Energetic Materials

Deutsche Ausgabe: DOI: 10.1002/ange.201606894
Internationale Ausgabe: DOI: 10.1002/anie.201606894

3,6-Dinitropyrazolo[4,3-*c*]pyrazole-Based Multipurpose Energetic Materials through Versatile N-Functionalization Strategies

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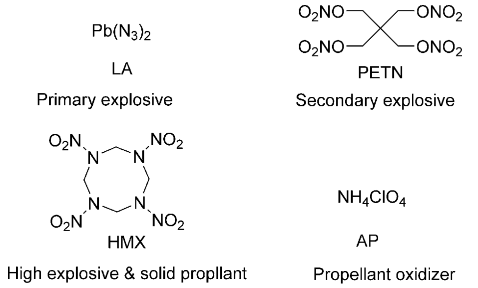
Abstract: *A family of 3,6-dinitropyrazolo[4,3-c]pyrazole-based energetic compounds was synthesized by using versatile N-functionalization strategies. Subsequently, nine ionic derivatives of the N,N′-(3,6-dinitropyrazolo[4,3-c]pyrazole-1,4-diyl)dinitramidate anion were prepared by acid-base reactions and fully characterized by infrared, multinuclear NMR spectra, and elemental analysis. The structures of four of these compounds were further confirmed by single-crystal X-ray diffraction. Based on their different physical and detonation properties, these compounds exhibit promising potential as modern energetic materials and can be variously classified as green primary explosives, high-performance secondary explosives, fuel-rich propellants, and propellant oxidizers.*

Energetic materials, which are typically small-molecule organic compounds, are required to store and rapidly release a large amount of chemical energy on demand.[1] Traditional energetic materials, such as gunpowder, dynamite, and 2,4,6-trinitrotoluene (TNT), represent a series of the most influential chemicals in human history and continue to have impact today.[2] However, although gunpowder is still effective for ammunition, it is certainly no longer the most explosive force available to armies or aerospace agencies. Modern explosives and propellants must be highly dense, thermally stable, environmentally friendly, and nitrogen- and oxygen-rich.[3] In addition, for the typical subclasses of energetic materials, such as primary explosives, secondary explosives, fuel-rich solid propellants, and propellant oxidizers, versatile application purposes require a variety of energetic functionalized groups, for example, azido, nitramino, nitrooxy, and perchlorate, in the molecular design (Scheme 1).[4] For example, the primary explosive lead azide (LA) is sufficiently sensitive to trigger the entire detonation process, while the secondary explosive pentaerythritol tetranitrate (PETN) is more powerful but less sensitive. With its high-energy content and high specific impulse, cyclo-1,3,5,7-tetramethylenene-2,4,6,8-tetranitramine (HMX) can be utilized for both high explosives and rocket propellants,[5] whereas the oxidizer ammonium perchlorate (AP) shows excellent performance as an oxygen carrier.[6]



Scheme 1. Classic energetic materials with different energetic groups and applications.

Fused-heterocycle ring frameworks that contains a π-conjugated system with an attached explosophore nitro group are of particular interest in the development of new energetic materials.[7] Currently, the most accessible method for the structural modification of fused heterocyclic rings is the formation of energetic salts through the NH-acidic moiety.[8,9] Although the formation of energetic salts based on fused-heterocyclic rings tends to enhance impact and friction stability, their density and detonation properties are basically not competitive with the parent frameworks.[8,9] Furthermore, some formula-related properties for the resulting energetic salts, such as oxygen balance and nitrogen content, will be strictly limited by the parent fused rings.

In a continuing search for high-energy-density materials, our current interest is focused on the structural modification of the well-known energetic fused-ring 3,6-dinitropyrazolo-[4,3-*c*]-pyrazole (DNPP) (**1**).[9,10] In this work, compound **1,** synthesized according to the reported method,[9] was treated with formaldehyde and dilute sulfuric acid to obtain the *N,N′*-dihydromethyl intermediate **2** (Scheme 2). Nitration of **2** was carried out by using fuming nitric acid and acetic anhydride. In the presence of ammonium nitrate and trifluoroacetic anhydride, N-nitration of **1** gave 1,3,4,6- tetranitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (**4**). A modified procedure using 1,8-diazabicycloundec-7-ene (DBU) and *O*-tosylhydroxylamine ($TsONH_2$) was carried out in organic solvents and gave **5** in good yield. In an initial attempt to prepare the dinitramino compound **6**, fuming nitric acid and trifluoro-

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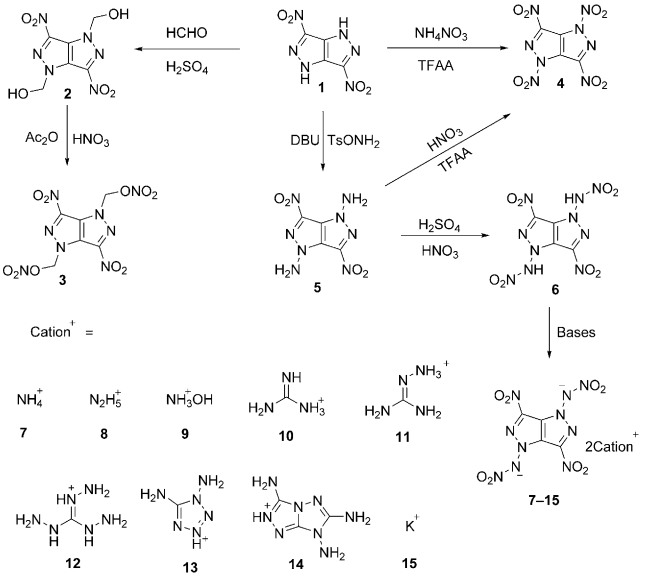
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201606894.



Scheme 2. Synthesis of N-functionalized 3,6-dinitropyrazolo[4,3-*c*]pyrazoles and their energetic salts. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, Ts = 4-toluenesulfonyl, TFAA = trifluoroacetic anhydride.

acetic anhydride were used as the nitration medium but only gave the unexpected product **4**. A possible mechanism includes cleavage of the N−NH_2 bond, resulting in the transformation of **5** into **1.** This, followed by an N-nitration reaction gave rise to the tetranitro product **4**. However, an alternate nitration route employing concentrated sulfuric acid and fuming nitric acid gave the *N*,*N*-dinitramino compound **6** in good yield. By treating **6** with different bases, a series of energetic derivatives (**7**–**15**) were prepared. In this work, all of the newly prepared compounds were fully characterized. The structures of compounds **6**, **7**, **9**, and **15** were further confirmed by single-crystal X-ray diffraction (Figure 1).

Crystals of **6**·H2O and **7** were grown from a mixture of chloroform and methanol, **9**·2MeOH was grown from methanol, and **15** was grown from water. Their crystal structures are shown in Figure 1. Energetic compound **6**, which crystallizes in the monoclinic space group with I2/a symmetry, contains one lattice water molecule, and consists of four molecules per unit cell. The structure of **7** crystalizes in the monoclinic space group with $P2_1/c$ symmetry, and has two units in the unit cell ($Z = 2$). The crystal density of **7** is 1.854 g cm^{-3} at 150 K. The unit cell of **9**·2 MeOH crystallizes in the monoclinic $P2_1/c$ space group, with two molecules and four MeOH molecules per unit cell. The unit cell of **15** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 2$), with a calculated density of 2.154 g cm^{-3} at 150 K. Based on the crystal structures, the central fused-pyrazole ring, two C−NO_2 groups, and two pyrazole N-functionalization N(H) moieties of **6**·H_2O, **7**, **9**·2 MeOH, and **15** are nearly planar; however, both N−NO_2 groups are twisted out of the plane.

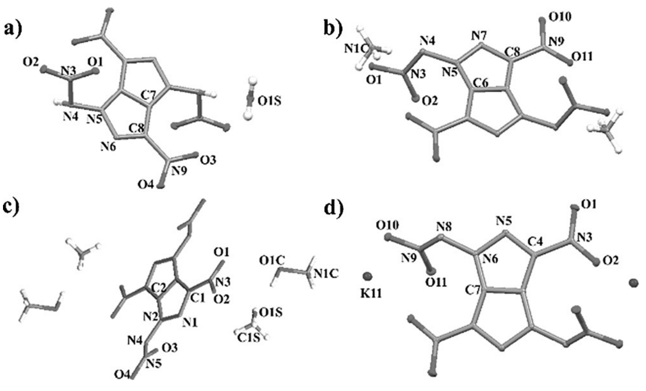


Figure 1. Single-crystal X-ray structures of a) **6**·H_2O, b) **7**, c) **9**·2 MeOH, and d) **15**.[14]

The heats of formation of **3**–**6** and energetic anions were obtained by using the isodesmic reaction approach by using the Gaussian 03 suite of programs.[11] The solid-phase heats of formation of energetic salts **7**–**15** were calculated on the basis of the Born–Haber energy cycle.[12] As shown in Table 1, all of the DNPP derivatives are endothermic with positive heats of formation. With a large number of N−N and N−O bonds, the heats of formation of **3**–**15** are higher than those of RDX and HMX, ranging from 0.38 to 3.25 kJ g^{-1}. The densities of **3**–**15** were measured with a gas pycnometer. With measured densities and calculated heats of formation in hand, the detonation performances of **3**–**15** were evaluated by using EXPLO5 v6.01.[13] The detonation velocities lie in the range 8295 to 9507 m s^{-1}, values superior to that of **1** (8250 m s^{-1}) and in some cases essentially comparable to HMX (9320 m s^{-1}). Similarly, **3**–**15** have favorable detonation pressures, falling between 26.9 and 41.8 GPa. Compounds **4** (40.4 GPa), **6** (41.8 GPa), and **9** (41.3 GPa) show remarkable values that are higher than that of HMX (39.5 GPa). Compounds, **3** (9.2 %), **4** (22.2 %), **6** (15.1 %), **9** (8.3 %), and **15** (16.2 %) show positive oxygen balances. Of **3**–**15**, neutral compounds **3**–**6** and energetic salts **7**–**9** and **12**–**15** are relatively sensitive to impact (IS ≤ 10 J); however, the other ionic derivatives **10** and **11** possess better stabilities, with impact sensitivities of 35 and 30 J, respectively. A similar trend is observed in friction-sensitivity tests, where **4**, **6**, **8**, **12**, **13**, and **15** are friction sensitive (FS ≤ 80 N), whereas **3**, **5**, **7**, **9** and **14** are less friction sensitive (FS = 120 N), and **10** and **11** are friction insensitive (FS = 360 N).

The N-nitro and N-nitramino functionalities enhance the density and oxygen balance greatly, which gives **4** (d, 1.95 g cm^{-3}; OB, 22.2 %) and **6** (d, 1.93 g cm^{-3}; OB, 15.1 %) promising application potential as high-density energetic oxidizers. With respect to ionic derivatives, the potassium salt **15** is highly sensitive to impact and friction but features better density and good thermal stability. These characteristics would enable **15** to be used as a potential green primary explosive.

In comparison to **15**, the other energetic salts **7**–**14** show better mechanical behavior and enhanced detonation properties, thereby highlighting their potential for application as high-performance secondary explosives. High values in terms of total nitrogen plus oxygen content and specific impulse were observed for **7**, **8**, **9**, and **13**, all of which outperform RDX and HMX, which suggests potential for use as high-performance solid rocket propellants.

In conclusion, 3,6-dinitropyrazolo[4,3-*c*]pyrazole-based energetic molecules (**3**–**6**) and nitrogen-rich ionic derivatives (**7**–**15**) were synthesized by using versatile N-functionalization strategies. Some representative 3,6-dinitropyrazolo[4,3-

Table 1: Physical and detonation properties of **3**–**15** and comparison with **1**, RDX, and HMX.

Compound	D[a] [g cm^{-3}]	T_d[b] [°C]	ΔH_f[c] [kJ mol^{-1}]/[kJ g^{-1}]	v_D[d] [m s^{-1}]	P[e] [GPa]	IS[f] [J]	FS[g] [N]	N[h] [%]	N + O[i] [%]	OB[j] [%]	I_{sp}[k] [s]
1	1.85	336	322.6/1.94	8250	27.4	15	160	42.4	74.7	−8	241
3	1.82	206	133.7/0.38	8674	33.1	10	120	32.2	78.2	9.2	245
4	1.95	145	550.9/1.92	9460	40.9	3	20	38.9	83.3	22.2	269
5	1.84	230	467.0/2.04	8864	33.9	7	120	49.1	77.2	−14.0	246
6	1.93	128	595.2/1.87	9507	41.8	2	20	44.0	84.3	15.1	274
7	1.81	181	423.1/1.20	8977	35.9	10	120	44.7	84.1	0	270
8	1.85	174	738.9/1.93	9399	39.5	5	60	51.3	84.8	−4.2	280
9	1.88	170	531.2/1.38	9495	41.3	7	120	43.8	85.4	8.3	282
10	1.68	190	454.7/1.04	8295	26.9	35	360	51.4	80.7	−14.7	239
11	1.71	153	692.9/1.49	8612	29.3	30	360	54.1	81.5	−17.2	247
12	1.70	141	1144.8/2.17	8884	30.8	10	80	58.5	82.8	−21.3	258
13	1.78	163	1683.3/3.25	9166	36.0	5	60	59.5	84.2	−9.3	280
14	1.83	203	1599.5/2.56	8993	33.1	10	120	58.1	78.6	−23.0	244
15	2.11	208	152.9/0.43	8306	31.2	2	20	35.5	68.0	16.2	226
RDX	1.80	205	80.0/0.36	8748	34.9	7	120	37.8	81.1	0	258
HMX	1.91	280	104.8/0.36	9320	39.5	7	120	37.8	81.1	0	266

[a] Density measured by gas pycnometer (25 °C). [b] Decomposition temperature (onset). [c] Heat of formation. [d] Detonation velocity (calculated with Explo5 v6.01). [e] Detonation pressure (calculated with Explo5 v6.01). [f] Impact sensitivity. [g] Friction sensitivity. [h] Nitrogen content. [i] Nitrogen and oxygen content. [j] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, $1600(c\text{-}a\text{-}b/2)/MW$ (MW = molecular weight). [k] Specific impulse.

c]pyrazole-based derivatives, especially **4**, **6**, and **9**, exhibit high densities and excellent detonation velocities and pressures, which outperform the current secondary-explosive benchmark HMX. Compared with DNPP, **4** and **6** also possess higher oxygen balances and densities that highlight their application potential as high-density energetic oxidizers. The potassium salt **15** is very sensitive mechanically but exhibits excellent density and good thermal stability, which make **15** a competitive candidate as a green primary explosive. In addition, according to the high values of total nitrogen plus oxygen content and specific impulse, some ionic representatives (**7**, **8**, **9** and **13**) also exhibit good possibilities for application in bipropellants.

Acknowledgements

Financial support of the Office of Naval Research (N00014-16-1-2089), the Defense Threat Reduction Agency (HDTRA 1-15-1-0028), the CFD Research Corporation, and the M. J. Murdock Charitable Trust (No. 2014120:MNL:11/20/2014) for funds supporting the purchase of a 500 MHz NMR spectrometer is greatly acknowledged. J. Zhang (ID No.P15349) acknowledges the Japan Society for the Promotion of Science (JSPS) for a JSPS research fellowship.

Keywords: detonation · energetic materials · fused heterocycle · N-functionalization · nitramines

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 12895–12897
Angew. Chem. **2016**, *128*, 13087–13089

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[1] a) J. P. Agrawal, R. D. Hodgson, *Organic Chemistry of Explosives*, Wiley, New York, **2007**; b) H. Gao, J. M. Shreeve, *Chem. Rev.* **2011**, *111*, 7377–7436.
[2] a) A. Alexander, T. M. Klapötke, *J. Am. Chem. Soc.* **2013**, *135*, 9931–9938; b) T. Brinck, *Green Energetic Materials*, Wiley, Hoboken, **2014**.
[3] a) M. H. V. Huynh, M. D. Coburn, T. J. Meyer, M. Wetzler, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10322–10327; b) K. B. Landenberger, O. Bolton, A. J. Matzger, *Angew. Chem. Int. Ed.* **2013**, *52*, 6468–6471; *Angew. Chem.* **2013**, *125*, 6596–6599; c) S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang, S. Pang, *Angew. Chem. Int. Ed.* **2013**, *52*, 14031–14035; *Angew. Chem.* **2013**, *125*, 14281–14285.
[4] Q. Yan, M. Gozin, F. Zhao, S. Pang, *Nanoscale* **2016**, *8*, 4799–4851.
[5] a) D. Fischer, T. M. Klapötke, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172–8175; *Angew. Chem.* **2014**, *126*, 8311–8314; b) P. Yin, D. A. Parrish, J. M. Shreeve, *J. Am. Chem. Soc.* **2015**, *137*, 4778–4786.
[6] a) P. W. M. Jacobs, H. M. Whitehead, *Chem. Rev.* **1969**, *69*, 551–590; b) Q. J. Axthammer, B. Krumm, T. M. Klapötke, *J. Org. Chem.* **2015**, *80*, 6329–6335.
[7] a) M. C. Schulze, B. L. Scott, D. E. Chavez, *J. Mater. Chem. A* **2015**, *3*, 17963–17965; b) T. M. Klapötke, P. C. Schmid, S. Schnell, J. Stierstorfer, *Chem. Eur. J.* **2015**, *21*, 9219–9228; c) J. Zhang, P. Yin, L. A. Mitchell, D. A. Parrish, J. M. Shreeve, *J. Mater. Chem. A* **2016**, *4*, 7430–7436.
[8] a) J. Zhang, J. M. Shreeve, *Dalton Trans.* **2016**, *45*, 2363–2368; b) C. Bian, X. Dong, X. Zhang, Z. Zhou, M. Zhang, C. Li, *J. Mater. Chem. A* **2015**, *3*, 3594–3601.
[9] J. Zhang, D. A. Parrish, J. M. Shreeve, *Chem. Asian J.* **2014**, *9*, 2953–2960.
[10] P. Yin, Q. Zhang, J. M. Shreeve, *Acc. Chem. Res.* **2016**, *49*, 4–16.
[11] M. J. Frisch, et al., Gaussian03, Revision D.01, Gaussian, Inc, Wallingford, CT, **2004** (see the Supporting Information for the complete reference).
[12] H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364–2367.
[13] EXPLO5, version 6.01, M. Sućeska, **2013**.
[14] CCDC 1477653 (**6**·H_2O), 1477654 (**7**), 1477655 (**9**·2 MeOH), and 1477656 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: July 15, 2016
Published online: September 15, 2016