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Challenging the limits of nitrogen and oxygen content of fused rings †

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Heat of formation and density have a significant influence on the detonation performance of a compound and are greatly influenced by the nitrogen and oxygen content of a material. Here a family of new materials with high oxygen and nitrogen content was synthesized and characterized. Compound 1 has a nitrogen and oxygen content of 85.3%, with a high density (1.93 g cm^{-3}) and high detonation properties (detonation velocity $v_D = 9503$ m s^{-1}; detonation pressure $P = 41$ GPa). The ammonium salt 3 has a nitrogen and oxygen content of 84.9%, a density of 1.86 g cm^{-3}, a detonation velocity of 9317 m s^{-1}, and acceptable sensitivities (8 J, 120 N) which are similar to those of **HMX**. The potassium salt (**5**) was characterized by single-crystal X-ray diffraction.

The design of new high-energy density materials (HEDMs) has attracted great interest in the global military technology field. In general, energetic materials with high densities and heats of formation are of great value in achieving high detonation velocities and pressures. The density of energetic compounds is influenced by the oxygen content as well as by other parameters. High oxygen content polynitro compounds, such as 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (**HMX**) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (**CL-20**), are of particular interest in the design of HEDMs.[1–4] In addition to the nitro group, the development of energetic compounds also focuses on compounds that contain the nitramino[5] or *N*-oxide group,[6] or uses backbones that have oxygen-containing moieties such as furazan,[7] furoxan[8] or oxadiazole.[9] It has been demonstrated that the higher the oxygen concentration, the higher the density and the higher the detonation performance. In addition to oxygen, increasing the nitrogen content of a compound is another route to achieving HEDMs. High-nitrogen content compounds possess a large number of inherently energetic N–N (160 kJ mol^{-1}) and N=N (418 kJ mol^{-1}) bonds which give rise to high positive heats of formation, thereby leading to high energetic performance.[10] For this reason, the azido group is often utilized in the design of energetic materials.[11–13] Additionally, N=C and N=N bonds in molecules can lead to π–π stacking, another way to realize HEDMs.[14] From this viewpoint, the pursuit of new energetic compounds which can challenge the limits of the oxygen and nitrogen content of existing compounds has attracted great interest from researchers all over the world.

Fused cyclic energetic materials, containing a coplanar polycyclic structure and conjugated system, have become a hot topic in the pursuit of HEDMs with high detonation performance and low sensitivity. In recent years, a large variety of fused rings have been reported.[15–17] Most of them possess good balance between high detonation performance and low sensitivity. As shown in Fig. 1, fused rings with high oxygen and nitrogen content always have a high density and a high detonation velocity. Among these fused rings, 6-aminotetrazolo[1,5-*b*]-1,2,4,5-tetrazine-4,7-*N*-oxide[18] has the highest oxygen and nitrogen content of 84.7% while having only two carbon atoms. However, fewer carbons also mean fewer positions to introduce more energetic groups, which limits energetic properties. 6-

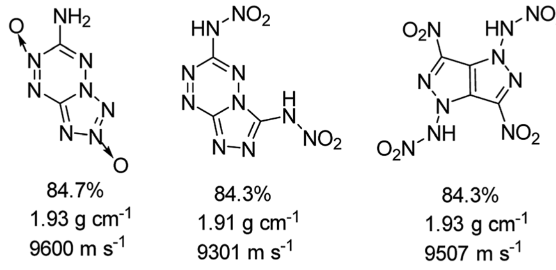

Fig. 1 Compounds with high nitrogen and oxygen content showing high detonation performance.

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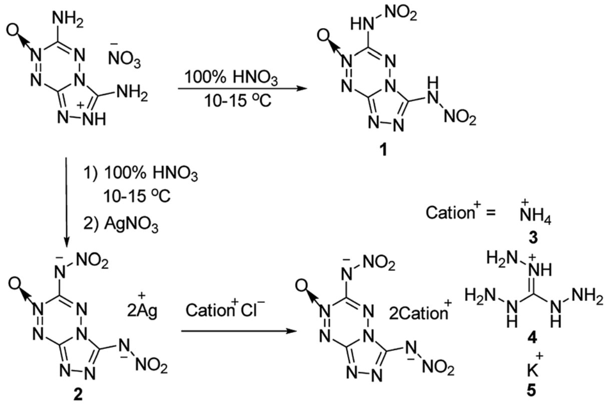
Dinitramino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine[19] and *N*,*N*′-(3,6-dinitropyrazolo[4,3-*c*]pyrazole-1,4-diyl)dinitramide[20] have slightly lower oxygen and nitrogen content (84.3%) since there are more carbons, which supply more positions for energetic groups. However, it is difficult to introduce energetic moieties at all of the functional positions. Therefore, more carbon atoms present in fused rings result in lower oxygen and nitrogen content.

Now with a triazolo-[1,2,4,5]tetrazine fused ring as the backbone, there are only three carbon atoms and three positions for introducing energetic groups. 3,6-Nitramino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine-7-*N*-oxide (**1**), which has the highest oxygen and nitrogen content (85.3%) among the fused ring compounds, was synthesized by nitrating 3,6-amino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine-7-*N*-oxide at ≥10 °C. The ammonium (**3**), triaminoguadinum (**4**) and potassium salts (**5**) were obtained by metathesis reactions of the silver salt (**2**) with respective bases in their hydrochloride form. Each of the new compounds was fully characterized by multinuclear NMR spectroscopy, infrared spectroscopy and elemental analysis. The potassium salt (**5**) was characterized using single crystal X-ray structural analysis.

The starting material was obtained by using a literature method.[21] Compound **1** was formed by nitrating the starting material with fuming nitric acid. While at lower temperatures, only one amino group was nitrated to a nitramino,[22] when the temperature was ≥10 °C, the pure dinitramino compound **1** was obtained (Scheme 1). At higher temperatures, **1** is not stable which results in low yield. Therefore, the temperature used was 10–15 °C. Compound **1** dissolves in water easily which precludes its extraction. Therefore, **1** was obtained as a precipitate by the addition of trifluoroacetic acid to the concentrated reaction mixture. Its silver salt (**2**) was precipitated by adding $AgNO_3$ directly to the diluted nitration reaction mixture. The salts (**3, 4** and **5**) were obtained by metathesis reactions of **2** with respective bases as their hydrochlorides.

All the compounds were fully characterized by using ^1H and ^{13}C NMR and IR spectra and elemental analysis. The crystal structure of **5** was characterized by single-crystal X-ray diffraction. The crystal was obtained from water at room temperature.



Scheme 1 Synthesis of compounds **1–5**.

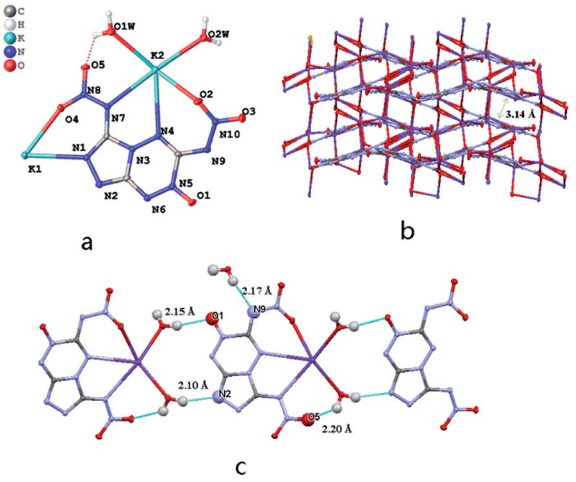


Fig. 2 (a) Single-crystal X-ray structures of **5**; (b) cross stacking in **5**; (c) hydrogen bonds in **5**.

Compound $\mathbf{5}\cdot 2H_2O$ crystallizes in the monoclinic space group with $P2_1/n$ ($Z = 4$) symmetry and a calculated crystal density of 2.043 g cm^{-3} at 100 K. The single-crystal X-ray structure and data are shown in Fig. 2a and Table S1,† respectively. The asymmetric unit of **5** contains four energetic cations , 8 potassium ions and 8 water molecules. The nitramino group on the triazole ring is nearly planar with a fused ring in which the dihedral angle is observed to be 4.162°. However, the dihedral angle between the nitramino group on tetrazine (adjacent to the *N*-oxide group) and the fused ring is 20.26° indicating that it is twisted out of the plane. In the anion, four hydrogen bonds (HBs) are formed with four different water molecules having bond lengths between 2.10 and 2.21 Å. Each hydrogen atom in a water molecule forms an HB with one anion (Fig. 2c). The distance between the two layers is 3.14 Å resulting in cross stacking (Fig. 2b). In the framework of **5** (Fig. 3a), each deprotonated energetic ligand is bonded to six adjacent potassium

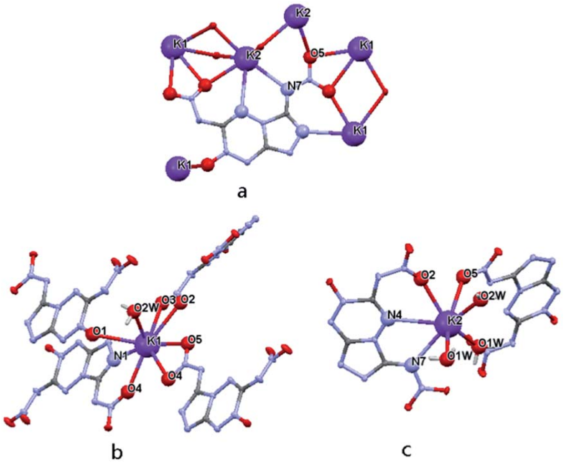


Fig. 3 (a) Deprotonated energetic ligand coordinated with potassium; (b) the coordination of potassium one (K1); (c) the coordination of potassium two (K2).

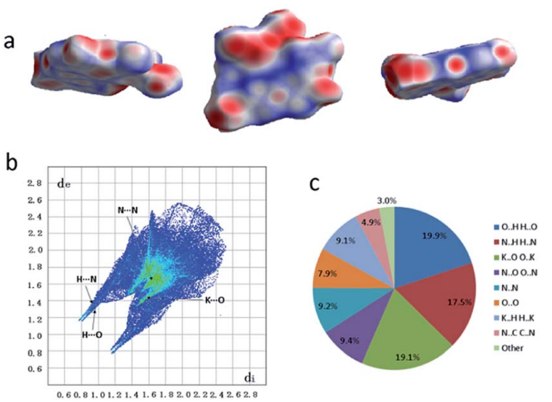


Fig. 4 (a) Hirshfeld surfaces for **5**; (b) 2D fingerprint plot in crystal stacking for **5**; (c) pie graph giving the percentage contributions of the individual atomic contacts for **5**.

ions *via* K–O and K–N bonds. The bond lengths of K–O and K–N are in the range of 2.71–3.08 Å and 2.85–3.52 Å, respectively. There are two types of potassium ions, one is coordinated with six oxygen atoms and one nitrogen atom from four energetic ligands and one oxygen atom from water (Fig. 3b); another is coordinated with two oxygen atoms and two nitrogen atoms from two energetic ligands and three oxygen atoms from water (Fig. 3c). Thus, an infinitely expanded three-dimensional (3D) structure is formed.

For further insight into the intermolecular interactions, the Hirshfeld surface of **5** and the 2D fingerprint spectra were analyzed as shown in Fig. 4a. The surface appears almost as a plate because of the fused ring backbone structures. The red and blue dots in the Hirshfeld surface analysis represent high and low close contact, respectively. The red spots on the side faces of the plate denote the close interactions of K···O, K···N and HBs which mainly come from water and potassium. The blue portion in the front faces of the plate denotes N···N and N···C, suggesting a fused structure. As can be seen in the two-dimensional fingerprint plot in Fig. 4b, because of two water molecules, the remarkable spikes on the bottom which demonstrate strong O···H and N···H HB interactions, contribute 37.4% of the total weak interactions. There is 14.1% of N···N and N···C interactions, which indicate π–π stacking from the fused ring. Because of the high content of oxygen, there is a high percentage of interactions between oxygen and other elements. As given in Fig. 4c, there are 19.1% K···O, 9.4% N–O and 7.9% O···O interactions, which suggests an increase in sensitivity for the metal salt (**5**) compared to the energetic salts **3** and **4**.

The oxygen balance values describe the conversion of the carbon and hydrogen in a compound into carbon monoxide and water which also indicates the oxygen content of a compound. A high oxygen balance value usually suggests high density. In this study, the neutral compound (**1**) and the potassium salt (**5**) have positive oxygen balances of 6.2% and 9.6%. Because of a higher hydrogen content, the ammonium and triaminoguandinium salts have negative oxygen values. The densities of these compounds are closely related to the oxygen balance. The density and heats of formation (HOF) of the new energetic materials were measured by using a gas pycnometer and the Gaussian03 (Revision D.01) suite of programs, respectively.[17] As shown in Table 1, the potassium salt (**5**) has the highest density at 2.08 g cm^{-3}, but has the lowest heat of formation (HOF) of 227.0 kJ mol^{-1}. The neutral compound **1** has a density of 1.93 g cm^{-3} and a HOF of 593.0 kJ mol^{-1}. With the introduction of the ammonium cation (**3**), the density and HOF are lowered to 1.86 g cm^{-3} and 466.1 kJ mol^{-1}, respectively. The triaminoguandinium salt (**4**) has the lowest density of 1.69 g cm^{-3} and has the highest HOF of 1248.5 kJ mol^{-1} (2.68 kJ g^{-1}).

The detonation properties of all new energetic materials were calculated by using the EXPLO5 (v6.01) program.[27] As shown in Table 1, **1** has the highest detonation velocity of 9503 m s^{-1} and a detonation pressure of 41 GPa. The ammonium (**3**) and triaminoguandinium (**4**) salts follow with detonation velocities of 9317 m s^{-1} and 9050 m s^{-1}, respectively. The potassium salt (**5**) has the lowest detonation velocity of 7838 m s^{-1}.

The thermal stabilities of these new energetic materials were determined by differential scanning calorimetry. All compounds have a sharp exothermic peak which results from rapid decomposition. As shown in Table 1, the decomposition temperature (onset temperature) of **1** is 114 °C, which is similar to that of most dinitramino compounds.[28,29] The potassium salt (**5**) has the highest decomposition temperature at 180 °C. Compared to the neutral compound, the ammonium salt (**3**) has a higher thermal stability decomposing at 150 °C. The

Table 1 Physical and detonation properties of the new energetic materials

Compound	N + O[a] (%)	Ω[b]	T_{dec}[c] (°C)	d[d] (g cm^{-3})	$\Delta_f H$[e] (kJ mol^{-1}/kJ g^{-1})	v_D[f] (m s^{-1})	p[g] (GPa)	IS[h] (J)	FS[i] (N)
1	85.3	6.2	114	1.93	593.0/2.30	9503	41.0	1	5
3	84.9	−11.0	150	1.86	466.1/1.60	9317	36.8	8	120
4	83.6	−30.9	111	1.69	1248.5/2.68	9050	30.6	9	120
5	65.8	9.6	180	2.08	227.0/0.68	7838	27.3	8	80
HMX[j]	81.1	0.0	280[l]	1.90	84.0/0.29	9100	39.5[l]	7.5	120
CL-20[k]	82.2	11	220[m]	2.02–2.04	372.0/0.84	10 000	44.6[m]	2	80

[a] Nitrogen and oxygen content. [b] Oxygen balance for $C_aH_bO_cN_d$, 1600($c - a - b/2$)/MW (based on CO). [c] Thermal decomposition temperature (DSC, 5 °C min^{-1}). [d] Measured density of anhydrous compounds using a gas pycnometer (25 °C). [e] Calculated heat of formation. [f] Calculated detonation velocity. [g] Calculated detonation pressure. [h] Impact sensitivity. [i] Friction sensitivity. [j] Ref. 23. [k] Ref. 24. [l] Ref. 25. [m] Ref. 26.

triaminoguandinium salt (**4**) has the lowest thermal decomposition at 111 °C.

Standard BAM drop hammer and friction tester techniques were used to measure the impact (IS) and friction (FS) sensitivities.[30] As shown in Table 1, **1** is very sensitive to both impact and friction (1 J, 5 N). However, its salts possess acceptable sensitivities, with impact sensitivities between 8 J and 9 J and friction sensitivities between 80 N and 120 N. The ammonium (8 J, 120 N) and triaminoguandinium salts (9 J, 120 N) have sensitivity values similar to those of **HMX**, and are less sensitive than **CL-20**. The potassium salt (**5**) has a little higher friction sensitivity of 80 N.

In conclusion, a series of new energetic materials based on fused 1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine rings was synthesized and characterized by IR and NMR spectroscopy and elemental analysis. Compound **5** was characterized by single crystal X-ray structure analysis. A fused ring that contains two nitramino and one *N*-oxide moieties is reported for the first time. This gives rise to **1** which has the highest oxygen and nitrogen content (85.3%) of all reported fused ring compounds. Compound **1** has a high density of 1.93 g cm^{-3} and excellent detonation properties (detonation velocity $\nu_D = 9503$ m s^{-1}; detonation pressure $P = 41$ GPa). Unfortunately, practical applications are limited by its low decomposition temperature and high impact and friction sensitivities. The ammonium salt **3** has an acceptable density of 1.86 g cm^{-3}, with a detonation velocity of 9317 m s^{-1} and acceptable sensitivities (8 J, 120 N) similar to those of **HMX**, which makes it competitive as a green energetic material.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 Q. Yu, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Org. Lett.*, 2019, **21**, 4684–4688.

2 Y. Tang, W. Huang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Am. Chem. Soc.*, 2020, **142**, 7153–7160.

3 Y. Wang, Y. Liu, S. Song, Z. Yang, X. Qi, K. Wang, Y. Liu, Q. Zhang and Y. Tian, *Nat. Commun.*, 2018, **9**, 2444.

4 P. Yin, J. Zhang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2017, **56**, 8834–8838.

5 W. Zhang, J. Zhang, M. Deng, X. Qi, F. Nie and Q. Zhang, *Nat. Commun.*, 2017, **8**, 181.

6 Y. Liu, G. Zhao, Q. Yu, Y. Tang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Org. Chem.*, 2019, **84**, 16019–16026.

7 J. Ma, J. Tang, H. Yang, Z. Yi, G. Wu, S. Zhu, W. Zhang, Y. Li and G. Cheng, *ACS Appl. Mater. Interfaces*, 2019, **11**, 26053–26059.

8 C. He, Y. Tang, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2016, **4**, 8969–8973.

9 Y. Tang, C. He, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2015, **3**, 23143–23148.

10 Q. Zhang and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2013, **52**, 8792–8794.

11 Y. Liu, G. Zhao, Y. Tang, J. Zhang, L. Hu, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2019, **7**, 7875–7884.

12 G. Zhao, D. Kumar, L. Hu and J. M. Shreeve, *ACS Appl. Energy Mater.*, 2019, **2**, 6919–6923.

13 J. Ma, G. Cheng, X. Ju, Z. Yi, S. Zhu, Z. Zhang and H. Yang, *Dalton Trans.*, 2018, **47**, 14483–14490.

14 C. Zhang, F. Jiao and H. Li, *Cryst. Growth Des.*, 2018, **18**, 5713–5726.

15 Y. Tang, C. He, G. H. Imler, D. A. Parrish and J. M. Shreeve, *ACS Appl. Energy Mater.*, 2019, **2**, 2263–2267.

16 W. Huang, Y. Tang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Am. Chem. Soc.*, 2020, **142**, 3652–3657.

17 H. Gao, Q. Zhang and J. M. Shreeve, *J. Mater. Chem. A*, 2020, **8**, 4193–4216.

18 D. E. Chavez, D. A. Parrish, L. Mitchell and G. H. Imler, *Angew. Chem., Int. Ed.*, 2017, **56**, 3575–3578.

19 L. Hu, P. Yin, G. Zhao, C. He, G. H. Imler, D. A. Parrish, H. Gao and J. M. Shreeve, *J. Am. Chem. Soc.*, 2018, **140**, 15001–15007.

20 P. Yin, J. Zhang, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2016, **55**, 12895–12897.

21 L. Hu, P. Yin, G. H. Imler, D. A. Parrish, H. Gao and J. M. Shreeve, *Chem. Commun.*, 2019, **55**, 8979–8982.

22 L. Hu, C. He, G. Zhao, G. H. Imler, D. A. Parrish and J. M. Shreeve, *ACS Appl. Energy Mater.*, 2020, **3**, 5510–5516.

23 http://www.eurenco.com/wpcontent/uploads/2013/07/HMX.pdf.

24 http://www.eurenco.com/wpcontent/uploads/2013/07/CL20.pdf.

25 P. Yin, D. A. Parrish and J. M. Shreeve, *J. Am. Chem. Soc.*, 2015, **137**(14), 4778–4786.

26 J. Zhang and J. M. Shreeve, *J. Am. Chem. Soc.*, 2014, **136**, 4437–4445.

27 M. Suceska, *EXPLO5, v6.01*, Brodarski Institute, Zagreb, Croatia, 2013.

28 Y. Tang, J. Zhang, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *J. Am. Chem. Soc.*, 2015, **137**, 15984–15987.

29 P. Yin and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2015, **54**, 14513–14517.

30 G. Tao, Y. Guo, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem.*, 2010, **20**, 2999–3005.