Energetic Materials

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Energetic *N*-Nitramino/*N*-Oxyl-Functionalized Pyrazoles with Versatile π–π Stacking: Structure–Property Relationships of High-Performance Energetic Materials

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Abstract: *N-Nitramino/N-oxyl functionalization strategies were employed to investigate structure–property relationships of energetic materials. Based on single-crystal diffraction data, π–π stacking of pyrazole backbones can be tailored effectively by energetic functionalities, thereby resulting in diversified energetic compounds. Among them, hydroxylammonium 4-amino-3,5-dinitro-1H-pyrazol-1-olate and dipotassium N,N′-(3,5-dinitro-1H-pyrazol-1,4-diyl)dinitramidate, with unique face-to-face π–π stacking, can be potentially used as a high-performance explosive and an energetic oxidizer, respectively.*

The last decade has witnessed the rapid development of high energy density materials (HEDMs), which are of wide interest to both the military and civilian research communities. The various application requirements of HEDMs commonly require molecular diversity of energetic ingredients.[1] For example, the organic molecule RDX (1,3,5-trinitrotriazacyclohexane) serves as a secondary explosive in most munitions, whereas the inorganic salt LA (lead azide) plays a pivotal role as a primary explosive to initiate energy release.[2] Diverse criteria, that is, density, detonation performance, mechanical sensitivity and heat of formation, have been established gradually for comprehensive evaluation of different HEDMs.[3]

In comparison with traditional HEDMs, the modern design of energetic materials is based more on insight arising from multiple disciplines, including synthetic methodology, crystal engineering, and computational science.[4] Among them, crystal engineering of HEDMs is of importance in acquiring structural information.[5] In general, there are four π–π stacking types for classic energetic aromatic molecules, i.e., face-to-face, wavelike, crossing, and mixing.[6] Face-to-face crystal stacking is the most favorable type which is stable to mechanical stimuli because of free interlayer sliding. In contrast, mechanical stimuli from different orientations, the interlayer sliding of other packing types is limited to different degrees (Figure 1). For instance, the crystal packing in 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) features an almost perfect face-to-face π–π stacking (Figure 1 a), which is consistent with its highly insensitive and heat-resistant properties.[7] Compared to TATB, 1,1-diamino-2,2-dinitroethene (FOX-7) has wavelike stacking and sliding horizontally may cause hot spots between adjacent units, thereby resulting in molecular decomposition (Figure 1 b).[8] With respect to 2,4,6-trinitroaniline (TNA) and 1,3,5-trinitrobenzene (TNB), sliding along any orientation is deleterious due to crossing and mixing stacked types, respectively (Figure 1 c and d).[9]

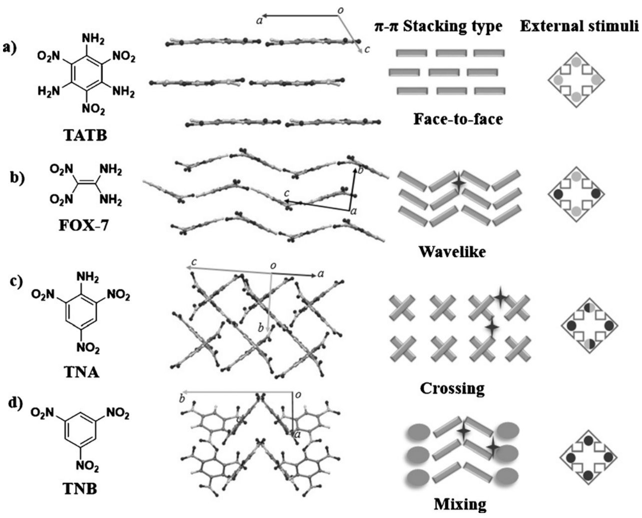

Figure 1. Representative energetic compounds and their diverse crystal stacking.

With our continuing goal of generating advanced HEDMs, *N*-nitramino and *N*-oxyl functionalization strategies are now employed to study the structure–property relationships of energetic pyrazoles. As a representative compound in the family of energetic azoles, 4-amino-3,5-dinitro-1*H*-pyrazole (**1**) has high density and a planar crystal structure (Scheme 1).[10] However, an undesirable crystal packing and low detonation performance may limit practical application. By selective or complete introduction of *N*-functionalized groups, the energetic derivatives (**2**–**5**) exhibit greater energetic performance.[11] Because these molecular compounds (**2**–**5**) are not stable enough to obtain crystal structures, structural confirmation was obtained by synthesizing the more stable salts. According to the difference in nitroamino and oxyl functionalities, these pyrazole frameworks show diversified dimensional structures, as can be seen in Scheme 1.

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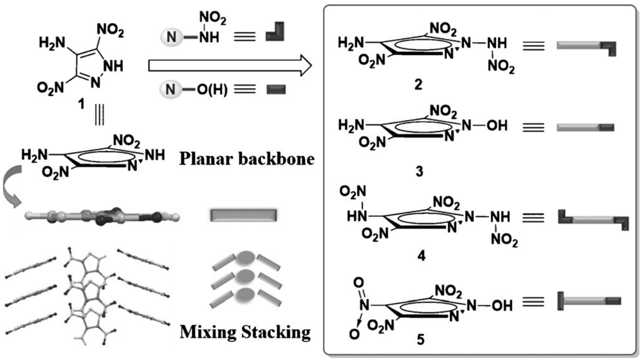
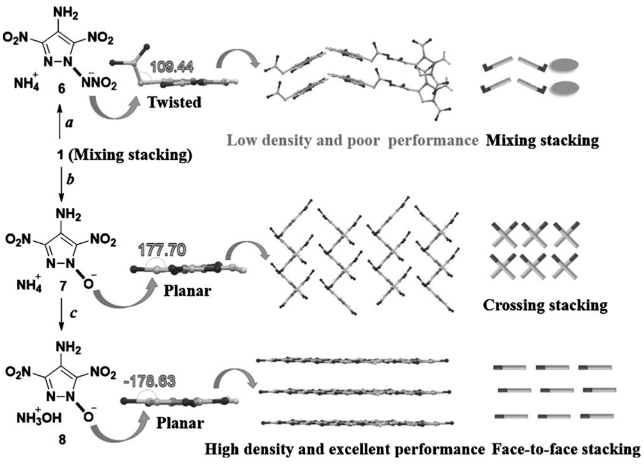


Scheme 1. Functionalization strategy of 4-amino-3,5-dinitropyrazole and structural models of energetic derivatives.

The selective introduction of the *N*-nitramino functionality was accomplished by amination and selective nitration using hydroxylamine-*O*-sulfonic acid (HOSA) and H_2SO_4/NH_4NO_3, respectively. Reaction with ammonia gave rise to ammonium *N*-(4-amino-3,5-dinitro-1*H*-pyrazol-1-yl)nitramidate **6**, which is suitable for X-ray single-crystal diffraction (Scheme 2).[12]



Scheme 2. Selective *N*-nitramino/*N*-oxyl functionalization and stacking types of pyrazoles. a) i) NH_2OSO_3H, Na_2HPO_4, Na_2CO_3; ii) conc. H_2SO_4, NH_4NO_3; iii) NH_3, MeOH. b) i) Conc. H_2SO_4, 30% H_2O_2; ii) Oxone; iii) NH_3, MeOH. c) i) 10% H_2SO_4; ii) 50% NH_2OH.

The *N*-nitramino unit is twisted out of the plane with an angle of 109.44° with the result that mixing stacking was found for the pyrazole backbone. These structural features disfavor thermal and mechanic stabilities as demonstrated by the relatively low decomposition temperature ($T_d = 124\,°C$), impact sensitivity (IS = 10 J), and friction sensitivity (FS = 80 N) (Table 1). Unfortunately, preparation of the hydroxylammonium salt from **6** was unsuccessful due to the highly hygroscopic nature of the target compound.

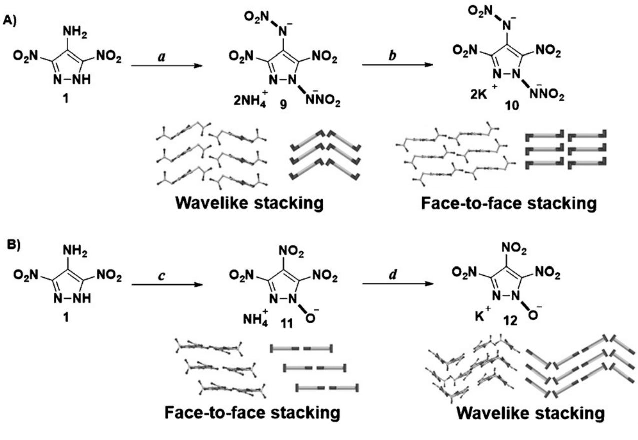
Table 1: Physicochemical properties of selected *N*-nitramino/*N*-oxyl-functionalized pyrazoles.

Comp.	d[a] [g cm^{-3}]	T_d [b] [°C]	ΔH_f[c] [kJ g^{-1}]	v_D[d] [m s^{-1}]	P[e] [GPa]	IS[f] [J]	FS[g] [N]
6	1.768	124	0.86	8762	33.8	10	80
7	1.775	176	0.16	8613	31.7	32	360
8	1.857	182	0.36	9004	37.6	35	360
RDX	1.806	205	0.36	8748	34.9	7	120

[a] Density measured by gas pycnometer (25 °C). [b] Decomposition temperature (onset). [c] Heat of formation. [d] Detonation velocity (calculated with Explo5 v6.01).[13] [e] Detonation pressure (calculated with Explo5 v6.01).[13] [f] Impact sensitivity. [g] Friction sensitivity.

The *N*-oxyl functionality was introduced selectively by oxidation of **1** using hydrogen peroxide and oxone, and the product was treated with ammonia to give **7** (Scheme 2). While the N−O functionality in the crystal structure of **7** is almost coplanar with the pyrazole backbone, the pyrazole rings are crossed with each other in three-dimensional crystal packing. Treating **7** with dilute sulfuric acid and aqueous hydroxylamine gives **8** in good yield. Interestingly, the modification by the hydroxylammonium cation results in a face-to-face stacking of **8** (Scheme 2). As expected, **8** exhibits the most desirable energetic properties, i.e., high density, excellent detonation performance and low impact and friction sensitivities (**8**, $d = 1.857\,g\,cm^{-3}$, $v_D = 9004\,m\,s^{-1}$, P = 37.6 GPa, IS = 35 J; FS = 360 N), which are comparable to those of the benchmark secondary explosive RDX ($d = 1.806\,g\,cm^{-3}$, $v_D = 8748\,m\,s^{-1}$, P = 34.9 GPa, IS = 7 J; FS = 120 N).

Analogous to the mono-nitramino functionalized **6**, dinitramino functionalization of **1** gave the similar twisted crystal structure of **9** (Scheme 3). In contrast to the coplanar feature of the selective *N*-oxyl unit, full oxyl functionalization of **1** led to a non-planar aromatic framework in **11**, which can be attributed to the increasing steric hindrance at the 4-positon. The mechanically sensitive features and poor thermal behavior resulting from their twisted structures make **9** and **11** unsuitable as secondary explosives.[11] However, their enhanced densities and oxygen balances provide a potential possibility for designing new ionic derivatives for energetic oxidizers and primary explosives. While secondary explosives are mainly evaluated by detonation performance, primary explosives and oxidizers are evaluated by oxygen balance, thermal behavior, density, and specific impulse.[14]



Scheme 3. A) Full nitramino and B) oxyl functionalization and stacking types of pyrazoles. a) i) NH_2OSO_3H, Na_2HPO_4, Na_2CO_3; ii) conc. H_2SO_4, HNO_3; iii) NH_3, MeOH. b) i) $AgNO_3$; ii) KI. c) i) Conc. H_2SO_4, 30% H_2O_2; ii) Oxone; iii) NH_3 (aq). d) i) 10% H_2SO_4; ii) K_2CO_3.

Metathesis reactions of silver nitrate and potassium iodide with **9** and **11** resulted in **10** and **12**, respectively. Their key physicochemical properties are given in Table 2 (detailed energetic properties, viz., detonation velocities and pressures can be found in the Supporting Information).

Table 2: Physicochemical properties of fully *N*-nitramino/*N*-oxyl-functionalized pyrazoles.

Comp.	T_d[a] [°C]	d[b] [g cm^{-3}]	Ω[c] [%]	ΔH_f[d] [kJ g^{-1}]	I_{sp}[e] [s]	IS[f] [J]	FS[g] [N]
9	139	1.801	5.1	0.46	270	12	120
10	272	2.161	18.1	−0.38	206	15	120
11	176	1.820	13.6	0.15	268	6	80
12	179	2.102	21.8	−0.38	223	3	60
ADN	159	1.810	25.8	−1.21	202	3–5	64–72
$Pb(N_3)_2$	315	4.800	−11.0	1.55	–	2.5–4	0.1–1

[a] Decomposition temperature (onset). [b] Density measured by gas pycnometer (25 °C). [c] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, $1600(c-a-b/2)/MW$, MW = molecular weight. [d] Heat of formation. [e] Specific impulse. [f] Impact sensitivity. [g] Friction sensitivity.

The densities of **9–12** range between 1.801 and 2.161 g cm^{-3}. The high densities of **10** and **12** arise from the presence of the potassium cation. Compared to the poor thermal stability of the ammonium salt (**9**), the potassium salt (**10**) exhibits a decomposition temperature of 272 °C relative to 139 °C. In stark contrast to the nitramines **9** and **10**, **11** and **12** exhibit similar thermal behavior with decomposition temperatures of 176 °C and 179 °C, respectively. These differences can be interpreted based on the change of π–π stacking: the reaction from **9** to **10** gave a favored face-to-face type from an unfavorable wavelike type, whereas face-to-face π–π stacking of **11** was changed to wavelike π–π stacking of **12**. Compared to ammonium dinitramide (ADN), the energetic properties of **10**, i.e., thermal stability, high density and positive oxygen balance will enable it to be applied as a potential heat-resistant energetic oxidizer in a propellant system (ADN: $T_d = 159\,°C$, $d = 1.810$ g cm^{-3}, $\Omega = 25.8\,\%$, $I_{sp} = 202$ s; **10**: $T_d = 272\,°C$, $d = 2.161$ g cm^{-3}, $\Omega = 18.1\,\%$, $I_{sp} = 206$ s). Additionally, based on the sensitive characteristic and positive oxygen balance, **12** exhibits the application potential to replace lead azide as a green primary explosive.

In conclusion, a family of new nitramino/oxyl functionalized energetic pyrazoles was prepared and characterized. The structure–property relationships were explored using X-ray single-crystal diffraction. By introducing nitramino or oxyl functionalities, the crystal packing can be modified diversely, giving rise to *N*-functionalized HEDMs with good energetic properties. Among them, **8** and **10** with face-to-face π–π stacking are the most promising energetic materials as a secondary explosive and an oxidizer, respectively. This work highlights an *N*-functionalization strategy as a useful tool to study structure–property relationship of HEDMs.

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Keywords: energetic materials · N-functionalization · pyrazoles · structure–property relationship · π–π stacking

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