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Synthesis and Properties for Two *N*-amino Derivatives of 4,8-Dihydrodifurazano[3,4-b,e]pyrazine

LI Ya-nan, LIU Ning, LIAN Peng, GE Zhong-xue, WANG Bo-zhou
(*Xi'an Modern Chemistry Research Institute, Xi'an* 710065, *China*)

Abstract: Two energetic compounds——4-aminodifurazano[3,4-b,e]pyrazine (ADFP) and 4,8-diaminodifurazano[3,4-b,e]pyrazine (DADFP) were prepared via *N*-amination reaction and their structures were characterized by IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. The themal properties of ADFP and DADFP were analyzed by differential scanning calorimetry and thermogravimetry techniques. Results show that DADFP melts concomitantly with decomposition at 284.3 ℃. The melting point of ADFP is 218.1 ℃ and its first decomposition temperature is 247.1 ℃, which indicate that ADFP and DADFP have good thermal stability.

Key words: organic chemistry; 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DADFP); 4-aminodifurazano[3,4-b,e]pyrazine (ADFP); *N*-amination reaction; synthesis; properties
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1 Introduction

Heterocyclic-based compounds, such as pyrazole, triazole, tetrazole, tetrazine, furazan and furoxan derivatives, have most often been utilized in energetic compounds due to their higher positive heat of formation, density, nitrogen content, oxygen balance and better thermal stability than those of their carbocyclic analogues, which are attributed to their large number of C—N, N—N, C = N and N = N bonds[1-8]. Combustion products of heterocyclic-based compounds contain large amounts of nitrogen, which is environmentally friendly. So, a number of heterocycle-based energetic compounds were reported and extensively used as high-energy explosives and ingredients of propellants[4,9]. Some of nitrogen-rich energetic compounds were synthesized using the *N*-amino compounds as raw materials[3,8]. *N*-amination reaction is an effective method to obtain *N*-amino compounds using imino compounds as start materials[10]. In 1997, I. B. Starchenkov[11] and his colleague reported the synthesis of 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP) and its derivatives, but the data of complete characterization and performance were not reported.

In this paper, two nitrogen-rich energetic compounds, 4-aminodifurazano[3,4-b,e]pyrazine (ADFP) and 4,8-diaminodifurazano[3,4-b,e]pyrazine (DADFP), were synthesized using 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP) as start material via *N*-amination reaction. The properties of ADFP and DADFP were estimated by a B3LYP method on 6-31G(d,p) basis set of Gaussian 09 procedure[12-13]. The main themal properties of ADFP and DADFP were analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG) techniques.

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Biography: LI Ya-nan(1984-), male, engineer, majoring in synthesis and property of energetic materials. e-mail: lyn2003080094@126.com
Corresponding Author: WANG Bo-zhou(1967-), male, professor, majoring in synthesis and property of energetic materials. e-mail: wbz600@163.com

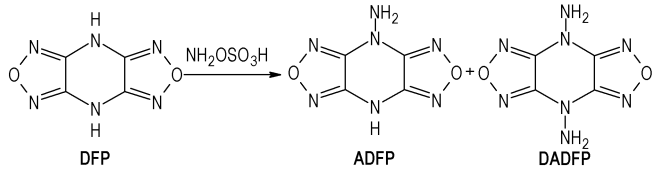
2 Experiment

2.1 Methods and materials

Melting points were determined using an open capillary tube. The IR spectra were recorded by NEXUS 870-based Fourier infrared spectrometer employing KBr pellet. ^{1}H NMR and ^{13}C NMR spectra were recorded with AV 500-type (500 MHz) superconducting NMR instrument. DMSO-d_6 was used as the solvent and tetramethyl silane (TMS) as the internal standard. Elemental analysis were performed on Vario EL-Ⅲ Elemental Analyzer. Differential scanning calorimetry (DSC) and thermogravimetric (TG) were carried out in a platinum sample container using Shimadzu DSC-60 and Nicolet TA 2950, respectively. 1.0 mg sample was heated at 10 ℃·min^{-1}.

DFP was self-synthesized; hydroxylaminosulfuric acid, hydrochloric acid, sodium carbonate, sodium bicarbonate were AR grade, purchased from Chengdu Kelong Chemical Reagents Factory.

2.2 Synthetic route



Scheme 1 Synthetic route of ADFP and DADFP

2.3 Synthesis of DADFP and ADFP

2.3.1 Synthesis of DADFP

To a solution of 0.5 g(0.003 mol) DFP and 0.95 g (0.009 mol) sodium carbonate in 14.5 mL water at 70 ~ 75 ℃, a solution of 1.53 g(0.012 mol) hydroxylaminosulfuric acid in 6.5 mL water was added for 10 min. The pH was kept at 8 ~9 by the addition of sodium bicarbonate. The mixture was kept at 70 ~75 ℃ for 2 h and then cooled to 15 ~

20 ℃. The precipitate was filtered off, washed with water and acetone, and dried to give 0.11 g off white solid, yield 18.6%. m.p.: 282.3 ~ 283.8 ℃.

^{1}H NMR (DMSO-d_6, 500 MHz), δ: 5.788 (s, 4H, —NH_2); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 149.93; IR (KBr, ν/cm^{-1}): 3312, 3246 (—NH_2), 1666 (C = N), 1613, 1443, 1021 (furazan ring); Anal (%). calcd for $C_4H_4N_8O_2$: C 24.50, N 57.13, H 2.06; found: C 24.41, N 57.23, H 2.01; MS (m/z): 180[M–NH_2]$^-$.

2.3.2 Synthesis of ADFP

The above alkaline filtrate was collected, and then the pH value of filtrate was neutralized to 1 ~ 2 with hydrochloric acid under the condition of cooling with ice water. The white precipitate was filtered, washed with water, and 0.153 g white solid was obtained with a yield of 28.1%. m.p.: 217.8 ~ 219.4 ℃.

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 5.751 (s, 2H, —NH_2), 11.913 (s, 1H, —NH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 146.89, 150.22; IR (KBr, ν/cm^{-1}): 3325 (—NH_2), 3283 (—NH), 1654 (C = N), 1618, 1445, 1003 (furazan ring); Anal (%). Calcd for $C_4H_3N_7O_2$: C 26.53, N 54.14, H 1.67; found: C 26.38, N 54.21, H 1.76; MS (m/z): 180[M–H]$^-$.

3 Results and discussion

3.1 Properties of ADFP and DADFP

ADFP was soluble in dimethyl sulfoxide, acetonitrile, acetone and methanol, and insoluble in water, diethyl ether and petroleum ether. DADFP was soluble in dimethyl sulfoxide, concentrated sulfur acid and acetonitrile, and insoluble in toluene, water and diethyl ether. The structures of ADFP and DADFP were optimized by Gaussian 09 in order to obtain their stable geometric configuration. The explosive parameters were obtained by VLW equation[12] using density and heat of formation as basic data, which were computed by Gaussian 09[13]. The date were shown in table 1. Data show that ADFP and DADFP have better detonation performances than RDX and high positive heat of formation.

Table 1 Properties of ADFP, DADFP and RDX

performances	ADFP	DADFP	RDX[14]
appearance	white solid	offwhite solid	white crystal
density/g · cm^{-3}	1.85	1.78	1.82
nitrogen content /%	54.14	57.13	37.84
melting point /℃	217.8–219.4	282.3–283.8	203.3
thermal decomposition peak/℃	247.1,288.8	284.3	244.6
detonation velocity /m · s^{-1}	9524.20	9620.84	8386
detonation pressure /GPa	43.26	40.84	33.7
heat of formation /kJ · mol^{-1}	1164.47	1335.32	–89.28
detonation energy /kJ · kg^{-1}	8980.11	9279.03	5355

3.2 Thermal properties of ADFP and DADFP

3.2.1 ADFP

The DSC and TG-DTG analyses revealed that ADFP was thermally stable up to 230.5 ℃. The DSC curve (Fig. 1) exhibited a melting point at 218.1 ℃ and two thermal decomposition peaks at 247.1 ℃ and 288.8 ℃, respectively. The TG-DTG curves (Fig. 2) showed that there were two stages in the decomposition process of ADFP with a mass loss of 30.77% before 262.0 ℃ at first stage and a total mass loss of 72.78% before 317.4 ℃, and a 16.87% residue at 484.0 ℃.

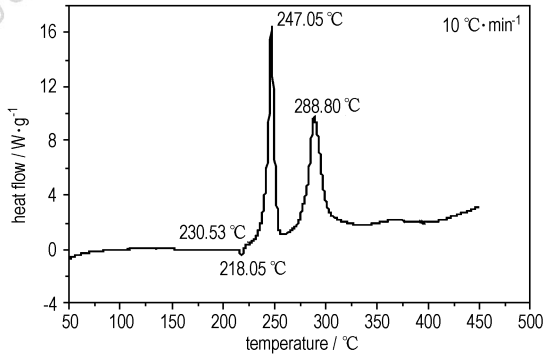


Fig. 1 DSC curve of ADFP

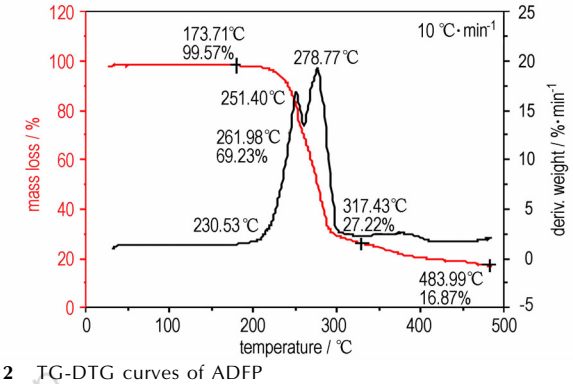


Fig. 2 TG-DTG curves of ADFP

3.2.2 DADFP

The DSC and TG-DTG analyses revealed that DADFP was thermally stable up to 273.5 ℃. The DSC curve (Fig. 3) exhibited a melting point at 284.3 ℃, and one thermal decomposition peak at 305.7 ℃ (Fig. 4). TG-DTG curves (Fig. 4) showed that there was one main decomposition stage with a mass loss of 68.98% before 394.7 ℃, and 24.78% residue at 497.4 ℃.

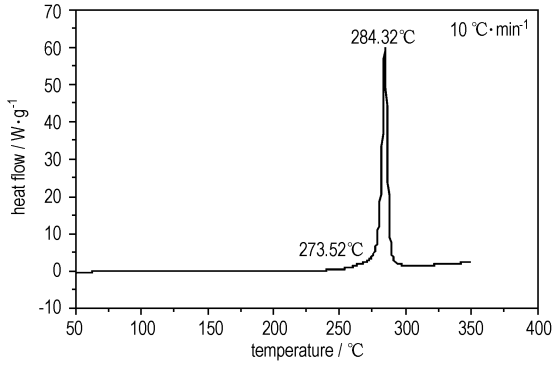


Fig. 3 DSC curve of DADFP

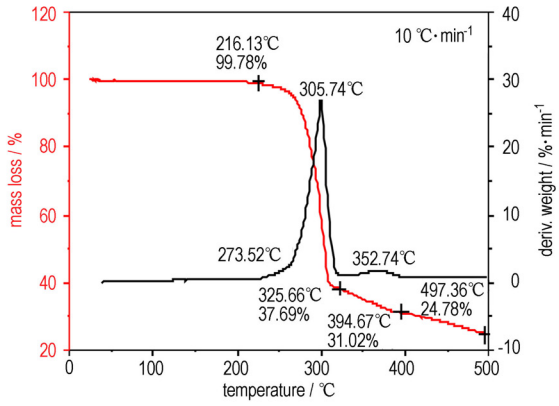


Fig. 4 TG-DTG curves of DADFP

4 Conclusions

(1) Two *N*-amino derivatives of DFP, ADFP and DADFP, were synthesized by *N*-amination reaction with a yield of 18.6%.

(2) ADFP and DADFP have better detonation performances than RDX. Especially, both of them have high positive heat of formation: 1164.47 kJ·mol^{-1} and 1335.32 kJ·mol^{-1}.

(3) The date indicate that ADFP and DADFP havegood thermal stability.

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