

# Synthesis and Properties [1,2,4]Triazolo[4,3-b][1,2,4,5]-Tetrazine *N*-Oxide Explosives

Guilong Wang,<sup>[a]</sup> Zhanda Fu,<sup>[a, b]</sup> Hongquan Yin,<sup>[a]</sup> and Fu-Xue Chen<sup>\*[a]</sup>

**Abstract:** To improve the detonation performance, 1,2,4,5-tetrazine and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine *N*-oxide explosives were prepared by oxidation reaction with trifluoroacetic peroxide acid. Thus, four compounds were synthesized and characterized. Among them, 3,6-bis((3-nitro-

1,2,4-oxadiazol-5-yl)amino)-1,2,4,5-tetrazine 1-oxide (TDOX) showed good detonation performance ( $D$ , 8926 ms<sup>-1</sup>;  $P$ , 34.8 GPa) and favorable thermal stability ( $T_d$ , 228 °C, onset). All compounds featured mechanic insensitivities ( $IS > 40$  J,  $FS > 360$  N).

**Keywords:** [1,2,4]Triazolo[4,3-b][1,2,4,5]tetrazine · 1,2,4,5-Tetrazine · *N*-Oxide · Explosives · Synthesis

## 1 Introduction

Introduction of N–O bond into a molecule of energetic compound can not only increase the oxygen balance but also allows more reasonable charge distribution and better crystal packing as well, consequently enhancing detonation performance [1–7]. Particularly, it is reasonable for 1,2,4,5-tetrazines to achieve good detonation performance by forming *N*-oxides [8–15].

1,2,4-Oxadiazole, an isomer of furazan, has recently received more attention in the field of high-performance insensitive energetic materials (HIEM) [16–21]. Combination of 1,2,4-oxadiazole and 1,2,4,5-tetrazine into one fused ring molecule led to high energy density and good stability (Scheme 1), while fused heterocyclic [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazines have been extensively investigated [22–31].

Our laboratory is particularly interested in the rational design of new energetic materials with tailored sensitivity and performance [32–37]. In previous work, we developed some new [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine explosives [38–39]. These fused ring explosives featured low sensitivity to impact and good detonation performance. To further improve the energy density, calculations suggested that it might be possible to improve the detonation performance properties by introducing *N*-oxide into the ring of [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine (Scheme 1).

Substituted tetrazine derivatives are readily accessible from 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (BT) [32]. Then, 3-nitro-1,2,4-oxadiazol-5-amine (NOA) [18] underwent nucleophilic substitution with BT in the presence of NaH to produce 1. Oxidation of 1 was accomplished with 3,6-bis((3-nitro-1,2,4-oxadiazol-5-yl)amino)-1,2,4,5-tetrazine 1-oxide (TDOX) using H<sub>2</sub>O<sub>2</sub> and trifluoroacetic anhydride (TFAA) (Scheme 2) after investigation of other oxidant reagents (see ESI, Scheme S1).

## 2 Experimental Section


**General:** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz (Bruker Avance 400) nuclear magnetic resonance spectrometers operating at 400 and 100 MHz, respectively. <sup>15</sup>N NMR spectra were measured on a 700 MHz (Bruker Avance 700) nuclear magnetic resonance spectrometers operating at 70 MHz. FT-IR spectra were taken using KBr pellets on a Bruker ALPHA FT-IR-Spektrometer. DSC (Shimadzu TA-60ws) was employed to measure the melt points and decomposition temperatures at a scan rate of 5 °C min<sup>-1</sup> in argon atmosphere. High resolution mass spectrometry was recorded on Bruker Apex IV FTMS.

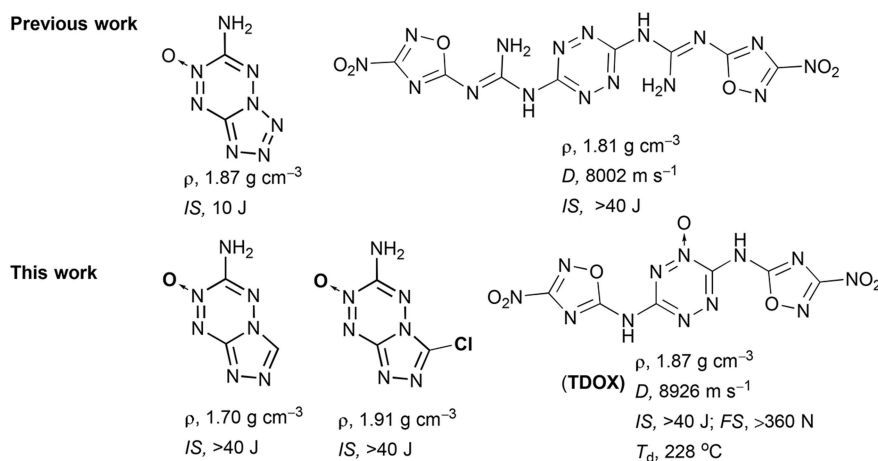
**Caution!** Although no dangerous situation was encountered in the synthesis of these energetic materials, it is recommended to carry out these procedures on a small scale and always use proper protective equipment.

***N,N*-Bis(3-nitro-1,2,4-oxadiazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (1):** BT (500 mg, 1.85 mmol) and NOA (530 mg, 4.1 mmol) were placed in a round-bottomed flask with a stir bar and anhydrous THF (50 mL). After cooled to 0 °C, NaH (60% dispersion in oil, 175 mg, 4.4 mmol) was added. The reaction mixture was stirred for 10 h at room temperature. Upon completion, it was diluted with water (100 mL) and acidified by 1.0 M HCl to pH 1. The resulting mixture was extracted with 3 × 100 mL of ethyl acetate. The organic lay-

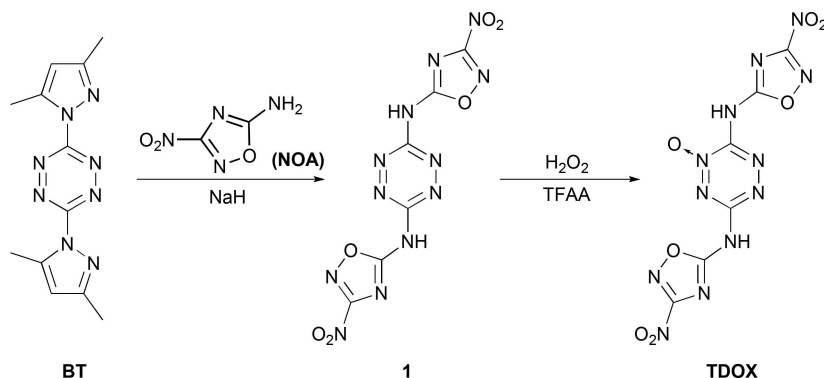
[a] G. Wang, Z. Fu, H. Yin, F.-X. Chen  
School of Chemistry & Chemical Engineering, Beijing Institute of Technology (Liangxiang Campus), No. 8 Liangxiang east road, Fangshan district, Beijing 102488, P.R. China  
\*e-mail: fuxue.chen@bit.edu.cn

[b] Z. Fu  
Department of Chemistry, Tangshan Normal University, Tangshan 063000, P.R. China

 Supporting information for this article is available on the WWW under <https://doi.org/10.1002/prep.201900014>



Scheme 1. 1,2,4,5-Tetrazine and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine N-oxides.



Scheme 2. Synthetic route of TDOX.

ers were combined, washed with  $2 \times 50$  mL of brine, dried over anhydrous sodium sulfate, and concentrated in vacuum. The residue was applied to a silica gel column with eluent methanol/dichloromethane (10:1, v/v), giving **1** (350 mg, 55.9% yield) as a red solid.  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 174.66, 170.38, 162.99$  ppm; HRMS  $[M-H]^-$  calc. for  $\text{C}_6\text{H}_2\text{N}_{12}\text{O}_6$  337.0147, found 337.0158; IR (KBr):  $\nu$  3354, 1653, 1616, 1576, 1533, 1449, 1398, 1304, 976, 953, 837, 739, 669, 592, 419  $\text{cm}^{-1}$ ;  $^{15}\text{N}$  NMR (70 MHz, DMSO- $d_6$ ):  $\delta = -23.79, -28.41, -59.23, -204.21, -239.86$  ppm.

**3,6-Bis((3-nitro-1,2,4-oxadiazol-5-yl)amino)-1,2,4,5-tetrazine 1-oxide (TDOX)**: TFAA (2.0 mL) was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL), 50%  $\text{H}_2\text{O}_2$  (0.65 mL) was added dropwise with an ice/water bath. **1** (170 mg, 0.503 mmol) was added slowly. After stirring for 12 h, the precipitate was filtered, washed with  $\text{CH}_2\text{Cl}_2$ , and air-dried, giving **TDOX** (78 mg, 43.8% yield) as a red solid.  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 169.27, 168.60, 158.21$  ppm; HRMS  $[M-H]^-$  calc. for  $\text{C}_6\text{H}_2\text{N}_{12}\text{O}_7$  353.0097, found 353.0111; IR (KBr):  $\nu$  2984, 2887, 1651, 1537, 1418, 1308, 1265, 1070, 943, 858, 729, 606, 559  $\text{cm}^{-1}$ ;  $^{15}\text{N}$  NMR (70 MHz, DMSO- $d_6$ ):  $\delta = -21.49, -29.40,$

$-31.59, -36.68, -37.42, -185.69, -188.15, -202.85, -276.59, -309.59$  ppm.

**6-Amino-[1,2,4]triazolo[4,3-b]1,2,4,5-tetrazine 7-oxide (5a)**: To a mixture of 50% hydrogen peroxide (7.5 mL) in  $\text{CH}_2\text{Cl}_2$  (75 mL) was added trifluoroacetic acid (15 mL) with stirring at  $< 10^\circ\text{C}$ . [1,2,4]triazolo[4,3-b]1,2,4,5]tetrazine-6-amine (**4a**) (1.5 g, 10.9 mmol) was added at  $0^\circ\text{C}$  and stirred for 30 min, then at room temperature for 12 h. The solvent was removed in vacuum and the residue was applied onto a silica gel column with ethyl acetate (EA) and petroleum ether (PE) 1:1, v/v, giving **5a** (500 mg, 30.0% yield) as a yellow solid.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 9.16$  (s, 1H), 8.28 (s, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 156.65, 138.64, 136.03$  ppm;  $^{15}\text{N}$  NMR (70 MHz, DMSO- $d_6$ ):  $\delta = 55.44, 35.25, -62.96, -76.67, -81.03, -178.26, -308.39$  ppm; IR (KBr):  $\nu$  3379, 3300, 3130, 1636, 1558, 1460, 1358, 1300, 1204, 1140, 1047, 970, 837, 721, 696, 552, 501  $\text{cm}^{-1}$ ; HRMS: calc. for  $\text{C}_3\text{H}_3\text{N}_7\text{O}$   $[M+H]^+$  154.0472 found: 154.0469.

**6-Amino-3-chloro-[1,2,4]triazolo[4,3-b]1,2,4,5-tetrazine 7-oxide (5b)**: Similarly, **5b** was isolated in 158 mg (36.0%) as a yellow solid from **4b** (400 mg, 2.3 mmol) with EA:PE = 1:3, v/v, as the eluent.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta =$

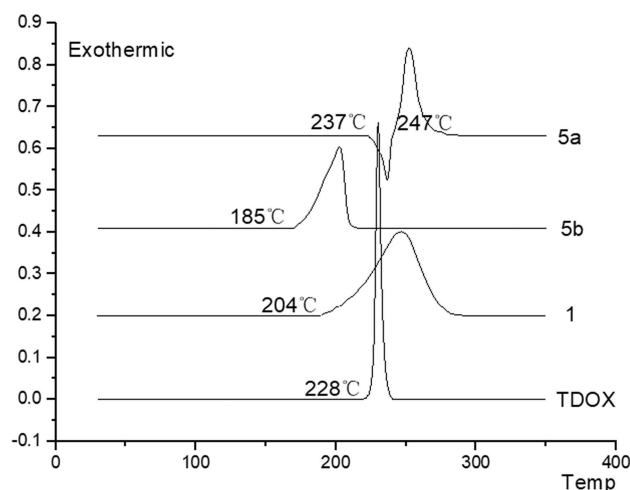
8.60 (s, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 148.41, 147.31, 132.49 ppm;  $^{15}\text{N}$  NMR (70 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = -52.18, -66.48, -73.41, -85.06, -175.83, -195.96, -309.09 ppm; IR (KBr):  $\nu$  3379, 3011, 1659, 1485, 1441, 1371, 1287, 1274, 1238, 1123, 924, 583, 527, 461  $\text{cm}^{-1}$ ; HRMS: calc. for  $\text{C}_3\text{H}_2\text{ClN}_7\text{O}$   $[M+H]^+$  188.0082 found: 188.0080.

### 3 Results and Discussion

Fused ring intermediates **2**, **3a–b** and **4a–b** were synthesized according to previous work [23,39]  $\text{H}_2\text{O}_2$  and trifluoroacetic acid (TFA) was employed to oxidize the tetrazine ring affording *N*-oxides **5a** and **5b** (Scheme 3). The chemical structures of these compounds were supported by HRMS, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR spectroscopy. By referring to other known compounds in the literature [3–4,7] we deduced that the oxygen atom was located at N7 position.

*N*-Oxide is in favor of the oxygen balance (OB), density and even thermal stability to *N*-heterocyclic explosives [40]. The thermal stabilities were determined with differential scanning calorimetry (DSC) at a scanning rate of  $5^\circ\text{C min}^{-1}$  (Figure 1). **1** showed good thermal stability with onset decomposition temperature at  $204^\circ\text{C}$ . After oxidation, **TDOX** showed a higher onset decomposition temperature at  $228^\circ\text{C}$ , comparable to that of RDX. The thermal decomposition temperature of **5a** was  $247^\circ\text{C}$ , which is lower than its parent compound **4a** ( $T_d = 280^\circ\text{C}$ ) [39]. As an exception, the decomposition temperature of chlorinated **5b** was  $185^\circ\text{C}$ , lower than its parent compound **4b** ( $T_m = 227^\circ\text{C}$ ) [39].

The calculated densities of **1** and **TDOX** are 1.84 and  $1.87\text{ g cm}^{-3}$ , respectively. Using a gas pycnometer at  $25^\circ\text{C}$ , **5a** has a density of  $1.70\text{ g cm}^{-3}$  which was greater than that of its precursor **4a** ( $1.64\text{ g cm}^{-3}$ ), while **5b** featured a den-

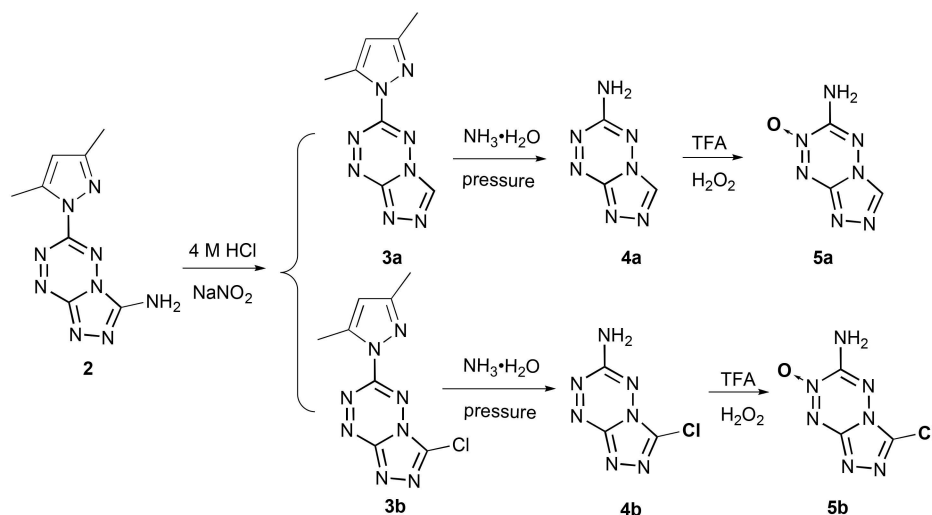


**Figure 1.** DSC plots of tetrazine and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine derivatives.

sity of  $1.91\text{ g cm}^{-3}$  that is much higher than that of **4b** (single crystal density,  $1.759\text{ g cm}^{-3}$ ). Obviously, introduction of oxygen into the molecular increased the density to different extent and thus favorable oxygen balance (OB) (Table 1).

The heats of formation of all compounds were calculated by using the program package Gaussian09. As shown in Table 1, **1** and **TDOX** have enthalpies of formation  $2.03\text{ kJ g}^{-1}$  and  $1.85\text{ kJ g}^{-1}$ , respectively. **5b** possess the highest  $4.37\text{ kJ g}^{-1}$ .

The detonation pressures and velocities were calculated using the software package EXPLO5 v6.01. **1** has the detonation velocity of  $8731\text{ m s}^{-1}$ , which exceeds that of TATB. **TDOX** ( $8926\text{ m s}^{-1}$ ) exhibits a comparable detonation velocity to RDX. The detonation velocity and detonation pressure of **5a** were  $8215\text{ m s}^{-1}$  and 25.5 GPa, respectively, com-



**Scheme 3.** Synthetic routes of **5a** and **5b**.

**Table 1.** Physical properties of 1,2,4,5-tetrazine and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine derivatives and comparison with TNT, RDX and TATB.

Compd.	$\rho$ [g cm <sup>-3</sup> ]	$T_m^{[c]}$ [°C]	$T_d^{[d]}$ [°C]	$\Delta H_f^{[e]}$ [kJ mol <sup>-1</sup> ]/[kJ g <sup>-1</sup> ]	$D^{[f]}$ [m s <sup>-1</sup> ]	$P^{[g]}$ [GPa]	OB% <sup>[h]</sup>	$IS^{[i]}$ [J]	$FS^{[j]}$ [N]
<b>1</b>	1.84 <sup>[a]</sup>	–	204	686.3/2.03	8731	32.5	–4.7	> 40	> 360
<b>TDOX</b>	1.87 <sup>[a]</sup>	–	228	657.7/1.85	8926	34.8	0.0	> 40	> 360
<b>5a</b>	1.70 <sup>[b]</sup>	237	247	524.3/3.42	8215	25.5	–36.6	> 40	> 360
<b>5b</b>	1.91 <sup>[b]</sup>	–	185	817.3/4.37	8546	32.2	–25.5	> 40	> 360
TNT <sup>[18]</sup>	1.65	81	295	–67/–0.29	6881	19.5	–24.7	15	353
RDX <sup>[16]</sup>	1.82	–	230	92.6/0.42	8997	35.2	0.0	7.4	120
TATB <sup>[32]</sup>	1.93	–	324	–140/–0.54	8114	31.2	–18.6	50	> 360

[a] Density was calculated with M06-2X/6-311 + + G(d,p). [b] Density measured by gas pycnometer (25 °C). [c] Melt temperature (peak, DSC, 5 °C min<sup>-1</sup>). [d] Decomposition temperature (onset, DSC, 5 °C min<sup>-1</sup>). [e] Heat of formation (calculated using Gaussian 09(vB.01)). [f] Detonation velocity, calculated with Explo5 v6.01. [g] Detonation pressure, calculated with Explo5 v6.01. [h] Oxygen balance (based on CO) for C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>N<sub>d</sub>, 1600(c-a-b/2)/MW (MW = molecular weight). [i] Impact sensitivity (BAM methods). [j] Friction sensitivity (BAM methods).

parable to those of TATB. Chlorinated compound **5b** was predicted with detonation velocity of 8546 m s<sup>-1</sup> and detonation pressure of 32.2 GPa.

The mechanical sensitivity was determined by using standard BAM fall hammer for the impact sensitivity (*IS*) and BAM friction tester for friction sensitivity (*FS*). **1**, **TDOX**, **5a** and **5b** all showed insensitivity towards impact (*IS* > 40 J, *FS* > 360 N), which is comparable to that of TATB (Table 1).

## 4 Conclusions

In summary, a series of insensitive explosives of 1,2,4,5-tetrazine and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine N-oxides were synthesized. Among them, **TDOX** showed high calculated density (1.87 g cm<sup>-3</sup>), low sensitivity (*IS* > 40 J, *FS* > 360 N) which is comparable to TATB, zero oxygen balance, good detonation pressure (34.8 GPa) and detonation velocity (8926 m s<sup>-1</sup>) which is superior to RDX.

## Acknowledgments

Financial support from the National Natural Science Foundation of China is acknowledged (21772011).

## References

- [1] D. E. Chavez, M. A. Hiskey, R. D. Gilardi, 3,3'-Azobis(6-amino-1,2,4,5-tetrazine): a novel high nitrogen energetic material, *Angew. Chem.* **2000**, 112, 1861–1863; *Angew. Chem. Int. Ed.* **2000**, 39, 1791–1793.
- [2] A. B. Sheremetev, N. V. Palysaeva, M. I. Struchkova, The first synthesis of 3-nitro-4-[(s-tetrazin-3-yl)amino]furazans, *Mendeleev Commun.* **2010**, 20, 350–352.
- [3] H. Wei, H. Gao, J. M. Shreeve, N-Oxide 1,2,4,5-tetrazine-based high-performance energetic materials, *Chem. Eur. J.* **2014**, 20, 16943–16952.
- [4] H. Wei, J. Zhang, J. M. Shreeve, *Synthesis, characterization, and energetic properties of 6-aminotetrazolo[1,5-b]-1,2,4,5-tetrazine-7-N-oxide: a nitrogen-rich material with high density*, *Chem. Asian J.* **2015**, 5, 1130–1133.
- [5] M. S. Klenov, A. A. Guskov, O. V. Anikin, A. M. Churakov, Y. A. Strelenko, I. V. Fedyanin, K. A. Lyssenko, V. A. Tartakovsky, *Synthesis of tetrazin-tetrazine 1,3,6,8-tetraoxide (TTTO)*, *Angew. Chem.* **2016**, 128, 11644–11647; *Angew. Chem. Int. Ed.* **2016**, 55, 11472–11475.
- [6] D. G. Piercey, D. E. Chavez, B. L. Scott, G. H. Imler, D. A. Parrish, *An energetic triazolo-1,2,4-triazine and its N-Oxide*, *Angew. Chem.* **2016**, 128, 15541–15544; *Angew. Chem. Int. Ed.* **2016**, 55, 15315–15318.
- [7] D. E. Chavez, D. A. Parrish, L. Mitchell, G. H. Imler, *Azido and tetrazolo 1,2,4,5-tetrazine N-Oxides*, *Angew. Chem.* **2017**, 129, 3629–3632; *Angew. Chem. Int. Ed.* **2017**, 56, 3575–3578.
- [8] M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, R. Gilardi, 3,6-Di(azido)-1,2,4,5-tetrazine: A precursor for the preparation of carbon nanospheres and nitrogen-rich carbon nitrides, *Angew. Chem. Int. Ed.* **2004**, 43, 5658–5661.
- [9] D. E. Chavez, M. A. Hiskey, D. L. Naud, *Tetrazine explosives*, *Propellants Explos. Pyrotech.* **2004**, 29, 209–215.
- [10] D. E. Chavez, M. A. Hiskey, R. D. Gilardi, *Novel high-nitrogen materials based on nitroguanyl-substituted tetrazines*, *Org. Lett.* **2004**, 6, 2889–2891.
- [11] M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud, R. D. Gilardi, *Synthesis, characterization and energetic properties of diazido heteroaromatic high-nitrogen C–N compound*, *J. Am. Chem. Soc.* **2005**, 127, 12537–12543.
- [12] D. E. Chavez, S. K. Hanson, J. M. Veauthier, D. A. Parrish, *Electroactive Explosives: Nitrate ester-functionalized 1,2,4,5-tetrazines*, *Angew. Chem.* **2013**, 125, 7014–7017; *Angew. Chem. Int. Ed.* **2013**, 52, 6876–6879.
- [13] A. Aizikovitch, A. Shlomovich, A. Cohen, M. Gozin, *The nitration pattern of energetic 3,6-diamino-1,2,4,5-tetrazine derivatives containing azole functional groups*, *Dalton Trans.* **2015**, 44, 13939–13946.
- [14] D. E. Chavez, D. A. Parrish, L. Mitchell, *Energetic trinitro- and fluoro-dinitroethyl ethers of 1,2,4,5-tetrazines*, *Angew. Chem.* **2016**, 128, 8808–8811; *Angew. Chem. Int. Ed.* **2016**, 55, 8666–8669.
- [15] A. M. Churakov, V. A. Tartakovsky, *Progress in 1,2,3,4-tetrazine chemistry*, *Chem. Rev.* **2004**, 104, 2601–2616.
- [16] Z. Fu, R. Su, Y. Wang, Y.-F. Wang, W. Zeng, N. Xiao, Y. Wu, Z. Zhou, J. Chen, F.-X. Chen, *Synthesis and characterization of en-*

- ergetic 3-nitro-1,2,4-oxadiazoles, *Chem. Eur. J.* **2012**, *18*, 1886–1889.
- [17] Y.-T. Gao, L.-M. Zhao, F.-Q. Pang, X.-J. Qi, J.-L. Huang, F.-X. Chen, *Synthesis and properties of energetic salts based on 3-nitro-5-nitroimino-1,2,4-oxadiazole*, *Chin. Chem. Lett.* **2016**, *27*, 433–436.
- [18] F. Pang, G. Wang, T. Lu, G. Fan, F.-X. Chen, *Preparation and characteristics of 1,2,4-oxadiazole-derived energetic ionic salts with nitrogen linkages*, *New J. Chem.* **2018**, *42*, 4036–4044.
- [19] T. M. Klapötke, N. Mayr, J. Stierstorfer, M. Weyrauther, *Maximum compaction of ionic organic explosives: bis(hydroxylammonium) 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolate) and its derivatives*, *Chem. Eur. J.* **2014**, *20*, 1410–1417.
- [20] H. Wei, C. He, J. Zhang, J. M. Shreeve, *Combination of 1,2,4-oxadiazole and 1,2,5-oxadiazole moieties for the generation of high-performance energetic materials*, *Angew. Chem. Int. Ed.* **2015**, *54*, 9367–9371.
- [21] Y. Tang, H. Gao, L. A. Mitchell, D. A. Parrish, J. M. Shreeve, *Enhancing energetic properties and sensitivity by incorporating amino and nitramino groups into a 1,2,4-oxadiazole building block*, *Angew. Chem.* **2016**, *128*, 1159–1162; *Angew. Chem. Int. Ed.* **2016**, *55*, 1147–1150.
- [22] V. A. Ershov, I. Ya. Postovskii, *Synthesis of compounds containing a new biheterocyclic system(s-triazolo[3,4-b]-s-tetrazine)*, *Khim. Geterotsikl. Soedin.* **1968**, *4*, 1134–1135.
- [23] D. E. Chavez, M. A. Hiskey, *Synthesis of the bi-heterocyclic parent ring system 1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine and some 3,6-disubstituted derivatives*, *J. Heterocycl. Chem.* **1998**, *35*, 1329–1332.
- [24] T. Wei, W. Zhu, J. Zhang, H. Xiao, *DFT Study on energetic tetrazolo-[1,5-b]-1,2,4,5-tetrazine and 1,2,4-triazolo-[4,3-b]-1,2,4,5-tetrazine derivatives*, *J. Hazard. Mater.* **2010**, *179*, 581–590.
- [25] Q. Wu, W. Zhu, H. Xiao, *Molecular design of trinitromethyl-substituted nitrogen-rich heterocycle derivatives with good oxygen balance as high-energy density compounds*, *Struct. Chem.* **2013**, *24*, 1725–1736.
- [26] T. W. Myers, J. A. Bjorgaard, K. E. Brown, D. E. Chavez, S. K. Hanson, R. J. Scharff, S. Tretiak, J. M. Veauthier, *Energetic chromophores: low-energy laser initiation in explosive Fe(II) tetrazine complexes*, *J. Am. Chem. Soc.* **2016**, *138*, 4685–4692.
- [27] T. W. Myers, K. E. Brown, D. E. Chavez, R. J. Scharff, J. M. Veauthier, *Laser initiation of Fe(II) complexes of 4-nitro-pyrazolyl substituted tetrazine ligands*, *Inorg. Chem.* **2017**, *56*, 2297–2303.
- [28] A. B. Sheremetev, N. V. Palysaeva, K. Yu. Suponitskii, M. I. Struchkova, *Nitroaminofurazans with azo and azoxy linkages: a comparative study of structural, electronic, physicochemical, and energetic properties*, *Russ. Chem. Bull.* **2012**, *1*, 119–128.
- [29] A. B. Sheremetev, N. V. Palysaeva, M. I. Struchkova, K. Yu. Suponitskii, M. Yu. Antipin, *Copper-catalyzed C–N coupling reactions of nitrogen-rich compounds-reaction of iodofurazans with s-tetrazinylamines*, *Eur. J. Org. Chem.* **2012**, 2266–2272.
- [30] N. V. Palysaeva, K. P. Kumpan, M. I. Struchkova, I. L. Dalingier, A. V. Kormanov, N. S. Aleksandrova, V. M. Chernyshev, D. F. Pyreu, K. Yu. Suponitskii, A. B. Sheremetev, *A direct approach to a 6-hetarylamino[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine library*, *Org. Lett.* **2014**, *16*, 406–409.
- [31] L. Hu, P. Yin, G. Zhao, C. He, G. H. Imler, D. A. Parrish, H. Gao, J. M. Shreeve, *Conjugated energetic salts based on fused rings: insensitive and highly dense materials*, *J. Am. Chem. Soc.* **2018**, *140*, 15001–15007.
- [32] Z. Fu, C. He, F.-X. Chen, *Synthesis and characteristics of a novel, high-nitrogen, heat-resistant, insensitive material NOG2T*, *J. Mater. Chem.* **2012**, *22*, 60–63.
- [33] Z. Fu, Y. Wang, L. Yang, R. Su, J. Chen, F. Nie, J. Huang, F.-X. Chen, *Synthesis and characteristics of novel, high nitrogen 1,2,4-oxadiazoles*, *RSC Adv.* **2014**, *4*, 11859–11861.
- [34] Q. Wang, H. Lu, F. Pang, J. Huang, F. Nie, F.-X. Chen, *Nitrogen-rich hypergolic ionic salts based on (2-methyltetrazol-5-yl) diazotates*, *RSC Adv.* **2016**, *6*, 56827–56830.
- [35] Q. Wang, F. Pang, G. Wang, J. Huang, F. Nie, F.-X. Chen, *Pentazadiene: a high-nitrogen linkage in energetic materials*, *Chem. Commun.* **2017**, *53*, 2327–2330.
- [36] X. Li, C. Wang, H. Li, F. Nie, H. Yin, F.-X. Chen, *Bishydrobis(tetrazol-1-yl)borate (BTB) based energetic ionic liquids with high density and energy capacity as hypergolic fuels*, *J. Mater. Chem. A* **2017**, *5*, 15525–15528.
- [37] X. Li, H. Huo, H. Li, F. Nie, H. Yin, F.-X. Chen, *Cyanotetrazolylborohydride (CTB) Anion-based ionic liquids with low viscosity and high energy capacity as ultrafast-igniting hypergolic fuels*, *Chem. Commun.* **2017**, *53*, 8300–8303.
- [38] G. Wang, T. Lu, G. Fan, C. Li, H. Yin, F.-X. Chen, *The Chemistry and Properties of energetic materials bearing [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine fused rings*, *Chem. Asian J.* **2018**, *13*, 3718–3722.
- [39] G. Wang, T. Lu, G. Fan, H. Yin, F.-X. Chen, *Synthesis and properties of insensitive [1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazine explosives*, *New J. Chem.* **2019**, *43*, 1663–1666.
- [40] P. He, J.-G. Zhang, X. Yin, J.-T. Wu, L. Wu, Z.-N. Zhou, T.-L. Zhang, *Energetic salts based on tetrazole N-Oxide*, *Chem. Eur. J.* **2016**, *22*, 7670–7685.

Manuscript received: January 10, 2019

Revised manuscript received: March 7, 2019

Version of record online: May 16, 2019