochemical and detonation performance of NIFDNP

The properties, such as density, enthalpy of formation, detonation velocity and detonation pressure for NIFDNP were shown in the Table 1. As seen in Table 1, NIFDNP has good detonation performances and physicochemical characteristics.

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Table 1 The properties of NIFDNP

properties	results	condition
appearance	white solid	eyeballing (tested)
density /g·cm^{-3}	2.04	Gaussian 09 program (caculated)
dissolubility	soluble in acetone and DMSO	experiment (tested)
melting point /℃	173 –175	melting point apparatus (tested)
detonation velocity /m·s^{-1}	9226	VLW method (caculated)
detonation pressure /GPa	40.56	VLW method (caculated)
enthalpy of formation (298 K)/kJ·mol^{-1}	437.6	Gaussian 09 program (caculated)
explosion heat /J·g^{-1}	6029	K-J formula (caculated)

3 Results

A new furazan fused ring energetic compound, NIFDNP, was first synthesized with a total yield of 14.3%. In addition, the target compound was found to have good detonation and physicochemical characteristics through calculation and test; which can result in extensive potential applications on gas generator, explosive mixture and propellants.

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