N-amino functionalization of nitroimidazoles: a new strategy for high performance energetic materials

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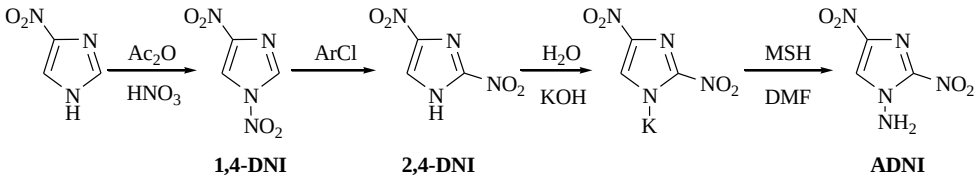
Submitted

An N-functionalized strategy, especially N-amination was utilized for the synthesis of nitroimidazole-based energetic materials, giving rise to a new family of highly insensitive N-amino nitroimidazoles with good to excellent properties, which not only gives rise to impact insensitive and thermally stable materials (IS: 0%, FS: 0%, H_{50}=104.2cm, T_d: 270 °C, 5S shotpoint 312℃), but also have favorable densities (1.774 g. cm^{-3}), good detonation properties (P: 31.9 GPa; v_D: 8500 $m.s^{-1}$). These properties are better than some known energetic compounds, such as TNT (P: 19.5 GPa; Dv: 6881 m. s^{-1}) and TATB (P: 31.2 GPa; vD: 8114 m s^{-1}), and are comparable to RDX (P: 35.0 GPa; vD: 8762 m s^{-1}). The synthesis of N-animo dinitroimidazole (ADNI) was optimized at hectogram level with total yield increase from 40% to 57.9%. and 2, 4, 6-trimethylbenzenesulfonic hydroxylamine (MSH) was optimized at 1 Kg level with total yield 33%. All of the structures were confirmed by single crystal X-ray diffraction.



Scheme 1. Synthesis of 1-amino-2,4-dinitro-imidazole (ADNI).

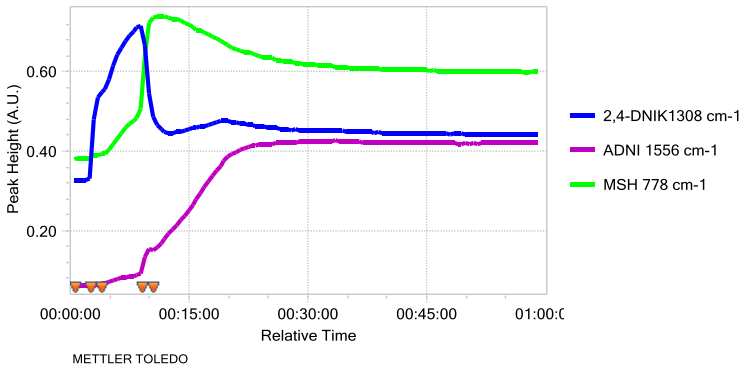


Figure 2. Reaction of 1-amino-2,4-dinitro-imidazole (ADNI) by on-line infrared analysis.

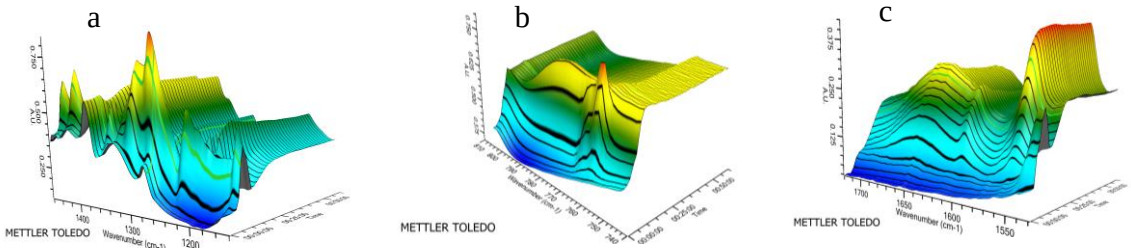


Figure 3. The real-time analysis of the concentration of 2,4-DNIK (a); MSH (b) and ADNI (c).

Single crystal X-ray structure analysis

Crystals of all the compounds for crystal-structure analysis were obtained by recrystalliz- ation from ethanol, whereas crystals of 2,4-DNI was obtained by recrystallization from acetonitrile. The structures of compounds 2,4-DNI, 2,4-DNI and ADNI are shown in Figure 1.

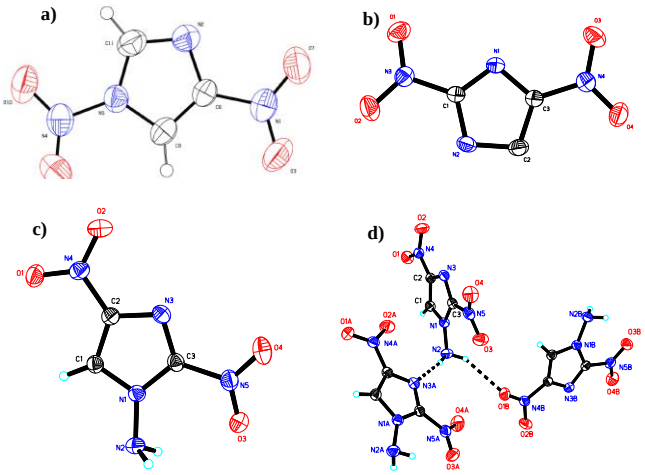


Figure 1. Thermal ellipsoid plot (50%) and labeling scheme for 1，4-DNI (a)， 2,4-DNI (b)，ADNI（c）, Crystal packing structure of ADNI (d).

High heats of formation is a peculiar advantage of nitrogen-rich heterocycles. Computation was performed by using the Gaussian 09 suite of programs to obtain the values of the heats of formation. Compound ADNI has a positive heat of formation of 200.8 kJ mol^{-1}, whereas its greater than the currently used explosives TNT (-67.0 kJ mol^{-1}) and RDX (80 kJ mol^{-1}). (Table 1). The thermal stabilities of all compounds were determined by differential scanning calorimetric (DSC) measurements. As shown in Figure 4. These nitroimidazole-based energetic materials decompose between 171 ^{o}C and 272 ^{o}C. which are comparable to RDX (205 ^{o}C). However, 5S

shotpoint up to 312℃ are better than a RDX (230 ^{o}C).

Table 1. Physicochemical properties of energetic compounds

Com.	ρ ($g.cm^{-3}$)	m.p. (℃)	v_D ($m.s^{-1}$)	P(GPa)	IS(%)	FS(%)	5S shotpoint (℃)
RDX	1.82	205	8700	34.8	80	76	230
HMX	1.91	285	9010	39.6	100	100	327
2,4-DNI	1.781	171~173	8130	28.1	0	14	322
ADNI	1.774	271~272	8174	29.3	0	0	312

In addition to thermal stabilities, impact and friction sensitivity measurements were according to the GJB772A-97 method 601.1 and 602.1 with approximately 50 mg (5.0 kg drop hammer） and 30 mg samples (1.5 kg pendulum hammer, pendulum angle of 90 degrees) tester, respectively. The ADNI shows both impact and friction insensitive characteristics with an impact sensitivity (IS) and a friction sensitivity (FS) both of 0%.

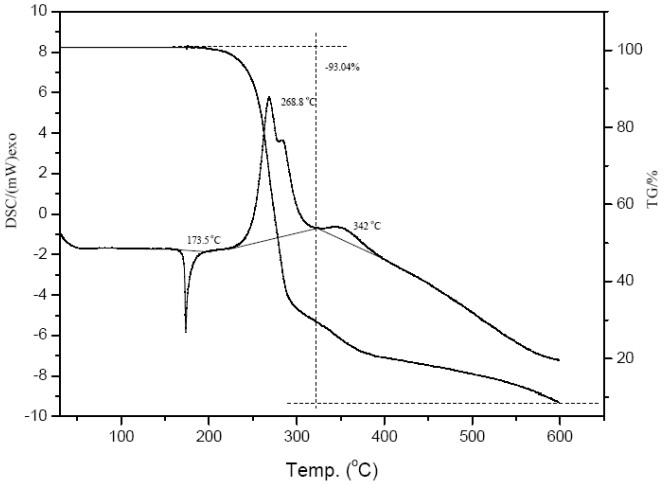


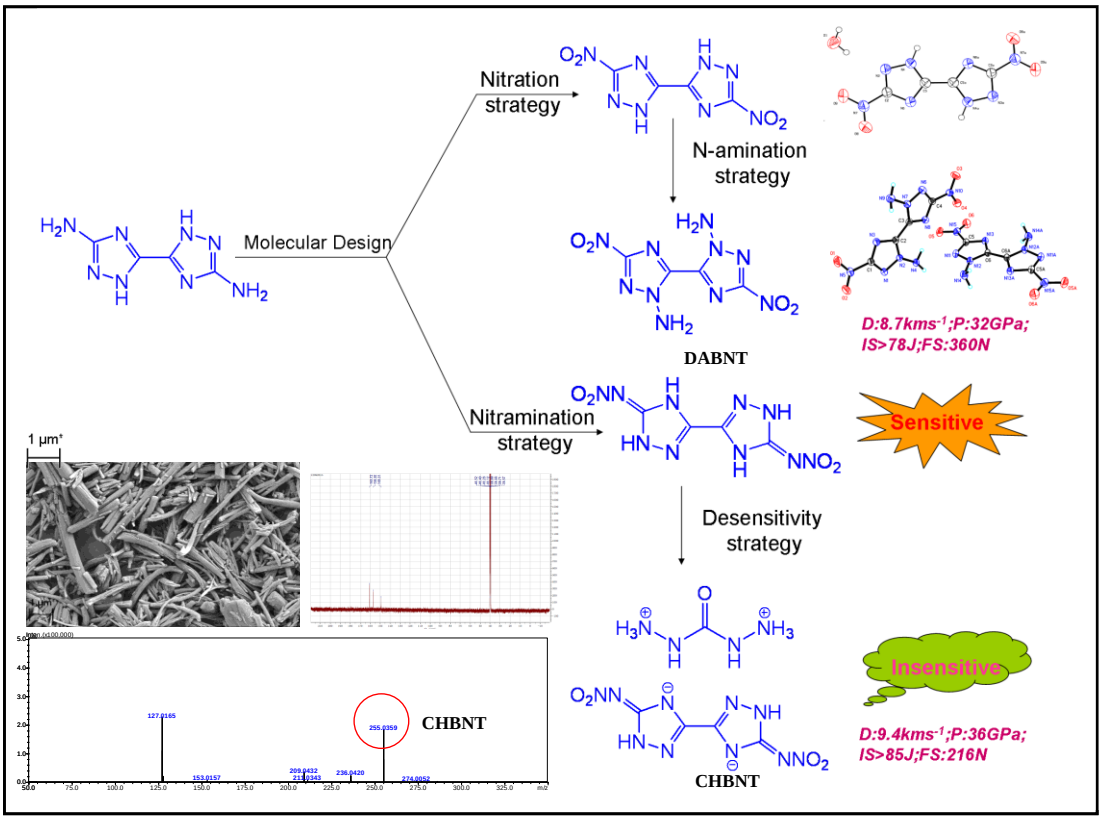
Figure 4. TG and DSC spectra of ADNI

A new type of on-line infrared analysis system has been developed for real-time analysis of each component in N-amino functionalization reaction instantly. And The synthesis of N-animo dinitroimidazole (ADNI) was optimized at hectogram level with total yield increase from 40% to 57.9%. Properties of these N-functionalized imidazole-based compounds show good performance. All compounds were characterized by using single crystal X-ray diffraction. The experimental measurements and theoretical calculations confirm that ADNI shows remarkable inter- and intramolecular interactions that contribute to closer packing and thus higher

density. Our results suggest that designing energetic compounds with π-stacking and hydrogen-bonding interactions may provide a powerful means for the development of next-generation explosives, pyrotechnics and propellants.

Rencent teamwork

Synthesis and scale of polynitroazole energetic compounds with low sensitivity and good detonation performance



A series of polynitro-triazole energetic compounds (PTECs) were synthesized and characterized through different synthesis strategies, including nitration, nitramination and N-amination. The new compounds have been subjected to small-scale safety testing and their responses to impact, friction and electrostatic discharge have been measured. Syntheses up to multi-gram have been carried out and material detonation properties have been predicted relative to RDX and HMX. Most of synthesized azole-ECs such as carbonic dihydrazidinium bis[3-(5-nitroimino-1,2,4-triazolate)](CHBNT), diamino-bis-1,2,-triazole (DABNT) have good thermal stabilities, low sensitivities and comparatively high detonation performance.

Synthesis and Application of Explosives Team (SAET)