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Multipurpose Energetic Materials by Shuffling Nitro Groups on a 3,3’-Bipyrazole Moiety[**]

Dheeraj Kumar[+], Yongxing Tang[+], Chunlin He, Gregory H. Imler, Damon A. Parrish and Jean’ne M. Shreeve*

Dedication ((optional))

Abstract: A family of 3,3’-bipyrazole-based energetic compounds having C-NO_2/N-NO_2 functionalities was synthesized by using various nitrating conditions. These nitro derivatives of bipyrazole are significantly more dense and energetic compared to the corresponding nitropyrazole analogues while maintaining the desired thermal stability and sensitivity. Depending on the number and nature of energetic nitro groups (C-NO_2/N-NO_2), different classes of energetic materials, such as green primary explosives, high-performance secondary explosives and heat-resistant explosives, were obtained. All the compounds were thoroughly characterized by IR, NMR [^{1}H, ^{13}C{^{1}H}, ^{15}N], elemental analysis, and differential scanning calorimetry (DSC). Four were also structurally characterized with single-crystal X-ray diffraction studies. Heats of formation and detonation performance were calculated using Gaussian 03 and EXPLO5 v6.01 programs, respectively.

In recent years, research on green high energy density materials (HEDMs) has aroused considerable attention because of increased environmental concerns.[1-3] Depending on their susceptibility to initiation, explosives are classified as secondary [RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) is the most commonly used secondary explosive], and primary explosives [lead azide (LA) is the most widely used primary explosive].[1] There are several issues with these commonly used materials. RDX is sensitive to external stimuli and toxic because of the presence of the nitramine moieties, and lead-based primary explosives pose serious threats to the environment as well as personal safety.[4] A subclass of secondary explosives called “heat resistant explosives,” with very high decomposition temperatures (T_d > 300 °C), are used for space exploration and drilling deep oil-wells. Hexanitrostilbene (HNS) is the best example of a heat resistant explosive and has been extensively used in space applications.[5] Advanced heat resistant explosives should be more powerful, less sensitive and thermally stable compared to HNS.

One of the best approaches for the design of green HEDMs is the incorporation of both fuel (nitrogen-rich rings) and oxidizer (oxygen-rich energetic groups) moieties into the same structure, so that clean and faster combustion can take place as a result of the intramolecular reaction.[6] During recent years, azoles, particularly nitro-azole derivatives have become very popular because of their high density, high positive heats of formation and good thermal stability.[7] There are few reports of multipurpose energetic materials based on bispyrazolylmethanes[8] and fused pyrazolo[4,3-*c*]pyrazole.[9] These bispyrazole-based skeletons, depending on the nature of the energetic groups (NO_2, N_3, N_2^+, ONO_2, $NHNO_2$, NH_2, etc.) are transformed into energetic materials belonging to different classes of HEDMs. Recently, we reported energetic compounds based on the 4,4′,5,5′- tetranitro-2*H*,2′*H*-3,3′-bipyrazole (TNBP) moiety.[10] However, no details related to the energetic properties of nitro derivatives of bipyrazole have been published. In contrast, the imidazole analogue of TNBP, 4,4′,5,5′- tetranitro-2,2′-bisimidazole (TNBI) is very well known and because of its good energetic performance along with excellent thermal stability and relatively insensitivity to stimuli, it was initially suggested as a potential replacement for RDX.[11]

Now, the detailed synthesis of bipyrazole and its nitro derivatives using a variety of nitrating conditions is described. Calculation and experimental studies show that as a function of the number and nature (C-NO_2/N-NO_2) of energetic nitro groups, different classes of energetic materials, *viz.*, green primary, high-performance secondary and heat-resistant explosives, can be synthesized. Interestingly these nitro derivatives of bipyrazole are found to be significantly more dense compared to their pyrazole analogues and hence exhibit better detonation properties compared to the corresponding nitropyrazole derivatives (Figure 1).[12]

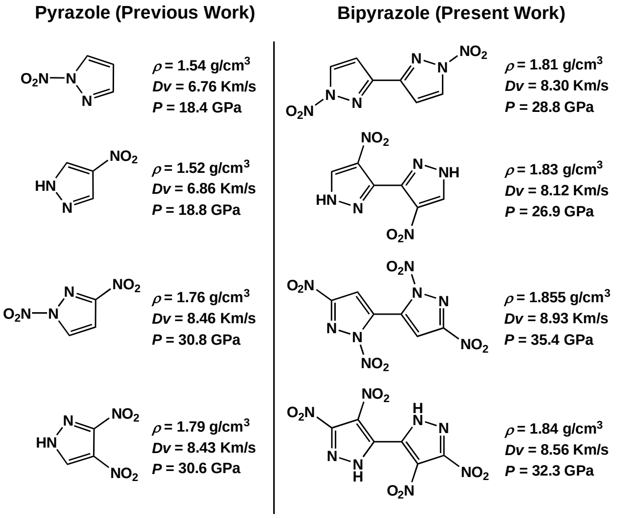

Figure 1. Comparison between the density and detonation properties of nitro derivatives of pyrazole and those of bipyrazole.[12]

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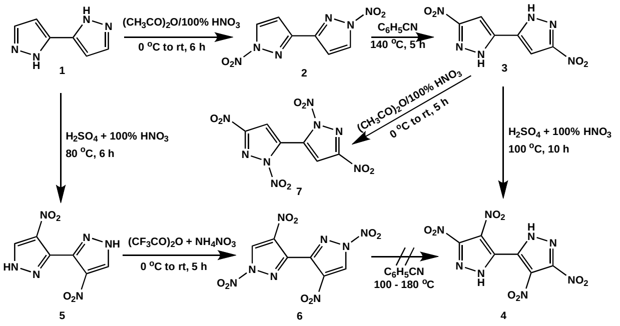

Scheme 1. Synthesis of compounds **2**–**7**.

The starting material 2*H*,2'*H*-3,3'-bipyrazole (**1**) was synthesized in two steps in 68% overall yield using a modified literature procedure.[13] Di-*N*-Nitro derivative **2** was obtained using a mixture of acetic anhydride and 100% nitric acid. The thermal rearrangement of **2** to **3** was carried out in benzonitrile at 140 °C. Finally, nitration of **3** with mixed acid (H_2SO_4 + 100% HNO_3) at 100 °C resulted in 4,4′,5,5′- tetranitro-2*H*,2′*H*-3,3′-bipyrazole (TNBP) (**4**) as a white solid.[14] In order to look for an alternate route to **4**, **1** was first nitrated with mixed acid (H_2SO_4 + 100% HNO_3) at 100 °C to give **5** (structural isomer of **3**) and further converted to 1,1',4,4'-tetranitro-1*H*,1'*H*-3,3'-bipyrazole (**6**) using trifluoroacetic anhydride and ammonium nitrate at 0 °C. Unfortunately, all efforts to convert **6** to **4** by heating **6** in benzonitrile at various temperatures (100–180 °C) always resulted in complicated reaction mixtures. The structural isomer of **6**, 2,2',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole (**7**) was synthesized from reaction of **3** with acetic anhydride and 100% nitric acid (Scheme 1).

All the compounds synthesized in this work were fully characterized by NMR [^{1}H, ^{13}C{^{1}H}, and ^{15}N], and FTIR spectral and elemental analyses. In the ^{1}H NMR spectra of **1**–**7**, signals corresponding to the bipyrazole C*H* protons were found to be in the range of 6.55 – 10.33 ppm, with the C*H* protons of di-*C*-NO_2 compound **5** (8.96 ppm) being more downfield compared to its structural isomer **3** (7.48 ppm). Similarly, C*H* protons of di-C-NO_2-di-N-NO_2 compound **6** (10.33 ppm) are more deshielded compared to its structural isomer **7** (7.77 ppm). In the ^{13}C{^{1}H} NMR of **1**–**7**, signals corresponding to bipyrazole carbons were found to be in the range of 99.9 – 156.6 ppm. The ^{15}N NMR spectrums were measured for **4** – **7** in DMSO and resonances were assigned based on GIAO NMR calculations (Figure 2). Signals corresponding to the C-*N*O_2 groups of bipyrazole were observed in the range of -15.85 to -28.9 ppm, whereas, signals for N-*N*O_2 were upfield shifted around -64.50 ppm. The resonances corresponding to bipyrazole ring nitrogen atoms were observed at -85.04 to -172.1 ppm. In compounds **6** and **7**, signals for ring nitrogen atoms attached to the nitro group were found to be more shielded (-110.6 to -116.6 ppm) compared to the other ring nitrogens (-85.04 to -87.7 ppm). TNBP (**4**) possess four well-resolved signals at -27.4, -28.9, -87.3 and -172.1 ppm.

Suitable crystals of **4** – **7** were obtained by slow evaporation of their saturated solutions in acetonitrile/water or methanol/water mixtures (Figure 3). Compounds **4** and **5** crystallize in the monoclinic space groups *P*2$_1$/c and C2/c, respectively, whereas **6** and **7** crystallize in the orthorhombic space groups *P*2$_1$2$_1$2 and *P*ccn, respectively. The asymmetric unit of **4** contains one molecule of water, and the asymmetric unit of **7** contains a one half molecule of **7** and one half molecule

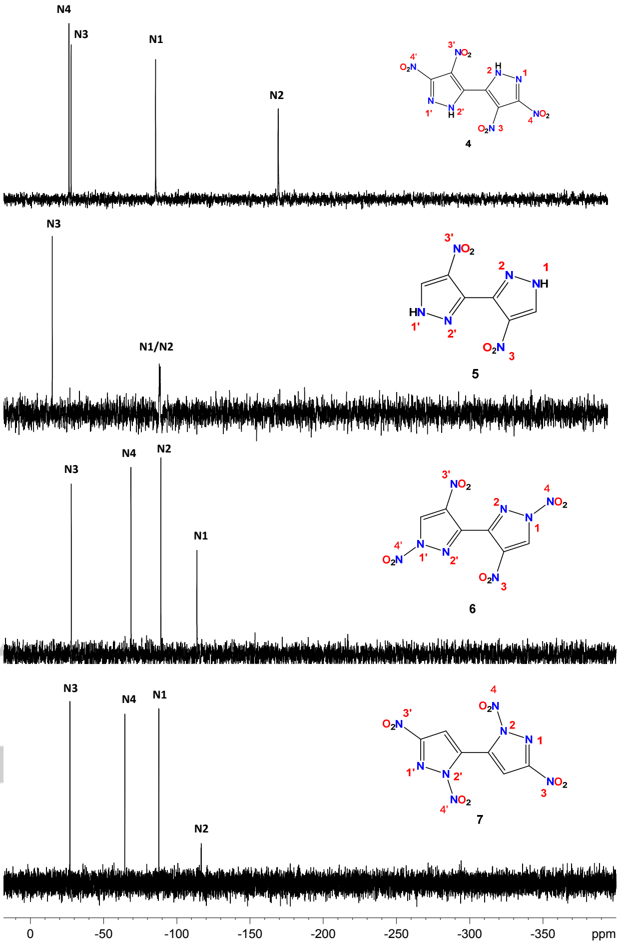

Figure 2. ^{15}N NMR spectra of **4** – **7**.

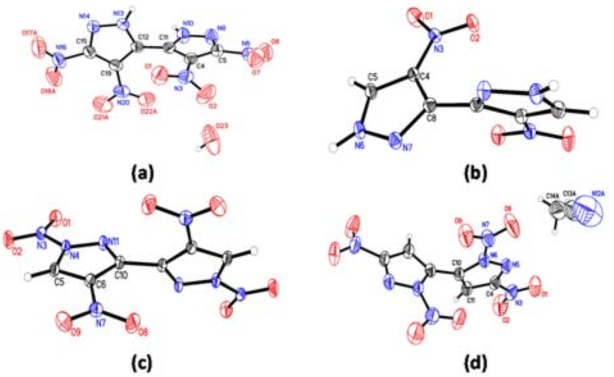

Figure 3. Single-crystal X-ray structures of (a) **4**.H_2O, (b) **5**, (c) **6** and (d) **7**.CH_3CN. [16]

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Table 1. Eneretic properties of **2**–**7**

	ρ[a] (g/cm^3)	Dv [b] (m/s)	P[c] (GPa)	ΔH_f[d] (kJ/mol)/(kJ/g)	T_m[e] (ºC)	T_{dec}[f] (ºC)	IS[g] (J)	FS[h] (N)	OB[i] (%)
2	1.81	8301	28.8	413.9/(1.85)	-	183	20	240	-28.6
3	1.81	8026	26.2	229.1/(1.02)	374	376	>40	>360	-28.6
4.H$_2$O	1.84	8556	32.3	42.7/(0.13)	209	243	30	360	+4.8
5	1.83	8120	26.9	221.0/(0.99)	305	365	>40	>360	-28.6
6	1.85	8869	34.5	407.1/(1.30)	-	206	2	40	+5.1
7	1.855	8926	35.4	444.1/(1.41)	-	152	2	60	+5.1
HNS	1.745	7629	24.5	78.0/(0.17)	-	320	5	>360	-17.77
RDX	1.80	8795	34.9	92.6/(0.42)	-	204	7.5	120	0
Pb(N$_3$)$_2$	4.80	5877	33.4	450.1/(1.54)	-	315	2.5-4	0.1-1	-11.0
TNBI	1.76	8070	28.5	265.2(0.84)	-	235	21	>240	-25.46

[a] Density measured - gas pycnometer at 25 °C; [b] Calculated detonation velocity; c] Calculated detonation pressure; [d] Heat of formation; [e] Melting point; [f] Temperature of decomposition (onset); [g] Impact sensitivity; [h] Friction sensitivity; [i] Oxygen balance (based on CO).

of acetonitrile, with acetonitrile solvate laying along a 2-fold rotation axis. All compounds exhibit high crystal densities [**4** (1.851 g/cm^3@293 K); **5** (1.860 g/cm^3@150 K); **6** (1.883 g/cm^3@150 K); **7** (1.647 g/cm^3@293 K)]. The relatively low crystal density for **7** results from the presence of acetonitrile solvent in its crystal structure. In **4** – **7**, the bridging C–C bond lengths are in the range of 1.466(3) to 1.473(1) Å. In **6**, both C-NO$_2$ [(1.435(2) Å] and N-NO$_2$ [(1.438(2) Å] bond lengths are nearly similar, whereas, in **7**, C-NO$_2$ [(1.452(2) Å] bond lengths are slightly longer than N-NO$_2$ [(1.434(2) Å]. In **4** – **7**, the dihedral angles between the two pyrazole rings are between 57.5(4) – 77.1(4)°. In **5**, the nitro groups are in the plane of the pyrazole rings [dihedral angle: 0.9(7) °], in **6** and **7**, they were slightly out of the plane of pyrazole rings [dihedral angle: 2.9(8) –8.3(7)°], whereas, in **4**, they were significantly out of the plane of the pyrazole rings [dihedral angle: 23.2(3) –25.6(2)°].

The physiochemical and energetic properties of **2**–**7** are given in Table 1. All the compounds, except **2** (T_d = 183 °C) and **7** (T_d = 152 °C) have higher decomposition temperatures than RDX (T_d = 204 °C) as determined with differential scanning calorimetry (DSC). Structural isomers **3** (T_d = 376; T_m = 374 °C) and **5** (T_d = 365; T_m = 305 °C) exhibit excellent thermal stability - significantly better than HNS (T_d = 320 °C). Primary explosive **6** (T_d = 206 °C) also shows very good thermal stability. Such high thermal stability is rare for metal free primary explosives. The experimental densities were measured using a gas pycnometer at 25 °C and the values range between 1.81 (**2** and **3**) and 1.855 (**7**) g/cm^3, better than RDX (1.80 g/cm^3) and HNS (1.745 g/cm^3). Compounds **4**.H$_2$O, **6** and **7** have positive oxygen balances whereas, **2**, **3** and **5** have negative oxygen balances. Values of impact and friction sensitivities were determined by using a BAM drophammer apparatus and BAM friction tester, respectively. Compounds **3** and **5** are found to be insensitive heat resistant explosives (*IS*: > 40 J, *FS*: > 360 N), compounds **2** (*IS*: 20 J, *FS*: 240 N) and **4**.H$_2$O (*IS*: 30 J, *FS*: 360 N) are less sensitive secondary explosives, whereas compounds **6** (*IS*: 2 J, *FS*: 40 N) and **7** (*IS*: 2 J, *FS*: 60 N) are highly sensitive primary explosives.

All the compounds have high positive heats of formation (ΔH_f) as calculated using the Gaussian 03 (Revision D.01) suite of programs. Except for 4.H$_2$O (ΔH_f = 42.7 kJ/mol), all other compounds have better ΔH_f values > RDX (+92.6 kJ/mol) and HNS (+78.0 kJ/mol). Using these values of heats of formation and experimental density, detonation parameters were obtained by using EXPLO5 (version 6.01).[15] The detonation pressures (*P*) range between 26.2 and 35.4 Gpa and the detonation velocities (*Dv*) between 8026 and 8926 m/s. Heat resistant explosives, 3 (*P*: 26.2 GPa, *Dv*: 8026 m/s) and 5 (*P*: 26.9 GPa, *Dv*: 8120 m/s) exhibit better detonation properties than HNS (*P*: 24.5 GPa, *Dv*: 7629 m/s), whereas, primary explosives 6 (*P*: 34.5 GPa, *Dv*: 8869 m/s) and 7 (*P*: 35.4 GPa, *Dv*: 8926 m/s) exceed LA (*P*: 33.4 GPa, *Dv*: 5877 m/s). Secondary explosive, 4.H$_2$O (*P*: 32.3 GPa, *Dv*: 8556 m/s) was also found to have energetic properties comparable to RDX and much better thermal stability (T_d = 243 °C) and insensitivity (*IS*: 30 J, *FS*: 360 N).

In summary, we have synthesized various energetic materials based on the 3,3'-bipyrazole moiety. These nitro derivatives of bipyrazole are found to be significantly more dense and energetic compared to the corresponding nitropyrazole analogues (Figure 1) while maintaining the required thermal stability and sensitivity. Also, different classes of energetic materials are obtained depending on the number and nature of energetic nitro groups (C-NO$_2$/N-NO$_2$). Di-*C*-Nitro derivatives, **3** and **5** belong to a class of insensitive heat resistant explosives. with significantly better density (ρ >1.83 g/cm^3), detonation properties (*P*: >26.2 GPa, *Dv*: >8026 m/s), thermal stabilities (T_d > 365 °C) and sensitivity (*IS*: > 40 J, *FS*: > 360 N) values compared to the well-known heat resistant explosive HNS. The tetra-*C*-nitro derivative (**4**.H_2O) belongs to the class of secondary explosives and has energetic properties approaching RDX, while having much better thermal stability and being less sensitive towards impact and friction. Di-*C*-di-*N*-nitro derivatives, **6** and **7** belong to the class of highly energetic metal free primary explosives. Particularly, **6** with very good thermal stability (T_d = 206 °C), which is very rare for metal free primary explosives, has an oxygen balance (*OB*: +5.1%) and energetic properties (*P*: 34.5 GPa, *Dv*: 8869 m/s) even better than $Pb(N_3)_2$. Also, **6** is relatively less sensitive to friction (*FS*: 40 N) compared to $Pb(N_3)_2$ (*FS*: 0.1-1 N), which is desired for safer transport. These new energetic compounds not only belong to different classes of explosives but also show improved properties relative to those of the corresponding representatives of each class (RDX, HNS, LA). The inexpensive and ready syntheses of these materials make them suitable for various military and civilian applications.

Acknowledgements

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Keywords: Pyrazole • nitroazoles • primary explosives • heat-resistant explosive • detonation • energetic material

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[16] CCDC 1852952 (**4**), 1852953 (**5**), 1852954 (**6**), and 1852956 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Entry for the Table of Contents

COMMUNICATION

Multipurpose Energetic Materials:

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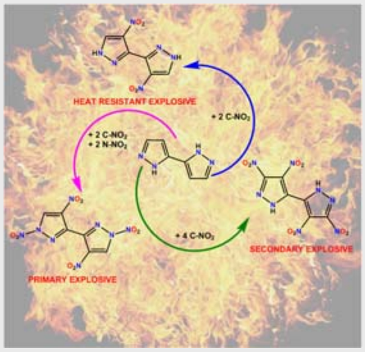

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