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A high density pyrazolo-triazine explosive (PTX)†

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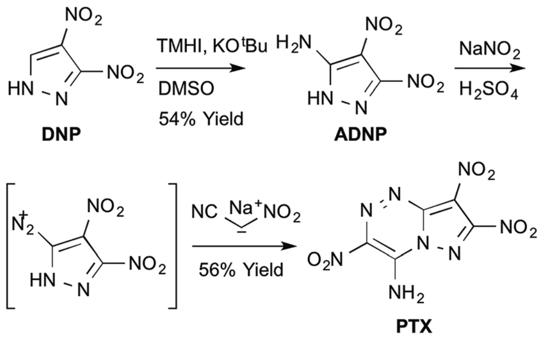
The fused-ring heterocycle 4-amino-3,7,8-trinitropyrazolo-[5,1-c][1,2,4]triazine (PTX) has promising explosive properties. The Cheetah thermochemical code used its calculated standard enthalpy of formation and its measured crystal density of 1.946 g cm^{-3} to predict HMX-like explosive performance, while measurements of its thermal stability, sensitivity to impact, friction, and spark showed greater safety margins.

The discovery and development of high performing and low-sensitivity explosives is an ongoing effort in the energetic materials community.[1–3] The main challenge to this effort is the trade-off between sensitivity and explosive performance. Insensitive high explosives such as 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), 2,2-dinitroethene-1,1-diamine (FOX-7), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), and 3,3′-diamino-4,4′-azoxyfurazan (DAAF), lack the explosive power of more sensitive but higher performing explosives like octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20).[3–5] Understanding how molecular features and material properties affect sensitivity and explosive performance in both high performing and insensitive explosives is essential in developing the next generation of explosives. Targeting molecules that combine features favorable for both explosive performance and stability may bridge the gap between them.

Low sensitivity explosives (TATB, FOX-7, DAAF, and LLM-105) are often flat molecules that display high thermal stabilities, N–H⋯O type hydrogen bonding, and π–π interactions.[1,6–8] The crystal lattice packing resulting from these features allows slipping between graphite-like layers in the explosive crystals, decreasing the likelihood of generating hotspots that inadvertently initiate the material to reactivity and ultimately detonation.[6–9] Higher performing explosives (HMX) have high density and better oxygen balance; in the cases of CL-20 and octanitrocubane, they have large positive heats-of-formation from their strained fused-ring/cage-like structures.[10]

With those molecular properties as guidelines for the rational design and discovery of new explosives, we investigated a fused pyrazolo-triazine explosive (PTX, Scheme 1), a molecule first synthesized in seven steps and 10% overall yield by Dalinger and coworkers.[11] The fused-rings produce a flat molecular geometry and π–π interactions. The nitrogen-rich heterocycles reduce the amount of carbon present, making a good oxygen balance easier to achieve with fewer explosophores. While density is difficult to predict, the presence of nitro and amino groups invites hydrogen bonding to increase molecular density. Herein we report an improved three step synthesis of PTX in 30% overall yield, its crystal structure, and its explosive properties.

The penultimate precursor to PTX is 5-amino-3,4-dinitropyrazole (ADNP, Scheme 1) which can be diazotized and condensed with the sodium salt of nitro-acetonitrile (NaNAN) to



Scheme 1 Synthesis of PTX *via* a VNS route.

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prepare PTX.[11] A few synthetic routes to ADNP have been reported[12] and involve the reduction of 5-azido-3,4-dinitropyrazole,[13,14] the Hofmann rearrangement of 3,4-dinitropyrazole carboxamide,[11] or substitution of *N*-protected 3,4,5-trinitropyrazoles.[15] We present an improved synthesis to ADNP from dinitro-pyrazole (DNP) by utilizing vicarious nucleophilic substitution (VNS) of the pyrazole C–H[16,17] as displayed in Scheme 1. The VNS amination reaction of DNP using trimethylhydrazinium iodide (TMHI) proceeds in 54% yield to provide ADNP contaminated with 10–15 mol% DNP. We found it unnecessary to purify ADNP before converting it into PTX. Insoluble material is filtered from the reaction after the diazonium intermediate has condensed with NaNAN into a soluble species, affording a pure crop of PTX from the filtrate in 56% yield. Solvent free X-ray quality crystals of PTX formed from an unstirred aliquot of the filtrate.

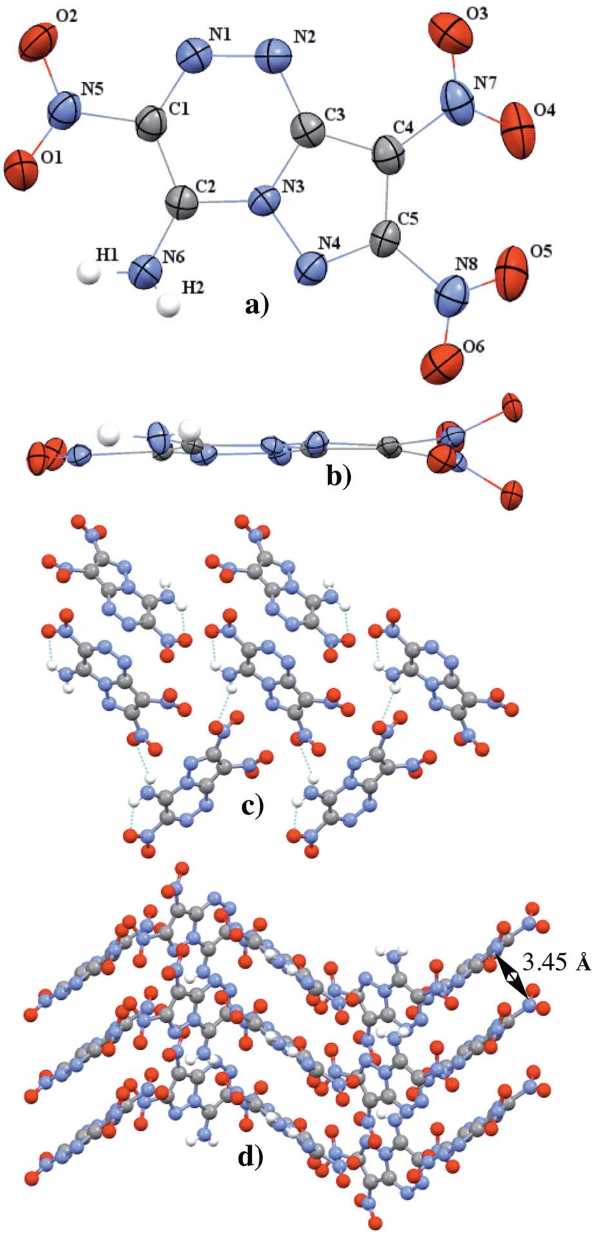

Fig. 1 (a and b) Thermal ellipsoids plot (50%) of PTX. (c) Crystal packing of PTX viewing down unit cell axis *a*, hydrogen bonds shown in blue. (d) Crystal packing of PTX showing molecular stacking planes.

Single crystal X-ray analysis was performed on PTX. Fig. 1b shows the planarity of the fused-ring structure, with all torsion angles of N5 and N6 substituents less than 7° and those of N7 and N8 substituents between 22–33°. Nitro group (N5) and amino group (N6) are presumably held co-planar with the fused-ring by intramolecular hydrogen bonding (H1–O1, 2.12 Å) (Fig. 1c). Intermolecular hydrogen bonds can also be seen in Fig. 1c as dashed lines between amino and nitro groups (H2–O6, 2.29 Å). The hydrogen bonds, along with π–π interactions and a serendipitous packing arrangement give the crystals an ultra-high density of 2.006 g cm^{-1} at 100 K. Fig. 1d shows the π–π interactions that result in molecular stacking planes with an interplanar distance of 3.45 Å. The presence of four unique molecular stacking plane orientations results in a mixed molecular stacking seen in Fig. 1d that prevents interlayer sliding within the crystal lattice. Interlayer sliding within a crystal lattice is a feature that contributes to the insensitivity of TATB, FOX-7, DAAF, and LLM-105, which have graphite-like stacking that allow such sliding.[6–9]

The explosive performance of PTX was calculated using the Cheetah thermochemical code.[19] A heat of formation was calculated by a method described by Rice[20] to be 88.44 kcal mol^{-1}. The measured ambient temperature diffraction density of 1.946 g cm^{-3} and the calculated heat of formation were used for the performance predictions. These data along with thermal stability and sensitivity are compared to those of HMX in Table 1. PTX should exhibit HMX-like performance with lower sensitivity and good vacuum thermal stability. The presence of intra- and intermolecular hydrogen bonding in PTX could account for lower sensitivity than HMX. However, the inability for interlayer sliding to occur within the crystal lattice may be a factor that prevents PTX from achieving the same insensitivity as molecules like TATB or FOX-7 despite similar intermolecular interactions and flat molecular geometries.

Table 1 Explosive performance and sensitivity

	PTX	HMX
ρ (g cm^{-1})	1.946@300 K	1.89^{a}
V_{det} (m s^{-1})	8998^{b}	9110^{a}
P_{CJ} (GPa)	36.04^{b}	39.0^{a}
H_{f} (kcal mol^{-1})	88.44^{b}	17.93^{a}
$T_{\text{onset}}/T_{\text{peak}}$ (°C)^{c}	246/288	265/285
Impact (cm)^{d}	58.4 ± 13.5	24.9 ± 4.9
Friction (N)^{e}	324–360	150 ± 40
Spark (J)^{f}	0.0625	0.025–0.125

[a] From LLNL explosives manual.[18] [b] Calculated values. [c] DSC decomposition temperature, onset is defined by a 0.01 W per g per °C threshold, with a 10 °C min^{-1} heating rate. [d] LANL type 12, 50% drop height, 2.5 kg. [e] 50% load Bruceton up/down method. [f] ABL spark 3.4% threshold initiation level (TIL).

Conclusions

In summary, we utilized VNS in an improved synthetic route to PTX. Its notable combination of calculated performance and decreased sensitivity makes PTX a promising explosive candidate that warrants further investigation. Additionally, these results exemplify the rational design and discovery of new explosive molecules *via* the combination of features that enhance performance (high density and good oxygen balance) while preserving molecular stability (hydrogen bonding, planar geometries, and π–π interactions).

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