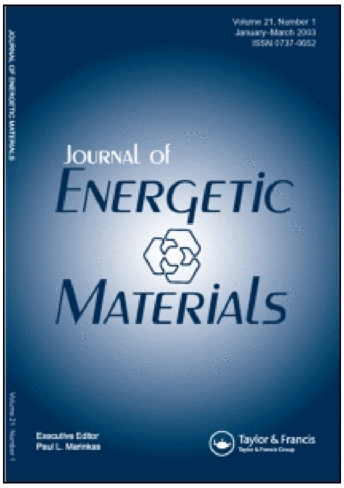

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Preparation and Properties of 2,4,8,10-Tetranitro-5*H*-Pyrido[3′,2′:4,5][1,2,3] Triazolo[1,2-a]Benzotriazol-6-ium Inner Salt as a Thermally Stable High Explosive

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The synthesis and explosive properties of 2,4,8,10-tetranitro-5H-pyrido[3′, 2′:4, 5] [1,2,3] triazolo [1,2-a] benzotriazol-6-ium inner salt (7) are given. This material is a very thermally stable high explosive that has a differential scanning calorimetry (DSC) onset of 365° C with fast decomposition occurring at 375°C. The material is readily prepared in three steps from inexpensive starting materials. The final compound is insensitive to initiation by spark and friction and has a drop height of 59 cm (Type 12, 2.5 kg weight, HMX = 23 cm). In addition, it has a failure diameter of less than 3 mm. A detonation velocity of 7.43 km/s and detonation pressure of 294 kbar were determined on 0.5 inch pellets at a density of 1.78 g/cm^3.

Keywords: synthesis, properties

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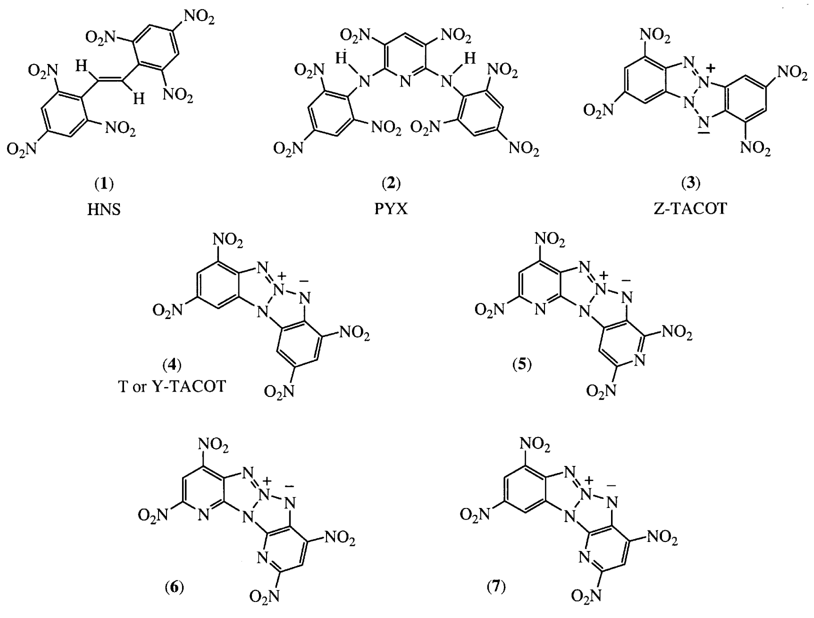
Introduction

Explosives with high thermal stability have a variety of military, space, and civilian uses. The major civilian use for these compounds is in shaped charges for increasing the yield of oil wells by penetrating the surrounding rock. The explosive in these "down-hole penetrators" must withstand temperatures in excess of 200°C for several days and still initiate and perform reliably. The most commonly used high-temperature explosive is HNS (2,2′,4,4′,6,6′-hexanitrostilbene) **(1)** (Figure 1), as it is readily prepared by the oxidative coupling of TNT by hypochlorite [1]. However, HNS suffers from a lengthy purification process involving recrystallization from DMF. Furthermore, HNS displays relatively poor performance with a detonation velocity of 7.07 km/s and a detonation pressure of only 199 kbar at density 1.685 g/cm^3 (96.8% of theoretical maximum density) [2]. In addition, its DSC exotherm of 315°C is too low in temperature for some applications.


(1) HNS

(2) PYX

(3) Z-TACOT

(4) T or Y-TACOT

(5)

(6)

(7)

Figure 1. Structures of some heat-resistant explosives.

Other thermally stable explosives have been prepared. PYX [2, 6-bis(picrylamino)-3, 5-dinitropyridine] **(2)** is a high-temperature explosive developed at Los Alamos that has excellent thermal stability (350°C) but suffers from the fact that the synthesis requires the use of an expensive picryl halide. Z-TACOT (1,3,7,9-tetranitro-6*H*-benzotriazolo[2,1-a] benzotriazol-5-ium inner salt) **(3)** and Y- or T-TACOT (2,4,8,10-tetranitro-5*H*-benzotriazolo [1,2-a] benzotriazol-6-ium inner salt) **(4)** (DSC exotherm at 354°C) were the first members of a family of thermally stable explosive based on the tetra-azapentalene ring system [3]. The high thermal stability inherent to tetra-azapentalenses is attributed to the zwitterionic resonance stabilized "inner salt" structure. Recently, derivatives of TACOT have been prepared in an effort to increase performance by improving the oxygen balance, density, and heat of formation. This was accomplished by substituting nitrogen for carbon in the benzene rings **(5)–(6)** [4]. Unfortunately, these compounds are expensive to manufacture, as the starting 1,2,3-triazolo-pyridines are not readily available. A hybrid structure containing both a benzene and a pyridine ring **(7)** was reported by Belgian workers [5–7]. They reported that this new material had a melting point >300°C but reported no explosive properties data. Because of the ease of preparation of this compound and its promising thermal stability, we undertook a study to characterize and determine its explosive performance.

Results

The preparation of (**7**) is outlined in Figure 2. The condensation of benzotriazole (**8**) with 2-chloro-3-nitropyridine (**9**)($0.56/g at the 100 kg scale in late 2003 from Aldrich Chemical Co.) proceeds to yield a single regioisomer (**10**) with substitution occurring on N1. The reaction, originally run in DMSO, was found to proceed equally well in refluxing acetonitrile. This allows for recovery of the solvent, which reduces the cost of the material on production scales. Tetra-azapentalene formation (**11**) occurs through a nitrene intermediate and requires a high-boiling solvent to advance(xylenes required one day at

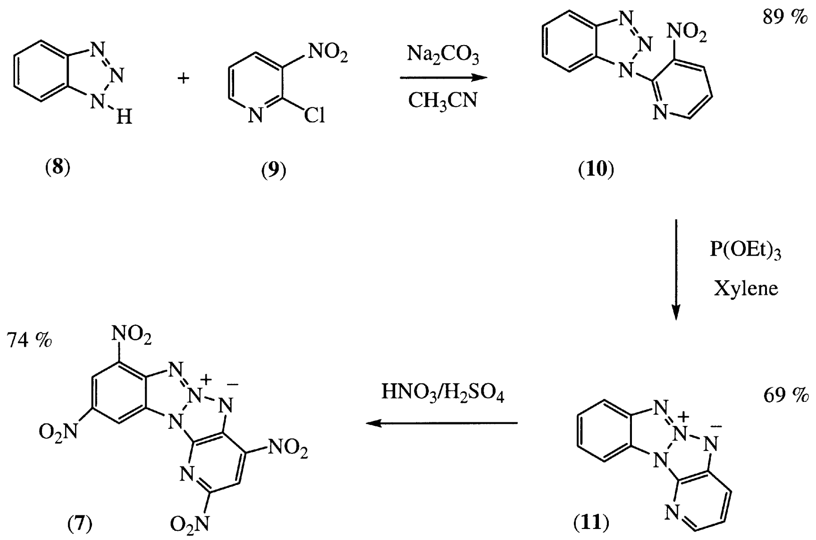


Figure 2. Synthesis route to (**7**).

reflux, while toluene necessitates a minimum of a week). The final nitration proceeds smoothly in mixed acid and is followed by trituration with organic solvent to remove residual acids.

The drop-height sensitivity of (**7**) was determined to be 59 cm (Type 12, 2.5 kg weight, HMX = 23 cm). When formulated with 5 weight% Kel-F 800®, the drop height increased to 155 cm. The material was insensitive to initiation by friction (BAM, >36 kg) and spark (0.36 J). A density was determined by He gas pycnometry to be 1.84 g/cm^3. The heat of formation was found to be +106 kcal/mol by combustion calorimetry. The DSC exotherm (365°C) indicated (**7**) is more thermally stable than both TACOT and PYX. Fast decomposition occurred at 375°C.

The explosive performance of (**7**) was determined on 0.5 inch pellets in a standard rate-stick/plate dent test at a density 1.78 g/cm^3 (96% of theoretical maximum density when formulated with Kel-F 800®), and a measured detonation velocity (V_D) of 7.43 km/s and detonation pressure (P_{CJ}) of 294 kbar were observed. In addition, a poly-ρ test was performed to determine detonation velocity as a function of density

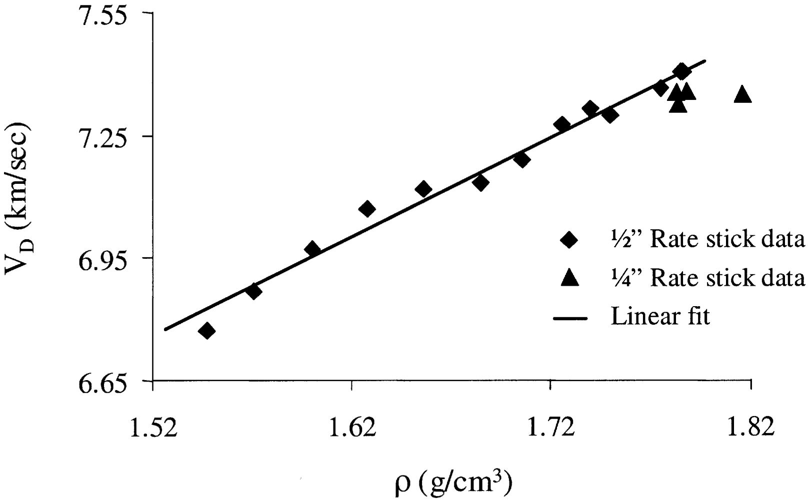


Figure 3. Detonation velocity as a function of density at 0.5 and 0.25 inch.

(Figure 3). Also shown in Figure 3 is the detonation velocity of a 0.25 inch rate stick, and it can be seen that very little degradation in velocity is observed at the smaller diameter. A 3 mm rate stick detonated cleanly. Although this small size was impossible to instrument accurately, it does demonstrate that (**7**) has a very small failure diameter.

Experimental

All starting materials were obtained from commercial sources. All NMR spectra were obtained on a JEOL Eclipse 300 spectrometer, and chemical shifts are reported relative to internal tetramethylsilane. The preparations that follow are modeled after the original Belgian workers [5]–[7].

1-(3-nitro-2-pyridyl)-1H-benzotriazole (***10***). A flask containing 11.91 g benzotriazole (**8**) (0.1 mol), 15.85 g 2-chloro-3-nitropyridine (**9**) (0.1 mol), 12.3 g anhydrous sodium carbonate, and 250 ml of acetonitrile was heated to reflux for 24 hr with vigorous stirring. The acetonitrile was then distilled and recovered, and 250 ml water added to the residue. The resulting solid was stirred vigorously for 1 hr and filtered. The filter cake was washed with water and air dried to yield 21.4g (89%) of product with sufficient purity for the next step. ^{1}H NMR (DMSO-d^6) δ 7.57–8.98 (m, 7H)^{13}C NMR (DMSO-d^6) δ 112.6, 119.8, 125.0, 125.7, 129.8, 131.2, 135.6, 139.7, 140.3, 145.3, 152.4.

5H-Pyrido[3′,2′:4,5][1,2,3]triazolo[1,2-a]benzotriazol-6-ium inner salt (***11***). To a flask containing 350 ml of xylenes and 65 ml triethyl phosphite (0.38 mol) was added 21.4 g of compound (**10**) (0.089 mol), and the mixture was refluxed 24 hr. The xylenes were then removed by distillation and recovered, and hexanes added to the dark semisolid residue. The pale yellow product was filtered, washed with hexanes, and air dried to yield 12.8 g (69%) of the desired product of sufficient purity for nitration. ^{1}H NMR (DMSO-d$_6$) δ 7.4–8.5 (m, 7H). ^{13}C NMR (DMSO-d$_6$) δ110.0, 115.7, 120.7, 121.8, 122.8, 123.0, 126.3, 135.4, 136.4, 142.2, 143.0.

2,4,8,10-tetranitro-5H-pyrido[3′,2′:4,5][1,2,3]triazolo[1,2-a] benzotriazol-6-ium inner salt (*7*). To 130 ml of 98% sulfuric acid was added 12.8 g of (**11**) at room temperature with vigorous stirring. After complete dissolution, 130 ml of 90% nitric acid was added with intensive cooling while maintaining the temperature below 30°C by the rate of addition. The mixture was then heated to 80°C for 2 hr, cooled and poured onto ice. The yellow-orange product was filtered, washed with water, and air dried to yield 17.8 g (74%) of crude material, which was consecutively triturated with acetone, acetonitrile, and methanol and air dried. ^{1}H NMR (DMSO-d$_6$) (85°C) δ 9.27 (s, 1H), 9.30 (d, $J=2.0$ Hz, 1H) 9.38 (d, $J=2.0$ Hz, 1H). ^{13}C NMR (DMSO-d$_6$) (85°C) δ 103.1, 111.2, 118.9, 122.8, 130.9, 132.5, 135.2, 139.6, 140.9, 153.6, 157.8.

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