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# HIGH-TEMPERATURE EXPLOSIVES FOR INSENSITIVE-MUNITIONS APPLICATIONS

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## ABSTRACT

We are developing new energetic structures expected to have superior insensitivity characteristics and superior performance characteristics relative to currently used insensitive high explosives. The chemical structures proposed herein are a series of zero- to low-hydrogen-content, polynitro, polycyclic heteroaromatic compounds based on novel nitrogenous heterocycles. By analogy to other nitrated nitrogenous heterocycles, which have been discovered to exhibit superior insensitivity properties, the proposed derivatives are predicted to have similarly attractive stability characteristics. The new compounds are expected to be high-density materials with explosive yields comparable to or better than hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) but with high melting points, comparable or better shock sensitivity, and significantly better thermal stabilities. This project is being conducted as a collaboration, via a Cooperative Research and Development Agreement (CRADA), with Pacific Scientific Energetic Materials Co., Chandler, AZ, which provides independent funding for its comparable contribution to this effort.

## BACKGROUND

Classical approaches to high-output secondary explosives have included the development of cyclic and cage nitramines, such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and CL-20. Although the representatives of this category of explosives exhibit superior explosive outputs, they are often more susceptible to degradation (including catastrophic reactive responses) via shock or thermal stimuli than is desired. More-recent alternative approaches to high-performance energetic materials have included: the incorporation of strain energy; more-energetic molecular features (e.g., difluoramino substituents); and high-density, low-hydrogen/high-nitrogen heterocyclic compounds. Nitro-

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aromatic and nitroheteroaromatic explosives tend generally to be more shock-insensitive and thermally stable. The superior thermal properties expected to be imparted by the heteroaromatic component of these structures may reasonably translate to other superior sensitivity characteristics (e.g., shock), on the basis of the generally recognized correlation of sensitivities to various stimuli that produce microscopic thermal events.

Examples of nitroaromatic and nitroheteroaromatic compounds of recent interest for demonstrated insensitivity properties include 5-nitro-1,2,4-triazolin-3-one (NTO) (Reference 1), 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) (Reference 2), 2,4-dinitroimidazole (2,4-DNI) (Reference 3), and aminonitroheterocyclic *N*-oxides (Reference 4).

One of the major goals in recent ordnance technology has been the development of high-explosive-yield materials that are nevertheless relatively insensitive to extraneous stimuli—i.e., insensitive high explosives (IHE) or insensitive munitions (IM). Accidental detonation, explosion, deflagration, or propulsive reactions of munitions pose extreme hazards to personnel and property and can inhibit military operations. As a result, the DOD Insensitive Munitions program began with an edict by the Chief of Naval Operations in May 1984 that all Navy munitions would have less-sensitive components. Many successive IM programs developed into joint cooperative efforts and have been reviewed by the Joint Army Navy NASA Airforce (JANNAF) Interagency Chemical Propulsion Committee.

## PROJECT DESCRIPTION

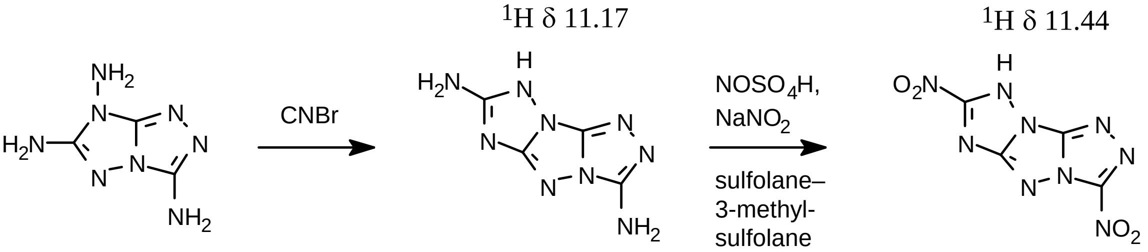
Based on experimental results and improved understanding of energetic materials' chemical reactivity arising from a past ILIR project ("Novel Thermally Insensitive Explosives/Oxidizers," concluded in FY 98), we modified the structural nature of desirable new target compounds for IM applications. The lessons from that previous ILIR project have led to different tactics in choosing attractive target compounds on the basis of synthetic tractability and predictable chemical reactivity as well as predicted performance.

The most important objective of the current program is to demonstrate the feasibility of preparing novel energetic materials based on *C*-nitro derivatives of extended (polynuclear) heterocyclic ring systems. These polynuclear systems may include nitroazines and/or nitroazoles as structural features for improving performance and safety relative to currently used high explosives.

This project addresses specific Navy technology issues in ordnance. A key technical issue in this field is that the heat soaking of submunition explosive fills at temperatures exceeding 280 °C over long flight times causes premature detonation; a technology problem for the hypersonic missile. Some of the nitroaromatic and nitroheteroaromatic compounds should be expected to be suitable high-temperature submunition explosive fills. Likely applications are lethality and propulsion in Theater Ballistic Missile Defense and kinetic warheads in Theater Air Defense.

## RESULTS

Known methodology for the preparation of certain polyazabicyclic systems has been extrapolated to still larger systems, resulting in improved thermal stability without the sacrifice of chemical stability. A relevant precedent is the preparation of a triaminopentaazapentalene (**1**), 7*H*-1,2,4-triazolo[4,3-*b*]-[1,2,4]triazole-3,6,7-triamine (Reference 5), which we have used as a precursor to form a larger polycyclic system (Figure 1). We extended the condensation to a trinuclear heterocycle, 8*H*-bis[1,2,4]triazolo[4,3-*b*:2´,3´-*d*][1,2,4]triazole-3,7-diamine (**2**), which consumes the N-amino substituent, obviates N-nitroazole products from oxidation, and expectedly improves thermal properties. A "nitro-Sandmeyer reaction" via diazotization followed by nitrite displacement—under unusual nonaqueous conditions (Reference 6), due to the poor aqueous solubility of amine reactant 2—produced a sulfone-soluble product consistent with the desired dinitro derivative (**3**), according to $^{1}$H and $^{13}$C NMR comparisons to model compounds such as NTO. This product must be purified and identified definitively.



**1**
(m.p. 250 °C)

**2**

**3** ($C_4HN_9O_4$)
[tentative]

FIGURE 1. Chemistry of the 8*H*-bis[1,2,4]triazolo[4,3-*b*:2´,3´-*d*][1,2,4]triazole System.

By similar methodology, 3,4,5-triamino-1,2,4-triazole (guanazine) has been cyclized with cyanogen bromide (Figure 2) to provide a new polycyclic high-nitrogen system (**4**) containing a guanidine component, identified by nuclear magnetic resonance spectrometry, elemental analysis, and X-ray crystallography (Figure 3).

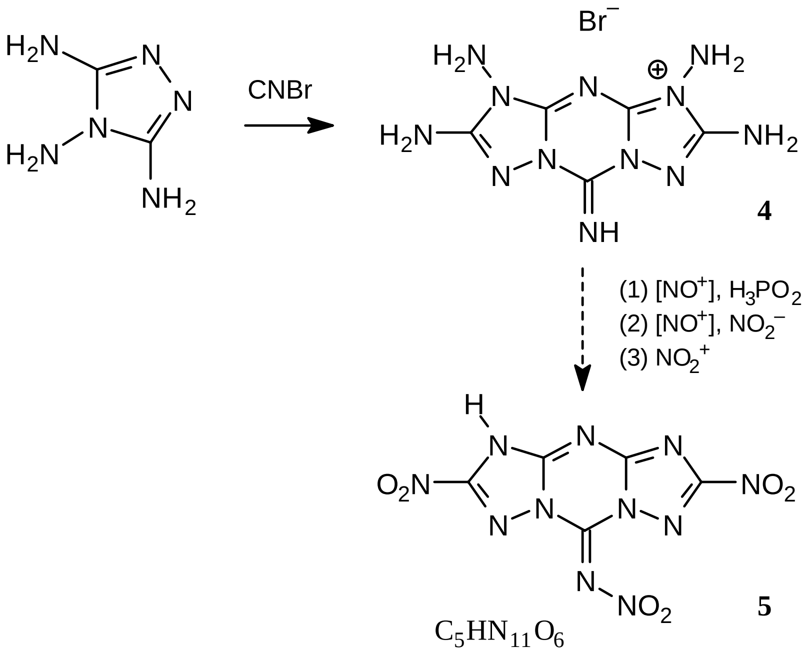


FIGURE 2. Chemistry of a New Bis[1,2,4]triazolo[1,3,5]triazine System.

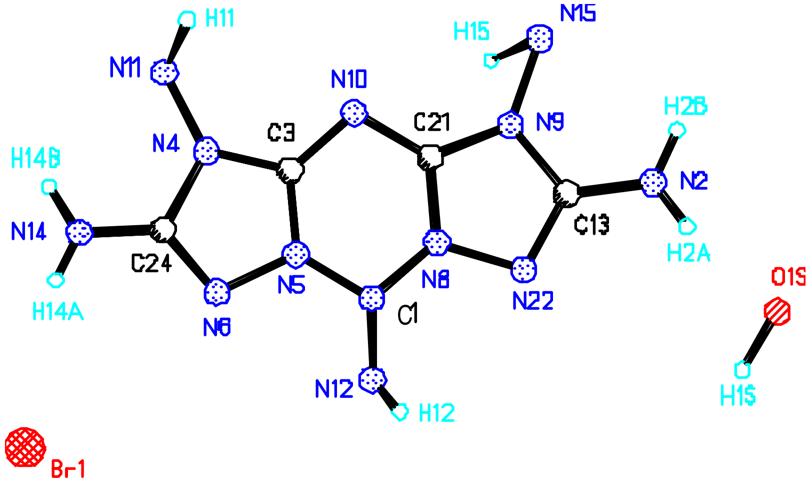
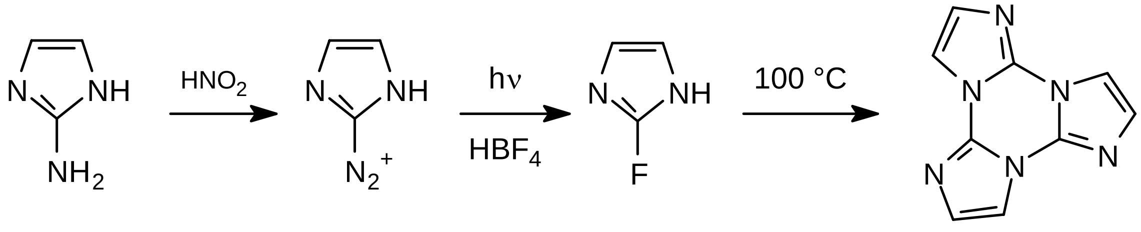


FIGURE 3. ORTEP Plot of a New Bis[1,2,4]triazolo[1,3,5]triazine Derivative (**4**).

A sequence of selective N-deamination—a transformation demonstrated on the *C,C,N*-triamino precursor (**1**) of Figure 1 (Reference 5)—amino-to-nitro conversion (via a nitro-Sandmeyer reaction or N-oxidation) and N-nitration would yield a new high-nitrogen energetic material (**5**) of expected high performance (oxygen-balanced to better than CO) and high thermal stability.

We recently investigated the development of a more convenient synthesis of 2-fluoroimidazole (**6**). As even the 4,5-unsubstituted derivative has been shown (Reference 7) to autocatalytically self-condense (Figure 4) to a trimer (**7**), monomer **6** is of interest: trimer **7** could potentially be directly nitrated in the 4,5-positions of each imidazole component—analogous to a known nitration of imidazole itself (Reference 8), making 4,5-dinitroimidazole—in order to prepare new energetic materials. 2-Fluoroimidazole has previously been prepared via a photochemically activated displacement by fluoride of imidazole-2-diazonium ion, using $HBF_4$ as a fluoride source (Reference 9). Our attempts to prepare **6** by a conventional Sandmeyer reaction, using aqueous HF without photochemical activation have been thus far unsuccessful.



**6** **7**

FIGURE 4. Preparation and Trimerization of 2-fluoroimidazole.

## CONCLUSIONS AND PROJECT STATUS

In this ILIR project, which is continuing in FY 01, synthetic methodology leading to proposed novel insensitive high explosives is being demonstrated and developed. New polycyclic heterocyclic systems (**2** and **4**) have been prepared as potential intermediates to expected new energetic materials, one of which (**3**) has been tentatively identified. The preparation of product **3** needs to be reproduced to isolate and definitively identify and characterize the product. The synthetic scheme leading to **5** will be continued in order to prepare this attractive target compound. As imidazole trimer **7** and its nitrated derivatives are of interest as additional target compounds, this desired intermediate may be prepared by the literature method in order to pursue prospective energetic products.

The collaboration with Pacific Scientific Energetic Materials Company through the CRADA will continue.

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