Polycyclic N-Oxides: High Performing, Low Sensitivity Energetic Materials

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Polycyclic N-Oxides: High Performing, Low Sensitivity Energetic Materials

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Polycyclic N-oxides were developed based on the heterocycles 1,2,4,5-tetrazine and 4*H*,8*H*-difurazano[3,4-*b*:3',4'-*e*]pyrazine. The new compounds are energetic and have excellent explosive properties, while maintaining low mechanical sensitivities. Most notably, compound 7 is thermally stable, insensitive, and and has superior detonation properties to the state-of-the-art insensitive high explosive, 1,3,5-triamino-2,4,6-trinitrobenzene.

Polycyclic systems have unique electronic properties due to the high degree of conjugation and π-stacking in these materials.[1] This makes them useful in organic electronic applications, such as molecular semiconductors, light emitting diodes, and field-effect transistors. The π-stacking within polycyclic systems results in efficient crystal packing and high crystal densities, which is attractive to the development of novel energetic materials since explosive performance (detonation velocity and detonation pressure) generally increase with density.[2]

A major challenge in the development of advanced energetic materials is to overcome the sensitivity versus performance trend observed with conventional explosives.[3] In general, the higher the explosive performance of a material the higher the sensitivity is towards destructive stimuli. However, π-stacking interactions within aromatic energetic materials been shown to result in lower sensitivities while maintaining good explosive performance properties.[4] Despite the potential benefits of energetic polycyclic systems, these systems are rare and seldom extend beyond four heterocycles.[5]

In order to expand our efforts in the arena of polycyclic systems, we embarked on the exploration of the construction of heterocyclic systems containing both linear and fused polycyclic components. This study represents our efforts to combine the 1,2,4,5-tetrazine ring and the fused heterocycle 4*H*,8*H*-difurazano[3,4-*b*:3',4'-*e*]pyrazine (DFP) in an attempt to construct novel polycyclic system energetics. DFP was chosen because of its very high density (1.99 g/cm^3), high thermal stability, and its ability to be substituted at both the 4 and 8 positions of the fused ring, which can allow for the formation of linear polycyclic systems.[6] DFP was first reported in the literature in 1996 in two separate efforts by Sheremetev[7a] and Adrianov.[7b] Subsequently, the chemistry of DFP was studied, including direct nitration and alkylation reactions[8] and macrocyclization reactions.[9] More recently, new energetic derivatives of DFP have been reported by Shreeve[10] and Wang.[11]

The 1,2,4,5-tetrazine heterocycle was selected due to to its high heat of formation, low carbon content, its propensity to undergo N-oxidation with a variety of oxidizing reagents, and its ability to be substituted at both the 3 and 6 positions. In addition to energetic materials, studies involving the 1,2,4,5-tetrazine heterocycle have surged recently due to their applications in bioorthogonal chemistry,[12] cocrystallization,[13] and electro- and photochemical reactions.[14] This is due to the high nitrogen content of the 1,2,4,5-tetrazine system, which makes it electron deficient, giving rise to unique optical and electronic properties and allowing it to undergo nucleophilic aromatic substitution reactions under mild conditions.[15]

The nucleophilic addition of DFP to aromatic electrophiles,[11,16] such as picryl chloride, led us to believe that a similar reaction with a chloro-substituted 1,2,4,5-tetrazine would be successful. Interestingly, the reaction of DFP with two equivalents of 3,6-dichloro-1,2,4,5-tetrazine in the presence of base led to an insoluble precipitate and recovery of one equivalent of 3,6-dichloro-1,2,4,5-tetrazine. The insoluble precipitate is very likely an oligomeric form of the DPF/1,2,4,5-tetrazine (Scheme 1). This implies that DFP substitution of the tetrazine ring further activates it toward nucleophilic attack. Unfortunately, the insoluble nature of the material precluded its analysis by NMR and elemental analysis suggests that a mixture of oligomers are produced.

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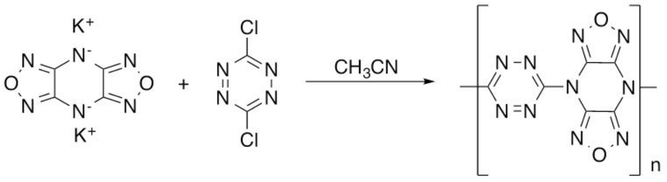
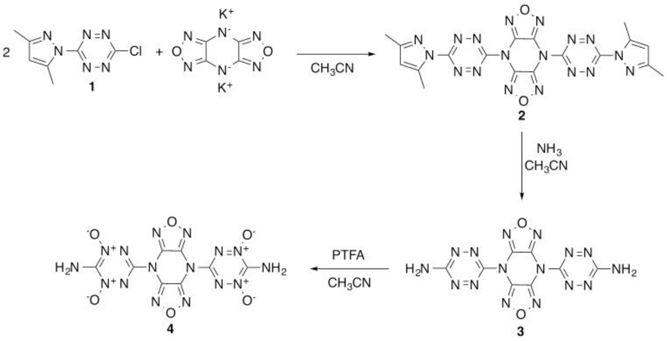


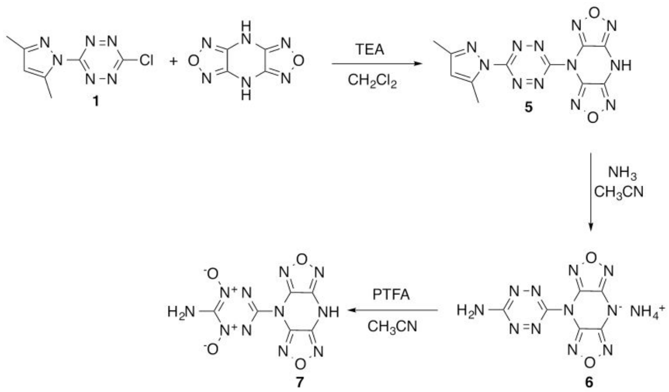
Scheme 1 Reaction of 3,6-dichlorotetrazine with the bis-potassium salt of DFP.

In order to prevent polymerization from occurring, the mono-chloro substituted compound, 3-chloro-6-(3,'5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**1**) was employed as the electrophile (Scheme 2). The reaction proceeded effectively in acetonitrile to give the desired product (**2**). Subsequent treatment of **2** with ammonia provided the desired diamino compound (**3**). It was found that only displacement of the 3,5-dimethylpyrazolyl groups occurred, with no side products being observed. Amino-1,2,4,5-tetrazines are excellent substrates for N-oxide formation with a variety of oxidizing reagents.[17] We studied both peroxytrifluoroacetic acid (PTFA) and hypofluorous acid (HOF) as oxidants. In both cases, the desired tetra-N-oxide compound (**4)** was obtained (Scheme 2).

While the ability to access symmetrical compounds such as **4** was a desired outcome, we felt that access to unsymmetrically substituted compounds would also be of interest. The use of a 1:1 ratio of **1** with DFP in the presence of triethylamine was successful at providing the monosubstituted product **5** (Scheme 3). Treatment of **5** with ammonia not only led to the displacement of the 3,5-dimethylpyrazole group, but also resulted in the deprotonation of the free N-H proton of the DFP substituent (**6**). Treatment of this intermediate with acid provides the protonated product, however, this step is unnecessary, as subjecting **6** to PTFA in acetonitrile not only leads to the formation of the di-N-oxide, **7**, but also protonates the DFP substituent (Scheme 3).

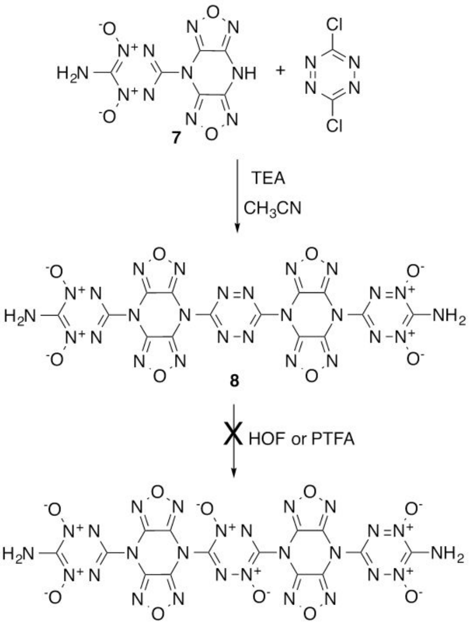


Scheme 2. Synthesis pathway to **4**.



Scheme 3 The synthesis of **7**.

With **7** in hand, we wondered whether it could act as a nucleophile and react with 3,6-dichloro-1,2,4,5-tetrazine to form the symmetrical compound **8** (Scheme 4). Treatment of **7** with triethylamine, followed by reaction with 3,6-dichloro-1,2,4,5-tetrazine in acetonitrile at ambient temperature provided **8**. We then investigated whether the central tetrazine ring could be oxidized further. Unfortunately, compound **8** is very insoluble and no reaction was observed with PTFA or HOF.



Scheme 4 Synthesis of **8.**

X-ray quality crystals of **4**, **7**, and **8** were grown from either N,N-dimethylformamide (DMF) or butyrolactone and in each case, solvates were formed.[18] Compound **4** formed a 1:2 DMF solvate. The crystal obtained was in the triclinic crystal system, in the P-1 space group. The DMF oxygen atom hydrogen bonds to the amino group on the tetrazine (Figure 1a). The tetrazine rings and the DFP ring system are staggered, with the DFP ring plane rotated 29.62 ° out of plane from the tetrazine rings. Compound **7** forms a 1:1 solvate with butyrolactone. The

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solvate exists in the monoclinic crystal system, in the $P2_1/n$ space group. In this case, the torsion angle between tetrazine and the DFP rings are only 16.59^{o} (Figure 1b). Compound **8** crystallizes in the unit cell accompanied by four solvated DMF molecules. Similar to compound **4**, compound **8** displays the triclinic crystal system in the P-1 space group. Each crystallographically independent molecule of **8** has unique torsion angles, implying that the polycyclic ring system allows for rotation around the bridging C-N bonds. The torsion angles between the terminal tetrazines and DFP in each molecule are 24.32 and 32.67 ^{o}, respectively. These angles are slightly smaller than the torsion angles between the central tetrazine to the DFP moieties of 28.25 and 33.96 ^{o} (Figure 1c).

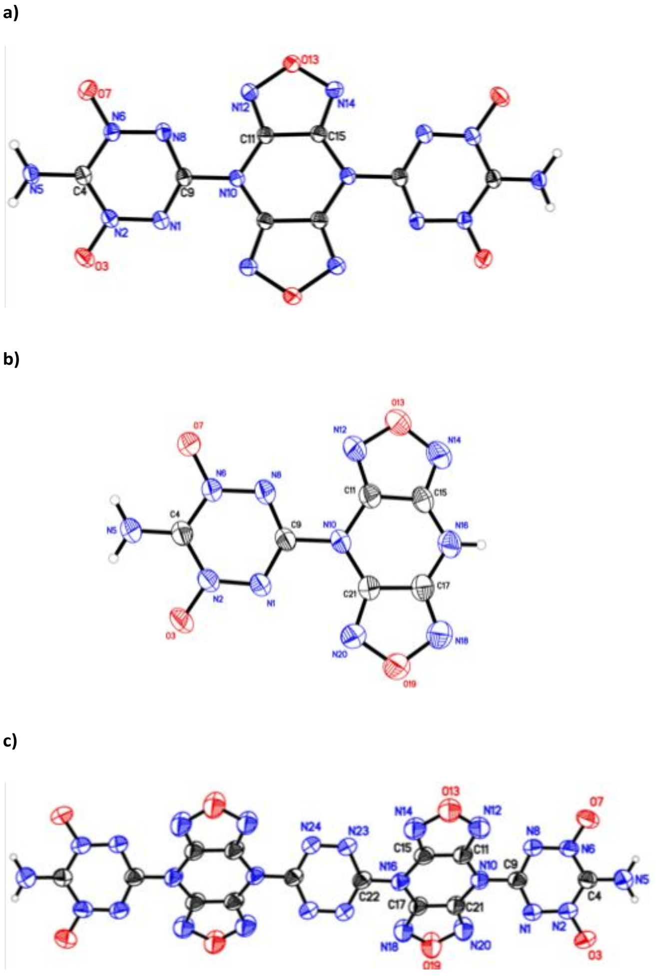

Figure 1. a) Molecular structure of **4** as it appears in the crystal structure. Non-H atomic displacement ellipsoids are 50% probability. The two solvated DMF molecules are omitted for clarity. b) Molecular structure of **7** as it appears in the crystal structure. Non-H atomic displacement ellipsoids are 50% probability. The butyrolactone molecule is omitted for clarity. c) Molecular structure of **8** as it appears in the crystal structure; the four solvated DMF molecules are omitted for clarity. Non-H atomic displacement ellipsoids are 50% probability.

The sensitivity data for compounds **4**, **7** and **8** are shown in Table 1. It should be noted that the crystal structures shown in Figure 1 are that of solvated materials, and are not the same as the unsolvated samples that were tested for sensitivity in Table 1. All three compounds were found to be much less sensitive to impact and friction than RDX. Compound **7** was found to be insensitive to impact. Overall the materials displayed excellent resistance toward destructive stimuli. The thermal stabilities of the materials were also observed to be excellent with each material's thermal onset of decomposition lying between 225 ^{o}C and 230 ^{o}C.

Table 1 Sensitivity Data for **4**, **7** and **8**

	Impact [J][a]	Spark [J][b]	Friction [N][c]
4	18.5	0.062	>360
7	>78.4	0.062	>360
8	35.7	0.062	>360
PETN	4.2	0.062	64.7
RDX	4.6	0.062	157
TATB	>78.4	0.125	>360

(a) LANL type 12, 50% drop height, 2.5 kg; (b) ABL spark 3.4% threshold initiation level (TIL); (c) 50% load Bruceton up/down method.

The heats of formation and density of compounds **4**, **7** and **8** were calculated using the method developed by Rice (Table 2).[19] These data were used to predict the explosive performance properties of these materials using the Cheetah thermochemical code.[20] The data are also displayed in Table 2. Overall, compound **4** and **8** display RDX-like performance in detonation velocity and detonation pressure, while displaying much better insensitivity. Additionally, compound **7** displays good performance, while being insensitive toward impact and friction.

Table 2. Performance Data for **4**, **7** and **8**

	V_D [km/s][a]	P_{CJ} [GPa][b]	Density [g/cm^3][c]	Enthalpy [kJ/mol][d]
4	8.8	33	1.889	1162
7	8.4	32	1.858	810
8	8.7	32	1.903	2128
RDX	8.8	34.9	1.80	70.3
TATB	8.43	30.1	1.93	134

(a) Calculated detonation velocity;[20] (b) calculated detonation pressure;[20] (c) calculated density at 23 °C;[19] (d) Calculated enthalpy of formation.[19]

In conclusion, we have developed a simple method for synthesizing polycyclic systems of varying lengths using nucelophilic aromatic substitution on 1,2,4,5-tetrazines under mild conditions. Oxidation of these materials yields energetic polycyclic N-oxides and opens a new avenue in the development of novel energetic materials. This work has demonstrated that by using only two types of heterocycles, the sensitivity and detonation properties of the materials may be tuned by varying the length of the polycyclic N-oxide system, allowing access to new materials that display high densities, high heats of formation, very low sensitivity toward impact and insensitivity toward friction, while maintaining excellent performance properties.

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Conflicts of interest

There are no conflicts to declare.

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