The Insensitive Energetic Material Trifurazano-oxacycloheptatriene (TFO): Synthesis and Detonation Properties

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Abstract: The high-energy insensitive compound trifurazano-oxacycloheptatriene (TFO) was first by synthesized through special etherification. The reaction mechanism and reaction conditions were discussed. TFO has a low melting point (78.6 °C) and good compatibility. TFO is insensitive to impact and friction and has similar detonation velocity (7.7 km s^{-1}) and detonation pressure (35.6 GPa) to RDX.

Keywords: Energetic material · Trifurazano-oxacycloheptatriene (TFO) · Furazan · Synthesis · Detonation properties

1 Introduction

New insensitive compounds with high-energy-density are development targets of energetic material researchers. As an energetic nitrogen heterocyclic group, furazan and furoxan feature high heats of formation, good thermal stabilities, big densities, and a high amount of active oxygen, which make them highly efficient structural units in the development of high-energy-density materials (HEDMs) [1–8]. Moreover, substituting a furazan ring or a furoxan ring for a nitro group, the density and detonating velocity can increase about 0.06–0.08 g cm^{-3} and 300 m s^{-1} [9–11], which leads to the synthesis of multi-furazan ring compounds and multi-furazan ring oxides, such as difurazans, chained furazans, macrocyclic furazans, ring-fused furazans, and other furazan or furoxan derivatives [8–16]. Many derivatives have shown good physicochemical properties and applied prospect.

Furazan-ether compounds are also the main research objectives. After ether bond was drawn into molecule, the flexibility of the compound rises, but the melting point reduces. So we designed and first synthesized bis(nitrofurazano)furoxan(BNFF^O) and bifurazano-furoxano-oxacycloheptatriene (BFFO), and found that the two compounds exhibit good promising applications in casting explosives and casting solid propellants [11,17,18]. However, it was also found the two compounds have high shock-wave sensitivity, which in turn limits their wide applications. The reason for the high shock-wave sensitivity should come from the active coordination oxygen atom of the central furoxan ring. Based on the above results, we further designed and synthesized bis(nitrofurazano)furazan (BNFF) and trifurazano-oxacycloheptatriene (TFO) (Scheme 1), and hoped to get the ideal results [19–22]. In this paper, we will report the synthesis and characterization of TFO.

## 2 Experimental Section

2.1 General Information

NMR spectra were recorded with a AV500 NMR spectrometer (BRUKER). IR spectra were determined with a NEXUS870 (THERMO NICOLET) with KBr pellets. Elemental analyses were performed with a Vario EL III elemental analyzer (ELEMENTAR). MS spectra were recorded with a GCMS-QP2010 mass spectrometer (SHIMADZU). UV/Vis spectra were measured with a UV-3600 spectrophotometer (SHIMADZU) in the range 200–800 nm. The differential scanning calorimetry (DSC) experiments were performed with a DSC200 F3 apparatus (NETZSCH) in a nitrogen atmosphere at a flow rate of 80 mL min^{-1}. The impact and friction sensitivities were determined by using a ZBL-B impact sensitivity instrument (NACHEN, China) and a MGY-2 friction sensitivity instrument (NACHEN, China), respectively. The mass of drop hammer was 5.0 kg. The sample mass for each test was 30 mg. All other reagents were purchased from commercial sources and used without further purification.

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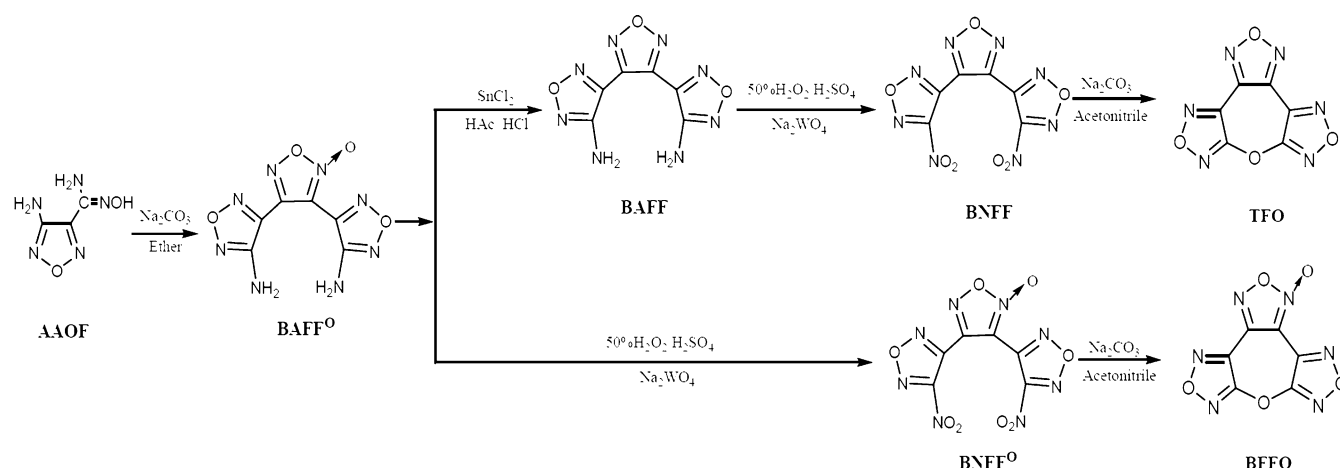
Scheme 1. Synthesis routes of TFO and BFFO.
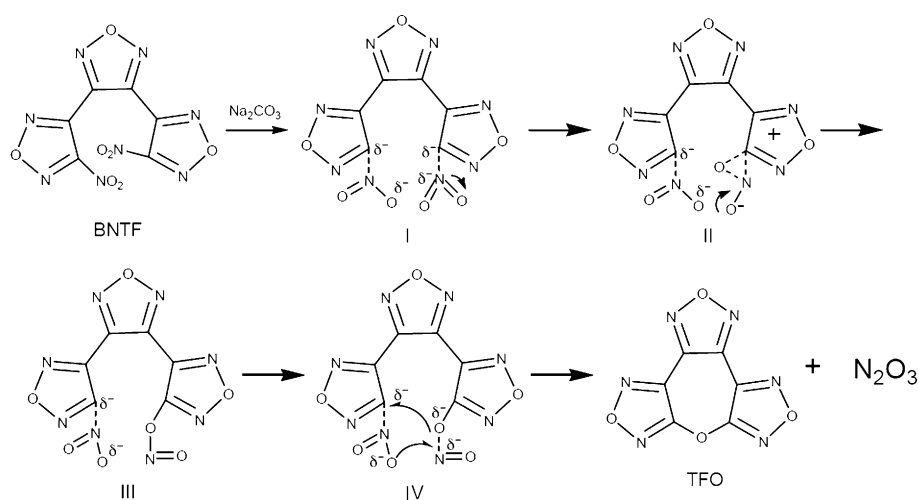
Scheme 2. Reaction mechanism of TFO.

2.2 Synthesis

Bis(nitrofurazano)furazan (BNFF) was prepared according to reference [21].

At room temperature, BNFF (10.0 g, 33.7 mmol) and anhydrous sodium carbonate (4.8 g, 45.1 mmol) were put into 25 mL anhydrous acetonitrile. After refluxing at 85 °C for 6 h, the reaction solution was transferred into water (80 mL), and extracted with chloroform (60 mL) for three times. The obtained organic phase was dried by anhydrous magnesium sulfate for 6 h and filtered. After the above filter was evaporated, white needle solids of TFO were obtained, yielding 4.2 g (55.2 %) [22]. ^{13}C NMR ([D$_6$]DMSO, 500 MHz): $\delta = 160.79$, 144.01, 137.28 ppm. IR: $\tilde{v} = 1569$, 1481, 1165, 1087, 1003, 985, 886 cm^{-1}. MS (EI) m/z (%): 220 [M$^+$, 45], 30 (100). C$_6$N$_6$O$_4$: calcd. C 32.73, N 38.18 %; found C 32.55, N 37.99 %.

3 Results and Discussion

Based on the synthesis of BNFF [21], we further synthesized trifurazano-oxacycloheptatriene (TFO) through special etherification. The reaction is similar to the synthesis of BFFO [11]. The difference between BFFO and TFO is the losing of the active coordination oxygen atom for reducing shock-wave sensitivity. The reaction mechanism should be as follows: (1) An intermolecular electron of a nitro group shifts from oxygen atom to nitrogen atom with the effect of weak base Na$_2$CO$_3$ to form a bipolar form (I); (2) The transfer of electron further results in forming a C—N—O ternary ring (II); (3) The C—N bond is broken to form a nitrite form (III); (4) The N···O bond of nitrite is weak with the effect of the other nitro group (IV). The positive and negative charges attack each other in the two groups, which result in the losing of —NO$_2$ and —NO groups, and the productions of C—O—C bond (TFO) and dinitrogen trioxide (N$_2$O$_3$). The inference can be supported with the release of red gas in synthesis process. The red gas was verified to be N$_2$O$_3$ (Scheme 2).
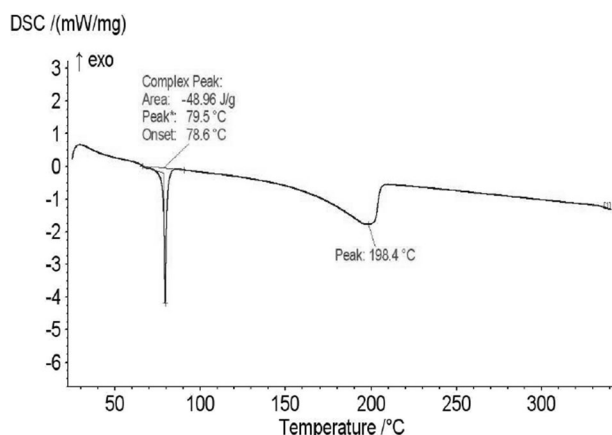
Figure 1. DSC curve of TFO at a heating rate of $10\,°C\,min^{-1}$.

In the synthesis process, anhydrous treatment is required. When the water content of acetonitrile is greater than 1.5 %, the yield is only 10 %. The reason is that one nitro group is easily hydrolyzed to a hydroxyl group with the effect of Na_2CO_3. The reaction temperature should be higher than 80 °C to allow the refluxing of acetonitrile. Reaction time should be at 3–5 h. The molecular yield of TFO can reach 55.2 % after extraction and separation.

IR spectra of TFO display the typical adsorption peaks of the ether bond (C—O—O) at 1165 and $1087\,cm^{-1}$. The adsorption peaks at 1003 and $985\,cm^{-1}$ indicate the presence of N—O—N pattern, which are also the characterized absorption peaks of furazan ring. The adsorption peaks of the C=N bond in the furazan ring appear are at 1569 and $1481\,cm^{-1}$. No adsorption peak in the $3000\,cm^{-1}$ region shows that there is no O—H, N—H, or C—H chemical bond in TFO molecular structure. UV/Vis spectra of TFO indicate the biggest adsorption peak at 275.6 nm is attributed to the $\pi \rightarrow \pi^*$ transition of C=N bond, which is red shifted due to the conjugated effect of furazan ring [23].

The DSC curve (Figure 1) indicates that the thermal behavior of TFO exhibits two stages. The first stage is a melting process, and the extrapolated onset temperature, peak temperature, and melting enthalpy at a heating rate of $10\,°C\,min^{-1}$ are 78.6 °C, 79.5 °C, and $48.96\,J\,g^{-1}$, respectively. The melting point is lower than that of BNFF as 82.6 °C and BFFO at 95.1 °C [11,21], which is good to be used as casting carrier. When the heating temperature is above 150 °C, the molten sample begins to slowly evaporate, so the thermal behavior presents a slight endothermic trend. At about 198.4 °C, the thermal behavior exhibits a transition toward the exothermic trend, so it can be concluded that TFO begins exothermic decomposition at this temperature. Thus, the decomposition temperature of TFO is higher.

The compatibilities of TFO with RDX, HMX, and TNT (0.5 g/0.5 g) were determined using the vacuum test method at 100 °C for 40 h, respectively. The experimental results (0.02, 0.04, and 0.07 mL) indicate that TFO is well compatible with other three typical energetic materials.

The impact and friction sensitivities of TFO are > 35.5 J and 4 % (3.92 MPa, 90°) respectively, so TFO is insensitive. The two sensitivities are all lower than these of BNFF as > 25.1 J and 8 % and BFFO as > 28.2 J and 16 % [11,21]. The impact sensitivity is also much lower than that of RDX (> 7.4 J) [24]. The loading density of TFO can reach $1.76\,g\,cm^{-3}$. The detonation velocity and detonation pressure of TFO calculated by our special software based on the empirical Kamlet-Jacobs (K-J) equations are $7.7\,km\,s^{-1}$ and 35.6 GPa, respectively, which are similar to these of RDX [$8.7\,km\,s^{-1}$, 33.8 GPa ($\rho = 1.765\,g\,cm^{-3}$)] [24], but lower than those of BNFF as $8.7\,km\,s^{-1}$ and 36.1 GPa ($\rho = 1.814\,g\,cm^{-3}$) [21]. The sensitivity declines significantly and the detonation velocity and detonation pressure also decrease slightly with the losing of coordination oxygen atom. But all data still indicate that TFO exhibits good application performances as casting carrier of explosive or solid propellant.

4 Conclusions

A novel energetic compound trifurazano-oxacycloheptatriene (TFO) was first synthesized through special etherification. TFO exhibits low melting point, good compatibility and excellent insensitivity to impact and friction. TFO is a good high-energy insensitive material used as casting carrier of explosive or solid propellant.

Acknowledgments

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