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Preparation, Characterization, and Properties of 7-Nitrotetrazolo [1,5-*f*]furazano[4,5-*b*]pyridine 1-Oxide

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The synthesis, characterization, and properties of 7-nitrotetrazolo[1,5-f]furazano[4,5-b]pyridine 1-oxide (NFP) are reported. NFP is prepared by the diazotization of 3,6-di(hydrazino)-3,5-di(nitro)pyridine followed by the extrusion of molecular dinitrogen and ring closure.

Keywords: Azido-tetrazolo tautomerism, Azido-nitro nitrogen heterocycles, high-nitrogen materials, synthesis, characterization, properties

Introduction

Azido-substituted pyridines have been known in the literature for several decades [1,2]. They are known to undergo photochemical or thermochemical dinitrogen elimination followed

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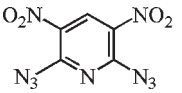
by ring expansion or cleavage and subsequent nucleophilic substitution to give diazepines, pyrroles [3], or heptenones [4], which display a variety of useful biological activities, pharmaceutical properties, and therapeutic applications [5–10]. Nitropyridofuroxans have revealed the great versatility and extensive reactivity in vicarious nucleophilic aromatic substitution and single-electron transfer processes [11,12].

At the Los Alamos National Laboratory, we have been interested in the preparation of high-nitrogen and heterocyclic compounds for applications in a wide variety of fields including energetic materials utilizing tetrazines [13–16], triazines [18,19], furazans, and triazoles [21]. Our interest in new pyridine-based energetic compounds was to probe the explosive performance of previously substituted pyridine compounds [22–24] and decrease the sensitivity to stimuli such as spark, friction, and impact.

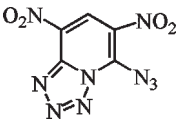
Experimental

Notations and Abbreviations

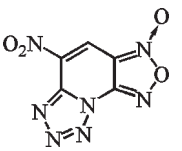
The following compounds appear in this study:



2, 6-Di(azido)-3, 5-di(nitro)pyridine, (**4**)



2-Azido-3, 5-di(nitro)-6-tetrazolopyridine, **(5)**



7-Nitrotetrazolo[1, 5-f]furazano[4, 5-b]pyridine 1 − Oxide, **NFP**

Materials

House water was purified with a Barnstead E-Pure deionization system. High-purity acetone, acetonitrile, and chloroform were purchased from Aldrich and used without further purification.

Deuterated solvents were purchased from Cambridge Isotope Laboratories. Other chemicals employed in the preparations were reagent grade.

Instrumentations and Measurements

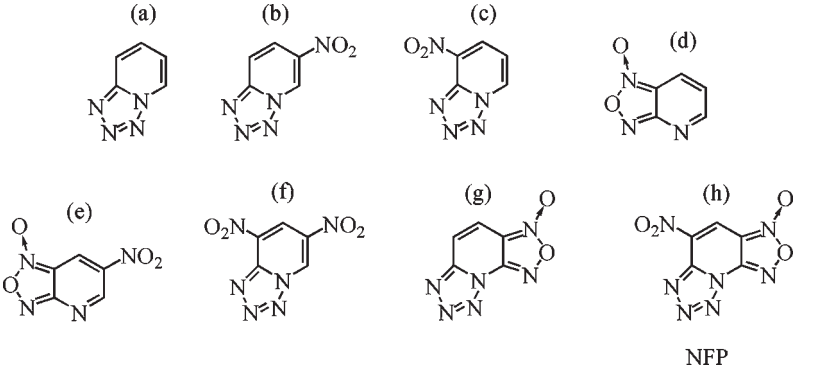
$^{1}H/^{13}C$ NMR spectra were obtained on a JEOL Eclipse 300 Fourier transform spectrometer, and chemical shifts are reported relative to internal tetramethylsilane. Melting points were determined by Differential Scanning Calorimetry (DSC) at 5°C/min using a TA Instruments DSC 2920 Modulated instrument. Elemental analyses were performed at Atlantic Microlabs (Norcross, GA) and Los Alamos National Laboratory.

Syntheses and Characterizations

2,6-di(azido)-3,5-di(nitro)pyridine (4). To a 100 mL-jacketed beaker containing 40 ml of 3 M HCl was added 0.5 g (2.18 mmol) of 2,6-di(hydrazino)-3,5-di(nitro)pyridine (**3**), and the suspension stirred until complete dissolution occurred. The temperature was then adjusted to −5°C, and a solution of 2.5 equivalents of $NaNO_2$ in 10 mL of water was added dropwise with vigorous stirring while maintaining the temperature below 3°C. The reaction was allowed to proceed at 0°C for 30 minutes during which a dark orange solid precipitated. It was filtered, washed thoroughly with cold water, and air-dried. In polar solvents, (**4**) is easily converted to (**5**) and rapidly undergoes ring closure to form **NFP**: (a) ^{1}H NMR (**5**, Acetone-d_6) δ 9.23 (s, 1 H); ^{13}C NMR (**5**, Acetone-d_6) δ 122.95, 131.09, 131.66, 137.29, 152.65 and ^{1}H NMR (**NFP**, Acetone-d_6) δ 9.42 (s, 1 H); ^{13}C NMR (**NFP**, Acetone-d_6) δ 121.64, 130.64, 130.75, 135.98, 151.39; (b) ^{1}H NMR (**5**, Acetonitrile-d_3) δ 9.04 (s, 1 H); ^{13}C NMR (**5**, Acetonitrile-d_3) δ 108.13, 123.77, 127.09, 145.37, 147.02 and ^{1}H NMR (**NFP**, Acetonitrile-d_3) δ 9.29 (s, 1 H); ^{13}C NMR (**NFP**, Acetonitrile-d_3) δ 118.30, 122.44, 131.42, 136.75, 152.21; (c) ^{1}H NMR (**NFP**, DMSO-d_6) δ 9.49 (s, 1 H); ^{13}C NMR (**NFP**, DMSO-d_6) δ 108.14, 122.37, 136.31, 144.87, 146.19; (d) Anal. Calc'd for $C_5HN_7O_4$: C, 26.92; H 0.45; N, 43.95. Found: C, 27.01; H, 0.65; N, 44.83.

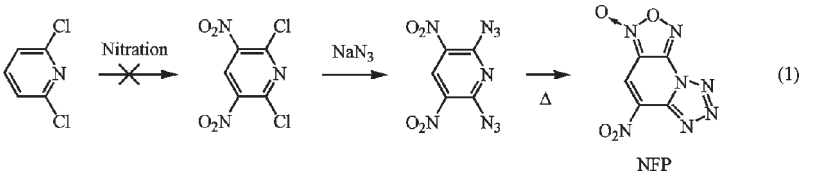
Results and Discussion

In 1990, Wilson *et al.* reported on the preparation of a series of disubstituted pyridines including nitro/tetrazolo, nitro/furoxano, or tetrazolo/furoxano, Scheme 1(a)–(g) [25]. Notably, absent among those compounds is the trisubstituted pyridine, 7-nitrotetrazolo[1,5-*a*]furazano[4,5-*b*]pyridine-1-oxide (NFP), Scheme 1 (h), containing all three moieties.



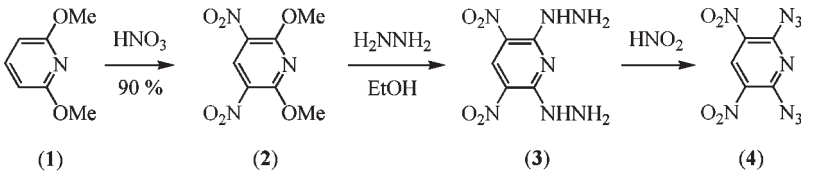
Scheme 1. Disubstituted and trisubstituted pyridines.

Unlike compound (g) illustrated in Scheme 1, the preparation of NFP was required to take a different path because the commercially available 2,6-dichloropyridine proved recalcitrant to all nitration protocols investigated, including nitric acid (90–100%), mixed acid, acetyl nitrate, and nitronium salts; see Equation (1).



(1)

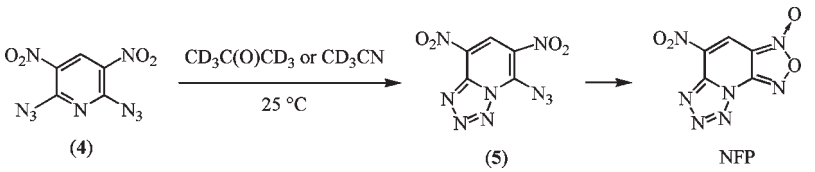
Attention was turned to another pyridyl precursor that has more activated moieties at the 2 and 6 positions toward the nitration. As described in the literature, 2,6-di(methoxy)-pyridine (**1**) was nitrated with 90% HNO_3 to 2,6-di(methoxy)-3,5-di(nitro)pyridine (**2**), which was further converted to 2,6-di(hydrazino)-3,5-di(nitro)pyridine (**3**) by treatment with hydrazine hydrate in ethanol [26]. Based on the protocol from our previous report [18], (**3**) underwent double diazotization to 2,6-di(azido)-3,5-di(nitro)pyridine (**4**), Scheme 2.



(**1**) (**2**) (**3**) (**4**)

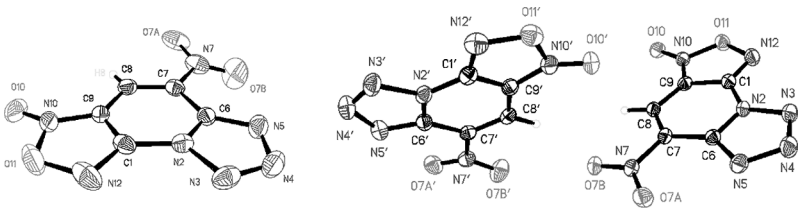
Scheme 2. Preparation of (**4**).

Azido-substituted pyridines are known to undergo azido-tetrazolo tautomerism (see above) that is attributed to the stabilization of the tetrazolo form due to the electron-deficient nature of the pyridine ring. In dry deuterated acetone and acetonitrile, NMR analysis indicated that (**4**) existed in the di(azido) form for 15–20 minutes, then transformed to (**5**), which further underwent transformation reaction with extrusion of dinitrogen followed by ring closure to form NFP in an additional 20–30 minutes, Scheme 3.



(**4**) (**5**) NFP

Scheme 3. Transformation of (**4**) to NFP.



(α-polymorph) (β-polymorph)

Figure 1. A drawing showing the results of X-ray analyses for the α- and *β*-polymorphs of NFP: ORTEP diagrams (25% ellipsoids) and labeling schemes are shown.

In a more polar solvent such as deuterated DMSO, the transformation from (**4**) to NFP occurred too fast for (**5**) to be observed on the NMR timescale. When crystalline (**4**) was stored at room temperature, the transformation to NFP slowly occurred over 8–10 days. In contrast to the study by Wilson *et al.* [25], the electron withdrawing nitro groups at the 3 and 5 positions in (**4**) stabilize the cyclization to form the tetrazolo substituent in (**5**) and to form the furoxan ring in NFP. In addition, the polarity of the solvent facilitates the ring closures of (**4**) shifting the equilibria to the right.

The structure of NFP was confirmed by single-crystal X-ray diffraction analyses. Yellow-brown orthorhombic crystals (α-polymorph) with a density of 1.853 g/cm^3 and light yellow monoclinic crystals (*β*-polymorph) with a density of 1.828 g/cm^3 were identified (figure 1)[27].

Physical and sensitivity properties of NFP have been determined. It displays a relatively fast burn rate and was insensitive to initiation by electrostatic discharge. It displays moderate sensitivity to initiation by friction and was slightly more sensitive to impact than HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). Differential Scanning Calorimetry was also performed to determine the thermal stability, and it was found to decompose at ∼160°C.

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[27] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-253213 for the NFP alpha polymorph and CCDC-253214 for the beta polymorph. Copies of the data can be obtained freely on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK); Tel.: (+44) 1223-336-408, Fax: (+44) 1223-336-033, and e-mail: deposit@ccdc.cam.ac.uk