Synthesis, Characterization and Thermal Properties of Energetic Compounds Derived from 3-Amino-4-(tetrazol-5-yl)furazan

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Five energetic compounds, 3,3-bis(tetrazol-5-yl)-4,4-azofurazan (DTZAF), 3-nitro-4-(tetrazol-5-yl)furazan (NTZF), hydrazinium 3-amino-4-(tetrazol-5-yl)furazan (HATZF), triaminoguanidinium 3-amino-4-(tetrazol-5-yl)furazan (TAGATZF) and guanylureaium 3-amino-4-(tetrazol-5-yl)furazan (MATZF), were prepared using 3-amino-4-(tetrazol-5-yl)furazan (ATZF) as starting material and their structures were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. The properties of NTZF were estimated: density is 1.67 g/cm^3, enthalpy of formation ＋415.41 kJ/mol and detonation velocity 8257.83 m/s. The main thermal properties of four compounds, DTZAF, HATZF, TAGATZF and MATZF, were analyzed by TG and DSC techniques and the results showed that their melting points are 251.9, 159.7, 205.4 and 211.4 ℃, respectively, and their first decomposition temperatures are 256.7, 258.6, 231.7 and 268.6 ℃, respectively. The fact that their decomposition temperatures were over 230 ℃ showed that they exhibit better thermal stability.

Keywords organic chemistry, 3-amino-4-(tetrazol-5-yl)furazan, energetic derivatives, synthesis, thermal property

Introduction

The currently widely used nitro-explosives such as TNT (trinitrotoluene), RDX (Royal demolition explosive), and HMX (high melting explosive) are the primary pollutants in the explosives industry and military testing of explosives.[1,2] In order to develop environment-friendly explosives, a number of heterocycle-based energetic compounds were reported and were extensively used as high-energy explosives and ingredients of propellants in recent years.[3,4] Among them, tetrazole and furazan derivatives are interesting high energy materials due to both tetrazole and furazan units being typical energetic constitutions with high positive heat of formation, high nitrogen content, good thermal stability deriving from their aromaticity.[5]

Recently, the nitrogen-rich heterocyclic energetic salts have been paid much more attention owing to their unique characteristics. They often possess lower vapor pressures and higher densities on comparison with non-ionic salts.[3] Shreeve *et al*. have made great contributions to this type of energetic materials. Their groups have prepared variety of nitrogen-rich energetic salts including triazolium-, tetazole-, tetrazine- and imidazolium-based salts.[6-9] In this year they reported the furazan-functionalized tetrazolate-based salts derived from 4-amino-3-(5-tetrazolyl)furazn. They demonstrated that these salts exhibit excellent thermal stability and high positive heats of formation since these salts combine the properties of a furazan fragment and a tetrazolate backbone.[10]

3-Amino-4-(tetrazol-5-yl)furazan (ATZF) is not only an energetic compound with high nitrogen content but also an important explosive intermediate.[11] Owing to the reactive amino and tetrazolyl groups in ATZF molecule, a variety of new energetic compounds could be derived.[12-14] 3,3-Bis(tetrazol-5-yl)-4,4-azofurazan (DTZAF) was therefore synthesized by oxidation of ATZF with potassium permanganate in an acidic medium and 3-nitro-4-(tetrazol-5-yl)furazan (NTZF) was prepared by amino oxidation. In addition, three kinds of nitrogen-rich energetic salts with ATZF as their anion were synthesized in order to decrease the acidity of the aimed compounds and improve their performances in energetic compositions including propellants, explosives, gasifiers and pyrotechnics.[15]

3-Amino-4-(tetrazol-5-yl)furazan (ATZF) was synthesized using 3-amino-4-cyanofurazan (CNAF) as a starting material through addition reaction, diazotization and cyclization or was prepared, alternatively, by a [3＋

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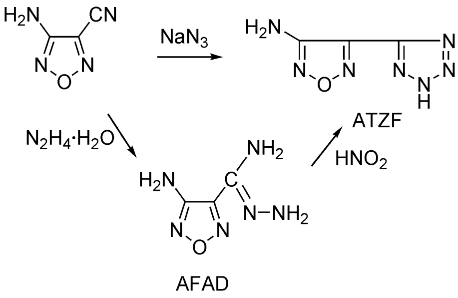
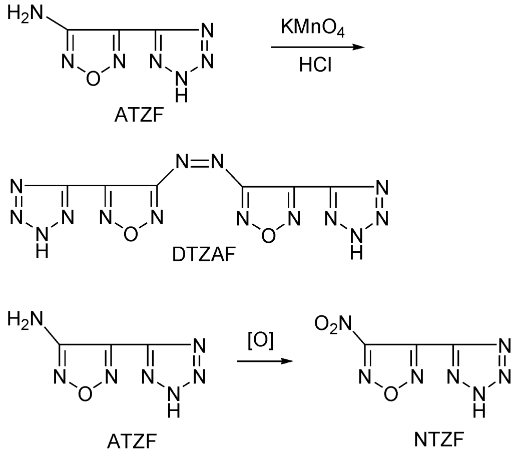
2] cycloaddition of 3-amino-4-cyanofurazan (CNAF) and sodium azide[4-6] (Scheme 1). The five derived energetic compounds, DTZAF and NTZF and three kinds of energetic salts of 3-amino-4-(tetrazol-5-yl)furazan (ATZF) were shown in Scheme 2 and 3, respectively. The [3＋2] cycloaddition mechanism of 3-amino-4-cyanofurazan (CNAF) and sodium azide was discussed. And the properties of 3-nitro-4-(tetrazol-5-yl)furazan (NTZF) were estimated. The main thermal properties of four compounds, 3,3-bis(tetrazol-5-yl)-4,4-azofurazan (DTZAF), hydrazinium 3-amino-4-(tetrazol-5-yl)furazan (HATZF), triaminoguanidinium 3-amino-4-(tetrazol-5-yl)furazan (TAGATZF) and guanylureaium 3-amino-4-(tetrazol-5-yl)furazan (MATZF), were investigated by DSC and TG techniques. The fact that nitrogen content of the five derived energetic compounds exceeds 50% and they exhibit better thermal stability makes them potentially useful as gas generants or energetic materials with low flame temperatures, while simultaneously increase impulse of gun or rochet propellants.

Scheme 1 The synthetic routes of ATZF



Scheme 2 The structures and synthetic routes of DTZAF and NTZF

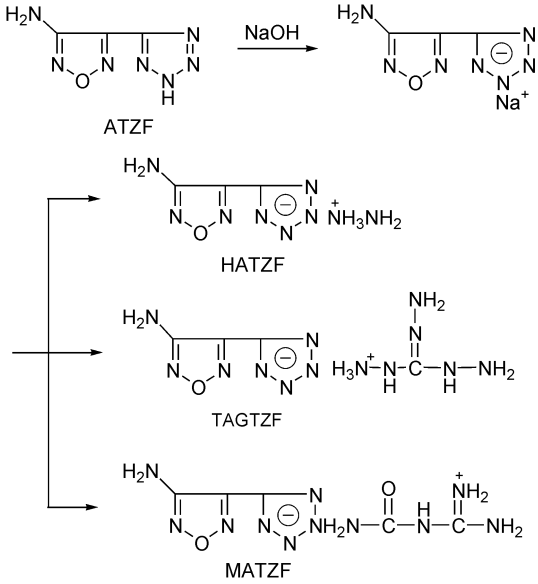


Experimental

General methods and materials

Melting point was determined using an open capillary tube. The IR spectrum was recorded utilizing a NEXUS870-based Fourier infrared spectrometer employing a KBr matrix. ^1H NMR and ^{13}C NMR spectra were recorded with an AV500-type (500 MHz) superconducting NMR instrument. DMSO-d_6 was the solvent and tetramethyl silane (TMS) was an internal standard. Elemental analysis was performed on a Vario EL-Ⅲ Elemental Analyzer. Differential scanning calorimetry (DSC) was carried out in a platinum sample container using a Shimadzu DSC-60. The 1.6—2.0 mg sample was heated at a rate of 10 ℃•min^{-1}. The product purity was recorded on an LC-2010A ht liquid chromatographer.

Scheme 3 Structures and synthetic routes of three ATZF energetic salts



Concentrated sulfuric acid, sodium nitrite, dimethyl formamide (DMF), anhydrous magnesium sulfate, potassium permanganate and sodium tungstate were all of AR grade; 50% hydrogen peroxide, 85% hydrazine hydrate, azide sodium, sodium hydroxide were all of CP grade; triaminoguanidine nitrate,[16] guanylurea hydrochloride[17] and 3-amino-4-cyanofurazan (CNAF)[18] were prepared in our laboratory.

Synthesis of 3-amino-4-aminohydrazolyfurazan (AFAD)

3-Amino-4-cyanofurazan (CNAF) (2.00 g, 18.18 mmol) was transferred into a three-necked round bottom flask fitted with a mechanical stirrer and a dropping funnel and 25 mL of acetonitrile was then added. 85% hydrazine hydrate was added dropwise to the reaction flask at ambient temperature. After hydrazine hydrate was added completely, it was stirred for another 6 h. The white precipitate was filtered and 1.80 g white solid was obtained with a yield of 70.4%. The product (purity 99.9%) was crystallized from ethanol with a melting point of 169—171 ℃ (capillary method).

^1H NMR (DMSO-d_6, 500 MHz) δ: 6.39 (s, 2H, NNH_2), 5.96 (s, 4H, CNH_2); ^{13}C NMR (DMSO-d_6, 500 MHz) δ: 154.71, 140.76, 137.68; IR (KBr) ν: 3470, 3415, 3322, 3234 (NH_2), 1662, 1610, 1500 (C＝N) cm^{-1}. Anal. calcd for $C_3H_6N_6O$: C 25.35, N 58.99, H 4.139; found C 25.35, N 59.15, H 4.225.

Synthesis of 3-amino-4-(tetrazol-5-yl) furazan (ATZF)

3-Amino-4-aminohydrazolyfurazan (AFAD) (2.00 g, 12.66 mmol) and 40 mL of 2.0% hydrochloric acid were added into a three-necked round-bottomed flask fitted with a mechanical stirrer and a dropping funnel. 10% $NaNO_2$ solution (10 mL) was added dropwise at 0 ℃. After complete addition, it was stirred further for 2 h at 15 ℃. The yellow precipitate was filtered and 1.65 g yellow solid was collected with a yield of 76.7%. The product (purity 99.7%) was crystallized from water with a melting point of 210—211 ℃. ^1H NMR (DMSO-d_6, 500 MHz) δ: 6.59 (s, 2H, NH_2); ^{13}C NMR (DMSO-d_6, 500 MHz) δ: 155.44, 147.49, 136.20; IR (KBr) v: 3458, 3357 (NH_2), 3050 (N—H), 1641, 1622 (C＝N) cm^{-1}. Anal. calcd for $C_3H_3N_7O$: C 23.53, N 64.05, H 1.961; found C 23.84, N 64.06, H 1.956.

DSC (10 ℃•min^{-1}): 215.79 ℃ (m.p.), 264.43 ℃ (T_p).

"One Step" synthesis of 3-amino-4-(tetrazol-5-yl)-furazan (ATZF)

CNAF (3.30 g, 30.00 mmol) and 6 mL DMF were added in a three-necked round-bottomed flask with a stirrer. To the reaction mixture, sodium azide (2.40 g, 36.92 mmol) was added and the resulting reaction mixture was poured into 42 mL water and its pH was adjusted to 1—2 with 10% hydrochloric acid, then extracted with ethyl ether (50 mL×4). The combined extracts were dried on $MgSO_4$, evaporated to dryness and 4.20 g yellow solid was obtained with a yield of 91.3%. The yellow product was crystallized from water with a melting point of 210—211 ℃ (capillary method).

Synthesis of 3-nitro-4-(tetrazol-5-yl)furazan (NTZF)

Na_2WO_4 (6.60 g, 0.011 mol) followed by addition of 50% hydrogen peroxide solution (90.00 g, 1.32 mol) were placed in a three-necked round-bottomed flask with a stirrer and dropping funnel in an ice-salt bath at －10 ℃, sulfuric acid (88.0 g) was added dropwise to the reaction flask under stirring at 5 ℃. Then, allow the reaction mixture warm to room temperature and CNAF (1.6 g, 14.55 mmol) was added slowly. After CNAF was added completely, the reaction mixture was stirred at room temperature for another 3 h and extracted with CH_2Cl_2 (50 mL×4). The combined extracts were washed with ice-water and dried on $MgSO_4$. The yellow precipitate thus obtained was concentrated on a rotary evaporator to leave 1.5 g solid with a yield of 83.3 %. The crude compound was crystallized from ethyl acetate with a melting point of 123—124 ℃. ^{13}C NMR (DMSO-d_6, 500 MHz) δ: 159.62, 146.96, 140.93; IR (KBr) v: 3250 (broad, N—H), 1566, 1345 (NO_2), 1622 (C＝N) cm^{-1}. Anal. calcd for $C_3HN_7O_3$: C 19.67, N 53.55, H 0.55; found C 19.63, N 54.01, H 0.58.

DSC (10 ℃•min^{-1}): 124.81 ℃ (m.p.), 224.02 ℃ (T_p).

Synthesis of 3,3'-bis(tetrazol-5-yl)-4,4'-azofurazan (DTZAF)

ATZF (0.80 g, 5.26 mmol) was transferred into a three-necked round-bottomed flask fitted with a mechanical stirrer and a dropping funnel, 13.5 mL 36% hydrochloric acid was then added. After the addition of hydrochloric acid, potassium permanganate (0.83 g, 5.25 mmol) dissolved in 5 mL of distilled water was added dropwise under stirring at room temperature. The stirring was continued for another 5 h at 50 ℃. The reaction mixture was then cooled to 0 ℃. The yellow precipitate was filtered, washed with ice-water and dried to obtain 0.75 g solid with a yield of 93.8%. The bright yellow product was crystallized from ethanol/water (V∶V＝1∶1). Its melting point is 249—250 ℃. ^{13}C NMR (DMSO-d_6, 500 MHz) δ: 161.83, 146.89 , 140.58; IR (KBr) v: 3490 (broad, N—H), 1636 (N＝N), 1058 (furazan) cm^{-1}. Anal. calcd for $C_6H_2N_{14}O_2$: C 23.84, N 64.90, H 0.662; found C 23.99, N 64.76, H 0.826.

Synthesis of hydrazinium 3-amino-4-(tetrazol-5-yl)-furazan (HATZF)

ATZF (0.20 g, 1.31 mmol) was transferred into a three-necked round-bottomed flask fitted with a reflux condenser, and 10 mL of distilled water was added at room temperature. 85% hydrazine hydrate (0.2 g) was then added dropwise at 70 ℃. The stirring was continued for another 3 h at 70 ℃ and then cooled down to 0 ℃. The precipitate thus obtained was filtered and washed with ice water and finally dried to obtain 0.22 g of solid with a yield of 91.7%. ^1H NMR (DMSO-d_6, 500 MHz) δ: 6.56 (s, 3H, NH_3^+), 7.15 (s, 4H, 2NH_2); ^{13}C NMR (DMSO, 500 MHz) δ: 155.59, 150.84, 139.99; IR (KBr) v: 3452, 3330 (NH_2), 3060, 2599, 2508 (NH_3^+), 1630, 1600 (C＝N) cm^{-1}. Anal. calcd for $C_3H_7N_9O$: C 1946, H 8.649, N 68.11; found C 19.32, H 8.652, N 67.9.

Synthesis of triaminoguanidinium 3-amino-4-(tetrazol-5-yl)furazan (TAGATZF)

ATZF (0.20 g, 1.31 mmol) was transferred into a three-necked round-bottomed flask fitted with a mechanical stirrer and a dropping funnel. 10 mL distilled water was added. After the addition of water, 0.5 mL 20% sodium hydroxide solution was added dropwise to the reaction flask under stirring. After 0.5 h, triaminoguanidine nitrate (0.22 g, 1.32 mmol) was added and the resulting reaction mixture was stirred for 3 h and then cooled down to 0 ℃. The precipitate thus obtained was filtered and washed with ice water and finally dried to obtain 0.32 g of the desired compound with a yield of 94.1%. ^1H NMR (DMSO-d_6, 500 MHz) δ: 4.51 (s, 6H, 3NH_2), 6.56 (s, 2H, NH), 8.60 (s, 3H, NH_3^+); ^{13}C NMR (DMSO, 500 MHz) δ: 159.08, 155.46, 150.59, 139.92; IR (KBr) v: 3425, 3333, 3213 (NH_2), 1683, 1632, 1632 (C＝N) cm^{-1}. Anal. calcd for $C_4H_{11}N_{13}O$: C18.68, H

6.226, N 70.82; found C 18.64, H 6.231, N 70.56.

Synthesis of guanylureaium 3-amino-4-(tetrazol-5-yl)furazan (MATZF)

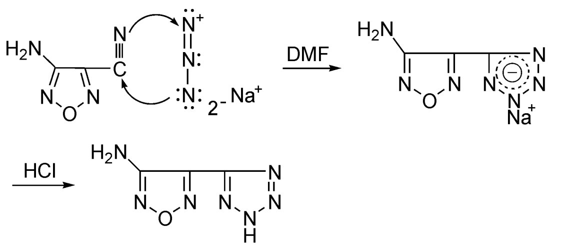
ATZF (0.20 g, 1.31 mmol) was transferred into a three-necked round-bottomed flask fitted with a mechanical stirrer and a dropping funnel, then 10 mL distilled water was added at constant temperature. After the addition of water, 0.5 mL 20% sodium hydroxide solution was added dropwise to the reaction flask under stirring at 70 ℃. The stirring was continued for another 0.5 h at 70 ℃. Guanylurea hydrochloride (0.18 g, 1.29 mmol) was added and the resulting reaction mixture stirred for 3 h and subsequently cooled down to ice temperature. The precipitate thus obtained was filtered and washed with ice water and finally dried to obtain 0.3 g product with a yield of 90.9%. ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 6.56 (s, 3H, NH_2 linked with furazan), 7.01 (s, 2H, NH_2^+), 8.07 (s, 4H, $2NH_2$), 9.70 (s, 1H, NH); ^{13}C NMR (DMSO, 500 MHz) δ: 206.69, 155.53, 154.52, 150.73, 139.93; IR (KBr) v: 3441, 3387, 3338 (NH_2), 1741 (C=O), 1631, 1653, 1603 (C=N) cm^{-1}. Anal. calcd for $C_5H_9N_{11}O_2$: C 25.10, H 6.695, N 64.44; found C 25.03, H 6.671, N 64.95.

Results and discussion

Reaction mechanism of tetrazole cyclization

Because sodium azide might be dissolved in dimethyl formamide (DMF), in DMF medium sodium 3-amino-4-(tetrazol-5-yl) furazan was produced by the [3+2] cycloaddition of sodium azide and cyano group in 3-amino-4-cyanofurazan (CNAF), followed by acidification by hydrochloric acid. The assumed reaction mechanism is as follows:[19]

Scheme 4 Mechanism of tetrazole cyclization



Performance evaluation of 3-nitro-4-(tetrazol-5-yl)-furazan (NTZF)

The structure of NTZF was optimized by Gaussian 98 in order to obtain its stable geometric configuration, and its density and enthalpy of formation were then computed. The explosive parameters were obtained by VLW equation using density and enthalpy of formation as basic data.[20] The predicted performance data of NTZF were: density 1.67 g/cm^3, detonation velocity 8257.83 m/s, C-J pressure 27.78 GPa and enthalpy of formation +415.41 kJ/mol.

Thermal studies

Thermal studies of DTZAF The DSC and TG analyses revealed that DTZAF was thermally stable up to 256.7 ℃. The DSC curve (Figure 1) of DTZAF exhibited a melting point, T_{max}, at 251.9 ℃ and two thermal decomposition peaks at 256.7 and 300.8 ℃, respectively. In the TG curve (Figure 2), DTZAF showed two stages of decomposition. The first stage amounts to 32.70% in the range of 250.2—264.7 ℃, and the second stage occurs with a weight loss of 58.73% in the range of 264.7—300.7 ℃.

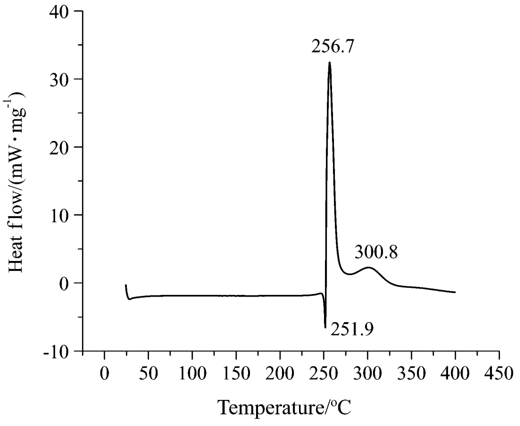


Figure 1 DSC curve of DTZAF.

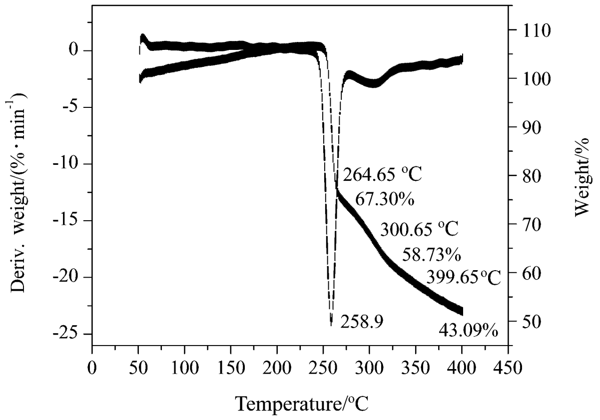


Figure 2 TGA curve of DTZAF.

Thermal studies of HATZF The DSC and TG analyses revealed that HATZF is thermally stable up to 230.3 ℃. The DSC curve (Figure 3) of HATZF exhibited a melting point, T_{max}, at 159.7 ℃ and four thermal decomposition peaks at 258.6, 272.3, 308.8 and 330.1 ℃, respectively. In the TG curve (Figure 4), HATZF showed the mass loss of 67.77% before 248.1 ℃, and only 6.75% residue at 289.5 ℃.

Thermal studies of TAGATZF The DSC and TG analyses revealed that TAGATZF is thermally stable up to about 206 ℃. The DSC curve (Figure 5) of TAGATZF exhibited a melting point, T_{max}, at 205.4 ℃ and three thermal decomposition peaks at 231.7, 281.6 and 327.4

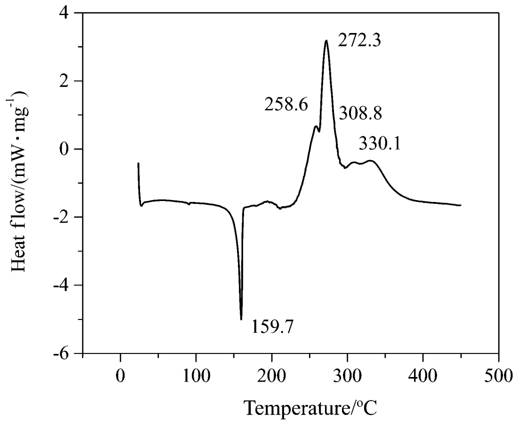


Figure 3 DSC curve of HATZF.

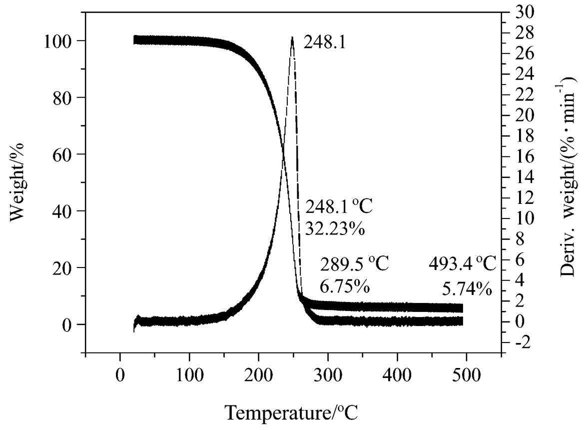


Figure 4 TGA curve of HATZF.

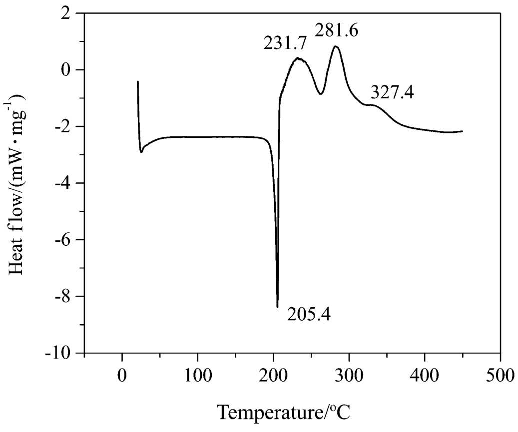


Figure 5 DSC curve of TAGATZF.

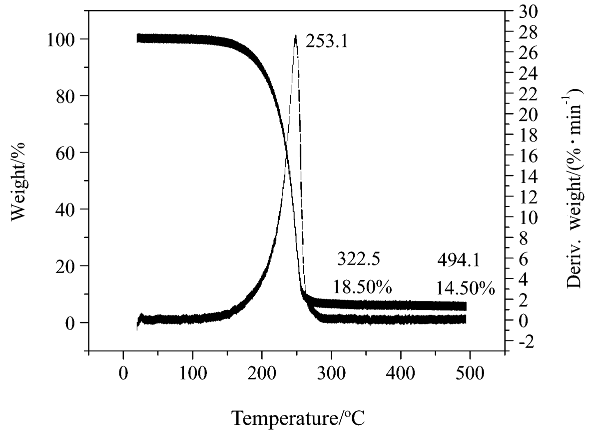


Figure 6 TGA curve of TAGATZF.

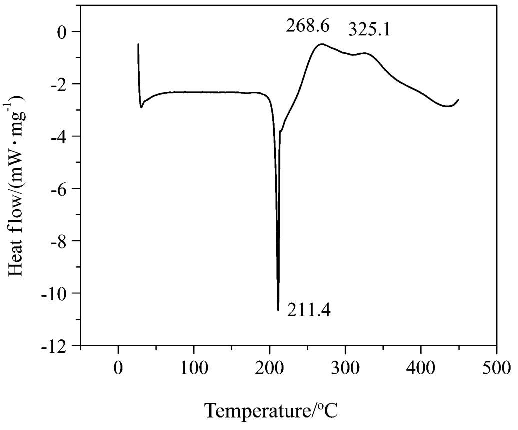


Figure 7 DSC curve of MATZF.

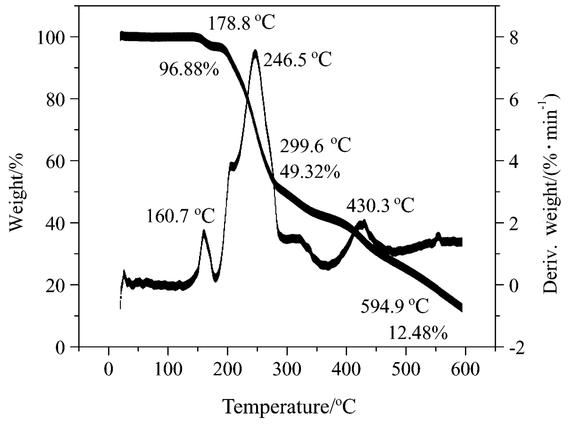


Figure 8 TGA curve of MATZF.

℃, respectively. In the TG curve (Figure 6), TAGATZF showed the mass loss of 81.48% before 322.5 ℃, and 14.50% residue at 494.1 ℃.

Thermal studies of MATZF The DSC and TGA revealed that MATZF is thermally stable up to 160.7 ℃. The DSC curve (Figure 7) of MATZF exhibited a melting point, $T_{\max}$, at 211.4 ℃ and two thermal decomposition peaks at 268.6 and 3225.1 ℃, respectively. In the TG curve (Figure 8), MATZF showed the mass loss of 50.68% before 299.6 ℃, and 12.48% residue at 594.9 ℃.

The above-mentioned DSC and TGA results showed that their melting points were 251.9, 159.7, 205.4 and 211.4 ℃ and their first decomposition temperatures were 256.7, 258.6, 231.7 and 268.6 ℃, respectively. The fact that their decomposition temperatures were over 230 ℃ showed that they exhibited excellent thermal stability and they might be potentially useful as gas generants or rochet propellants.

Conclusions

3-Amino-4-(tetrazol-5-yl)furazan (ATZF) was synthesized with a total yield of 54.0% using 3-amino-4-cyanofurazan (CNAF) as a starting material and with a yield of 91.3% by [3＋2] cycloaddition of 3-amino-4-cyanofurazan (CNAF) and sodium azide. Five new energetic compounds derived from ATZF were synthesized and characterized. The properties of 3-nitro-4-(tetrazol-5-yl)-furazan (NTZF) were estimated: density is 1.67 g/cm^3, enthalpy of formation ＋415.41 kJ/mol and detonation velocity 8257.83 m/s. The main thermal properties of four new compounds, DTZAF, HATZF, TAGATZF and MATZF, were investigated by DSC and TG techniques and the results showed that their melting points were 251.9, 159.7, 205.4 and 211.4 ℃ and their first decomposition temperatures were 256.7, 258.6, 231.7 and 268.6 ℃, respectively. The fact that their decomposition temperatures were over 230 ℃ showed that they exhibit better thermal stability.

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