

# High-energy hydroxytetrazoles: Design, synthesis and performance

Alexander A. Larin, Leonid L. Fershtat\*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prosp. 47, Moscow, 119991, Russian Federation

## ARTICLE INFO

### Keywords:

High-energy materials  
Nitrogen heterocycles  
Hydroxytetrazoles  
Detonation performance  
Energetic salts

## ABSTRACT

In recent years, the development of novel advanced high-energy density materials has significantly shifted toward nitrogen-containing heterocyclic derivatives, which demonstrate a great potential for multipurpose application patterns. Among known heterocycles hydroxytetrazole is of special importance due to its high nitrogen-oxygen content and a possibility to serve as anion counterpart and to form a diverse array of organic and inorganic energetic salts. In this review, we summarized the main achievements on the synthesis and performance of hydroxytetrazole-based energetic materials. Potential applications of the presented high-energy compounds and their environmental compatibility are especially emphasized.

## 1. Introduction

In recent decades, the design and synthesis of novel high-energy density materials (HEDMs) became an emergent area of research.<sup>1,2</sup> HEDMs remain leading positions in a development of dual-use technologies for military and civilian purposes including space technologies, mining and explosion welding. However, advanced military, space and civilian technologies bring new increased requirements to the synthesis and performance of HEDMs.<sup>3,4</sup> Novel energetic materials should have balanced functional properties including good detonation performance, high density and high enthalpy of formation. At the same time, such materials should possess moderate sensitivity toward various mechanical stimuli to guarantee safety concerns associated with their preparation, isolation and handling. Traditional energetic materials, such as trinitrotoluene (TNT), hexogen (RDX), octogen (HMX) suffer from harsh methods for their synthesis and a lack of environmental compatibility.<sup>5,6</sup> Serious ecological issues are also connected with the wide utilization of highly toxic primary explosives lead azide and lead styphnate thus demanding their replacement for metal-free environmentally benign alternatives.<sup>7</sup> Therefore, design and synthesis of novel HEDMs with a balanced set of properties remains one of the constant multidisciplinary tasks both in fundamental and applied research areas.

A search of novel powerful HEDMs continues to evolve and nowadays it is performed among a variety of high-nitrogen and nitrogen-oxygen heterocyclic compounds.<sup>8–10</sup> A utilization of hetarene scaffolds for the construction of high-energy structures has a number of advantages compared to the cyclic and caged nitramines. Polynitrogen and nitrogen-oxygen heterocyclic derivatives have higher densities due to

planarity and possess higher enthalpies of formation, thus providing high detonation performance of such materials.<sup>11–14</sup> In addition, due to high nitrogen-oxygen content, the amount of oxidizer in energy-rich compositions can be significantly reduced.<sup>15</sup> Therefore, the development of novel advanced HEDMs among azole and azine derivatives demonstrates a great potential for multipurpose application patterns.

In a series of nitrogen-rich heterocycles, tetrazole ring is of particular importance due to high thermal stability, good detonation performance and high level of environmental compatibility of the energy-rich tetrazole derivatives.<sup>16–19</sup> However, the tetrazole moiety has no oxygen in its structure. This disadvantage may be circumvented by an introduction of a hydroxyl motif on one of the ring nitrogen atoms to produce hydroxytetrazole scaffold (also known as tetrazole *N*-oxide).<sup>20</sup> As a result of regioisomerism, both 1- and 2-hydroxytetrazoles **A** and **A'** (Fig. 1) were successfully synthesized so far.

There are two main routes to an assembly of the hydroxytetrazole framework. The first one is based on a direct oxidation of the corresponding tetrazoles with oxone, which is a triple salt  $2\text{KHSO}_5\text{KH}\text{SO}_4\text{K}_2\text{SO}_4$  and is widely used as a convenient, bench-stable oxidant. This approach is quite facile and tolerates well various functional groups, but has rather narrow substrate scope associated with a low oxidation ability of the tetrazole ring. The second route involves an acid-promoted cyclization of geminal azidooximes due to azide-tetrazole tautomerism. This approach enables a regiospecific construction of 1-hydroxytetrazole scaffold **A** for a wide range of substrates. In this review, we summarized the known approaches for the synthesis of energy-rich hydroxytetrazoles and organic/inorganic salts thereof. Main physicochemical properties of the reported HEDMs as well as their detonation

\* Corresponding author.

E-mail address: [fershtat@bk.ru](mailto:fershtat@bk.ru) (L.L. Fershtat).

<https://doi.org/10.1016/j.enmf.2021.01.001>

Received 30 November 2020; Received in revised form 23 December 2020; Accepted 8 January 2021

Available online 12 January 2021

2666-6472/© 2021 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND

license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

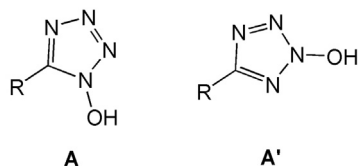


Fig. 1. The structures of regioisomeric hydroxytetrazoles.

performance are thoroughly discussed. In addition, potential application perspectives of the hydroxytetrazole-based HEDMs are emphasized.

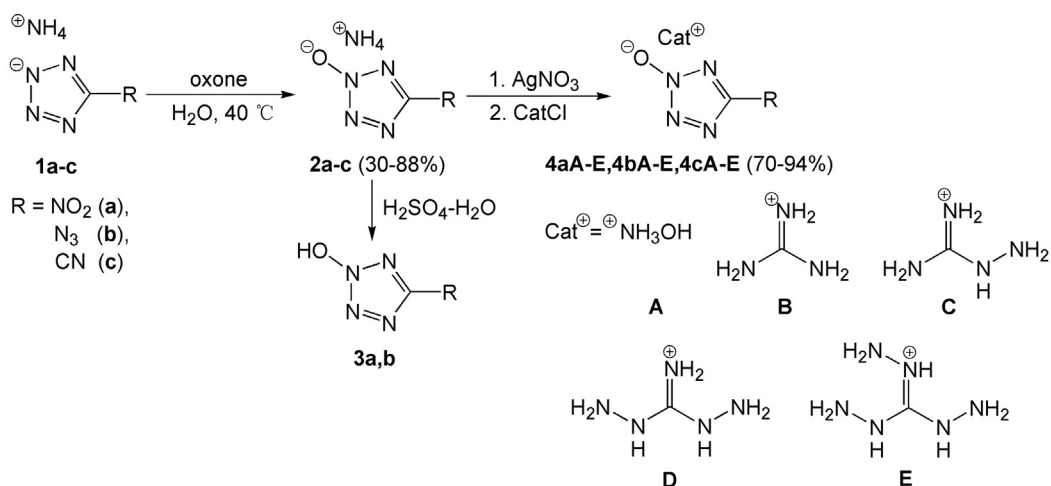
## 2. Oxidation of tetrazoles by oxone

Oxidation of tetrazolate-anions with oxone may serve as a direct approach to the assembly of hydroxytetrazole motif from available tetrazole derivatives. As a rule, this oxidation proceeds regioselectively resulting in a predominant formation of 2-hydroxytetrazole subunit. Arguably, this reactivity is attributed to the increased electron density on the N(2) atom of the tetrazole ring which is especially relevant in the case

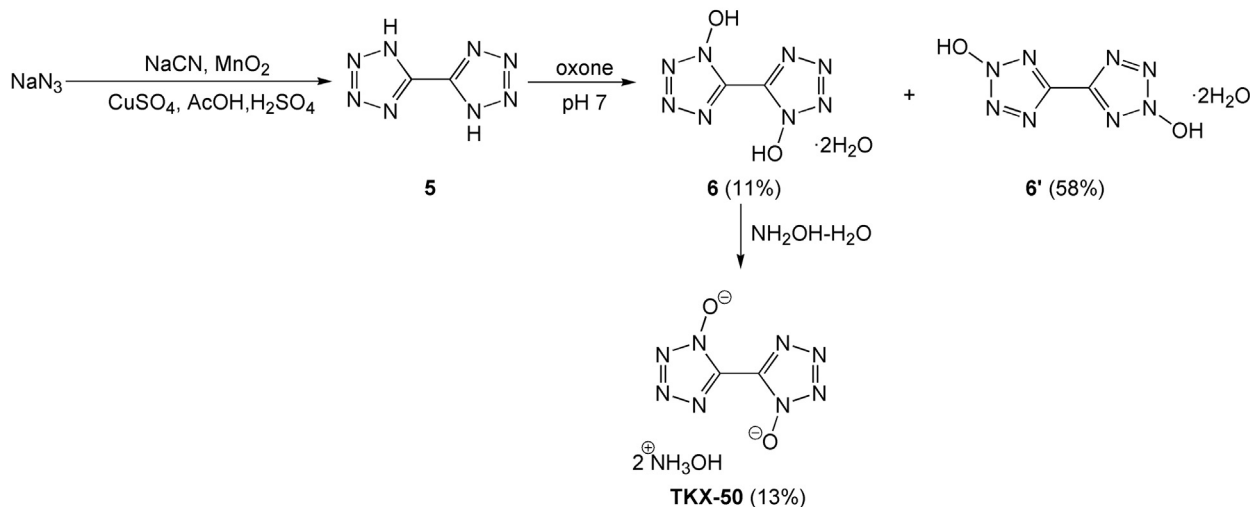
of various energetic derivatives incorporating electron-withdrawing explosophoric moieties (e.g. NO<sub>2</sub>, N<sub>3</sub>) at the tetrazole carbon atom. For example, an oxidation of ammonium salts of 5-nitro-, 5-azido- or 5-cyanotetrazoles **1a-c** resulted in a regioselective formation of 2*N*-oxides **2a-c**. Acidification of thus prepared salts **2a,b** afforded free 2-hydroxytetrazoles **3a,b** while double cation metathesis procedure provided a series of nitrogen-rich organic salts **4** (Scheme 1).<sup>21–23</sup>

Cycloaddition of NaN<sub>3</sub> and NaCN followed by oxidative C–C coupling of the parent tetrazole resulted in a formation of 5,5'-bitetrazole **5**. Oxidation of compound **5** with oxone afforded a mixture of 1,1'- and 2,2'-diolates **6** and **6'** with a predominance of the latter. The formed mixture can be easily separated by an addition of aqueous hydroxylamine: 1,1'-diolate **6** produced the corresponding dihydroxylammonium salt which is known as **TKX-50** (Scheme 2).<sup>24</sup> This HEDM demonstrated excellent detonation performance and moderate mechanical sensitivity representing a potential replacement for RDX and HMX. Physicochemical properties of **TKX-50** as well as of several other hydroxytetrazole salts are summarized in Table 1.

Isomeric 5,5'-bitetrazole-2,2'-diolate **6'** was also used as a synthetic platform for the preparation of a series of energetic salts **7–13** (Scheme 3). All transformations were performed by direct neutralization of the



Scheme 1. Synthesis of 2-hydroxytetrazoles and salts thereof.<sup>21–23</sup>



Scheme 2. First synthesis of **TKX-50**.<sup>24</sup>

**Table 1**  
Physicochemical properties and detonation performance of TKX-50,<sup>24</sup> 2a-c, 4aC.<sup>21–23</sup>

Compound	TKX-50	2a	2b	2c	4aC	RDX	HMX	TNT
$T_d/^\circ\text{C}^a$	170	173	151	184	185	210	279	290
$N/\%^b$	59.3	56.8	77.8	65.6	61.5	37.8	37.8	18.5
$\Omega_{\text{CO}}/\%^c$	-13.6	0	-22.2	-37.5	-19.5	0	0	-24.7
$\Omega_{\text{CO}_2}/\%^d$	-27.1	-10.8	-33.3	-62.5	-35.1	-21.6	-21.6	-74.0
$\rho/\text{g}\cdot\text{cm}^{-3e}$	1.918	1.730	1.689	1.554	1.697	1.858	1.944	290
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1f}$	446.6	152.0	534.0	325.9	256.4	86.3	116.1	-55.5
$D/\text{m}\cdot\text{s}^{-1g}$	9698	8885	8926	7749	8514	8983	9221	7459
$p/\text{GPa}^h$	42.4	32.2	32.5	22.2	28.5	34.1	41.5	23.5
$IS/\text{J}^i$	20	7	1	15	20	7.5	7	15
$FS/\text{N}^j$	120	120	20	112	216	120	112	353

<sup>a</sup> Decomposition temperature.

<sup>b</sup> Nitrogen content.

<sup>c</sup> Oxygen balance (based on CO) for  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ ,  $1600(c-a-b/2)/\text{MW}$ .

<sup>d</sup> Oxygen balance (based on  $\text{CO}_2$ ) for  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ ,  $1600(c-2a-b/2)/\text{MW}$ .

<sup>e</sup> Density.

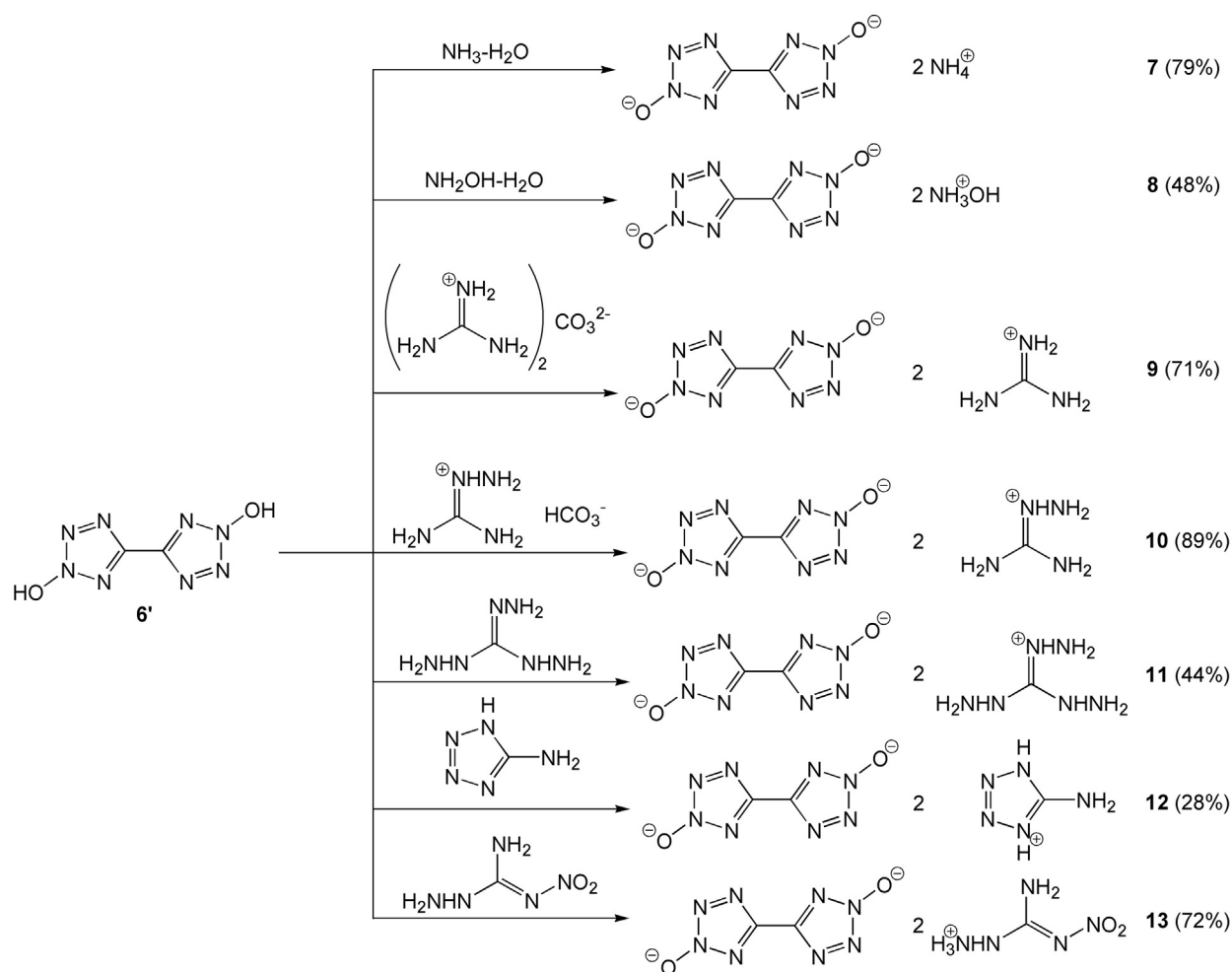
<sup>f</sup> Calculated enthalpy of formation.

<sup>g</sup> Detonation velocity.

<sup>h</sup> Detonation pressure.

<sup>i</sup> Impact sensitivity.

<sup>j</sup> Friction sensitivity.



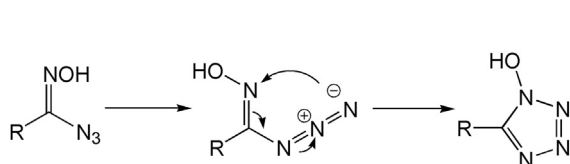
**Scheme 3.** Preparation of a series of energetic salts based on a 5,5'-bitetrazole-2,2'-diolate core.<sup>25</sup>

initial compound 6' with corresponding bases or their carbonate (bicarbonate) salts. Synthesized organic salts have good densities and high positive enthalpies of formation. Although dihydroxylammonium salt 8

and diaminotetrazolium salt 12 exhibit higher detonation velocities than RDX and HMX, their sensitivity to friction is also higher (Table 2).<sup>25</sup> At the same time, all prepared compounds have high nitrogen content

**Table 2**Physicochemical properties and detonation performance of 5,5'-bitetrazole-2,2'-diolate 6' and of the corresponding nitrogen-rich salts 7,8,12,13.<sup>25</sup>

Compound	6'	7	8	12	13	RDX	HMX	TKX-50
$T_d/^\circ\text{C}$	165	265	172	163	188	205	275	170
$N/\%$	65.8	68.6	59.3	61.7	67.0	37.8	37.8	59.3
$\Omega_{\text{CO}}/\%$	-9.4	-31.3	-13.6	-15.7	-25.5	0	0	-13.6
$\Omega_{\text{CO}_2}/\%$	-28.2	-47.0	-27.1	-31.3	-42.5	-21.6	-21.6	-27.1
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.953	1.664	1.822	1.832	1.633	1.858	1.944	1.877
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1}$	559.7	257.3	390.7	1043.8	608.1	86.3	116.1	446.6
$D/\text{m}\cdot\text{s}^{-1}$	9364	8212	9264	9350	8094	8983	9221	9698
$p/\text{GPa}$	40.9	25.8	37.2	38.2	25.2	38.0	41.5	42.4
IS/J	3	10	3	10	5	7.5	7	20
FS/N	5	360	60	48	360	120	112	120

**Scheme 4.** Plausible mechanism for the cyclization of geminal azido oximes.

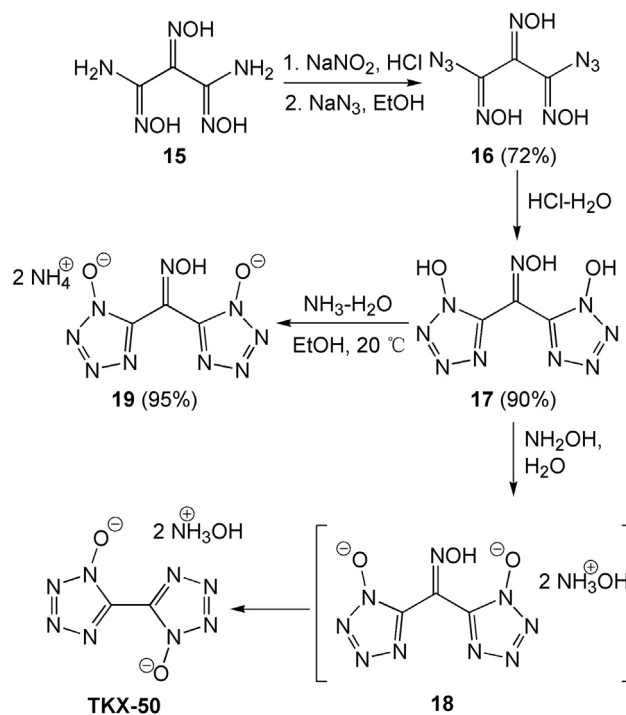
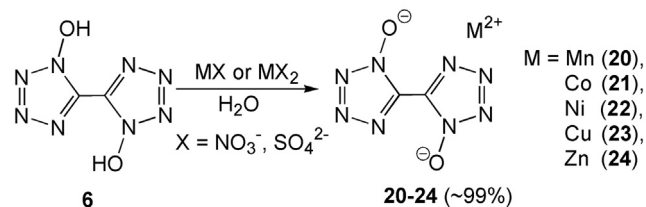
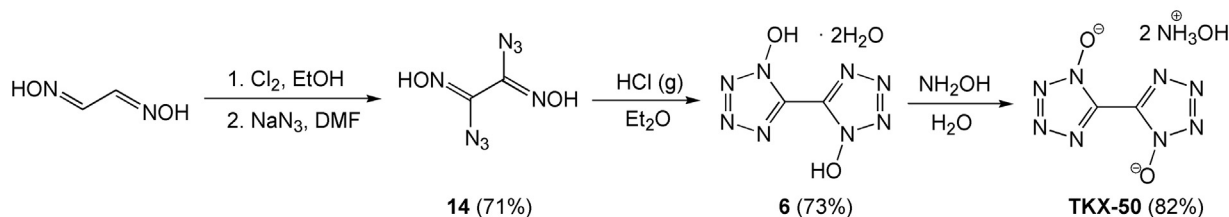
(>59%) which allows to consider these salts as environmentally benign HEDMs.

### 3. Cyclization of geminal azido oximes

A wide scope of energetic 1-hydroxytetrazoles was synthesized through a cyclization of geminal azido oxime derivatives. This approach usually provides higher yields of 1-hydroxytetrazoles comparing to the oxidation route and eliminates any regioselectivity issues. Arguably, cyclization occurs via an intramolecular nucleophilic attack of the terminal nitrogen atom of the azide moiety onto the oxime nitrogen atom followed by electronic shifts (Scheme 4).

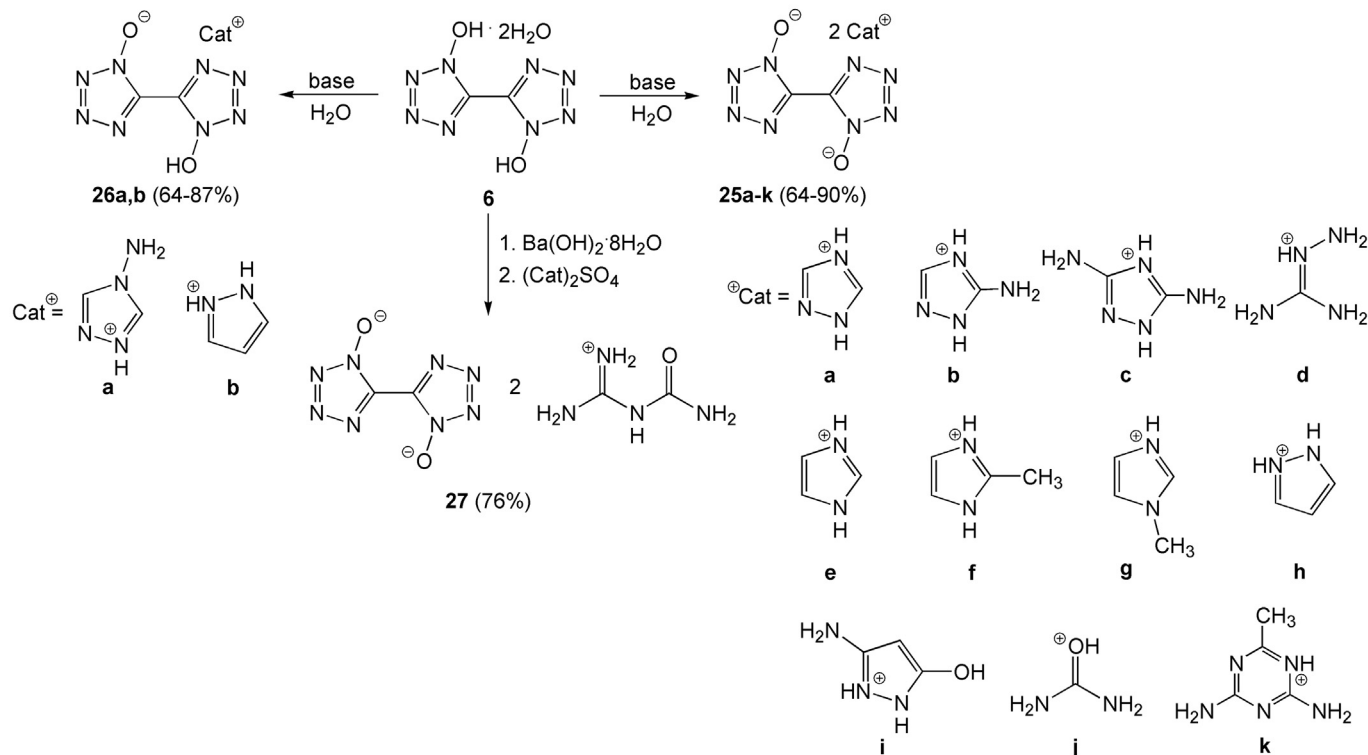
In particular, acid-promoted cyclization of diazidoglyoxime **14** afforded 5,5'-bitetrazole-1,1'-diolate **6** in a good yield. Substrate **14** was in turn prepared in two steps from unsubstituted glyoxime with an overall yield of 71% (Scheme 5).<sup>24</sup> This method may serve as a reliable and scalable procedure for the synthesis of **TKX-50** which is prepared in a yield of 42.5% starting from commercially available glyoxime. In-depth investigation showed that the thermal stability of **TKX-50** was slightly lower than that of RDX and was on the same level as that of CL-20.<sup>26</sup> Due to a favorable set of properties **TKX-50** was also investigated as a co-crystallization component.<sup>27–29</sup>

An alternative synthetic route to **TKX-50** was recently proposed.<sup>30</sup> This approach is based on a tandem conversion of bis-amidoxime **15** to the corresponding bis(azido oxime) **16**. Intramolecular cyclization of both azido oxime moieties in **16** afforded compound **17** incorporating two hydroxytetrazole subunits linked by an oxime moiety. Neutralization of bis(hydroxytetrazole) **17** with aqueous hydroxylamine unexpectedly resulted in a formation of **TKX-50** due to a possible loss of the oxime moiety. Although detailed mechanism for this transformation has been

**Scheme 6.** Alternative synthetic route to **TKX-50**.<sup>30</sup>**Scheme 7.** Preparation of non-heavy metal salts of 5,5'-bitetrazole-1,1'-diolate.<sup>31</sup>**Scheme 5.** Synthesis of **TKX-50** from unsubstituted glyoxime.<sup>24</sup>

**Table 3**  
Physicochemical properties and detonation performance of energetic coordination polymers **20–24**.<sup>31</sup>

Compound	<b>20</b>	<b>21</b>	<b>22</b>	<b>23</b>	<b>24</b>	TKX-50	Pb(N <sub>3</sub> ) <sub>2</sub>
<i>T<sub>d</sub></i> /°C	313	282	274	276	318	170	315
<i>N</i> /%	43.2	42.6	42.6	41.8	41.6	59.3	28.9
$\Omega_{CO_2}$ /%	0	0	0	0	0	-13.5	-11.0
$\Omega_{CO_2}$ /%	-14.4	14.1	-14.1	-13.8	-13.7	-27.1	-11.0
$\rho$ /g·cm <sup>-3</sup>	2.129	2.158	2.128	2.355	2.371	1.877	4.8
<i>Q</i> /kcal·g <sup>-1</sup>	0.609	0.755	0.627	0.724	0.773	1.532	0.375
<i>D</i> /m·s <sup>-1</sup>	6412	7164	6769	7968	7635	9698	5920
<i>p</i> /GPa	20.0	25.1	22.2	32.4	29.9	42.4	33.8
IS/J	16	12.5	32.5	20	60	20	2.5–4
FS/N	180	260	192	216	192	120	0.1–1

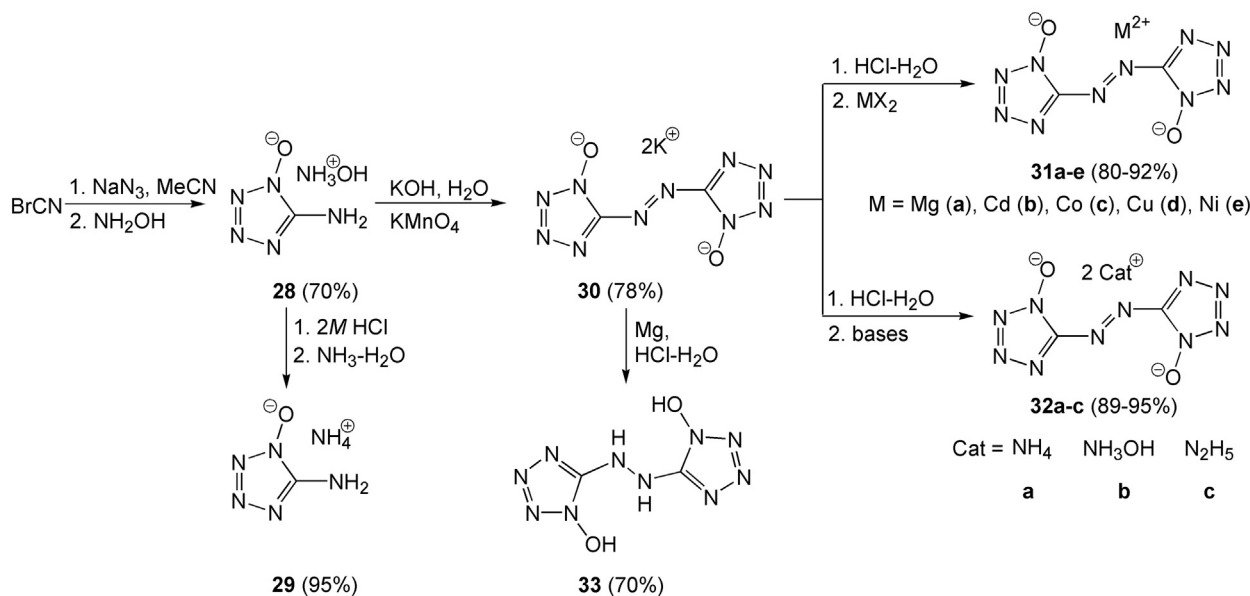
**Scheme 8.** Synthesis of mono- and bitetrazole-1,1'-diolate organic salts.<sup>29,33–38</sup>**Table 4**  
Physicochemical properties and detonation performance of energetic salts **25c,e,i,26a,b**.<sup>33</sup>

Compound	<b>25c</b>	<b>25e</b>	<b>25i</b>	<b>26a</b>	<b>26b</b>	RDX	HMX	TNT
<i>T<sub>d</sub></i> /°C	303	262	273	243	225	210	279	290
<i>N</i> /%	68.4	54.9	53.3	66.1	58.8	37.84	37.84	18.50
$\Omega_{CO_2}$ /%	-43.4	-57.5	-43.5	-31.5	-40.3	0	0	-24.7
$\Omega_{CO_2}$ /%	-69.5	-99.3	-78.3	-56.6	-74.0	-21.6	-21.6	-74.0
$\rho$ /g·cm <sup>-3</sup>	1.650	1.715	1.702	1.667	1.711	1.858	1.944	1.648
$\Delta H_f^\circ$ /kJ·mol <sup>-1</sup>	906.2	717.6	1385.3	885.0	751.1	86.3	116.1	-55.5
<i>D</i> /m·s <sup>-1</sup>	7405	7151	8151	8218	7693	8983	9221	7459
<i>p</i> /GPa	23.0	22.0	28.5	28.7	25.5	34.1	41.5	19.5
IS/J	>50	>50	>60	>50	>50	7.5	7	15

unknown so far, it proceeds arguably via an intermediate formation of dihydroxylammonium salt **18**. Unfortunately, the authors<sup>30</sup> did not provide the yield of TKX-50 which complicates its comparison with the previously reported synthetic route. Curiously, neutralization of bis(hydroxytetrazole) **17** with aqueous ammonia afforded expected diammonium salt **19** in a quantitative yield (Scheme 6). Compound **19** has higher thermal decomposition temperature (241 °C) than TKX-50,

however it has moderate density and enthalpy of formation which resulted in lower detonation velocity (8114 m·s<sup>-1</sup>).

5,5'-Bitetrazole-1,1'-diolate **6** was thoroughly studied by a number of research groups as a valuable scaffold for the preparation of a variety of both metal and metal-free energy-rich salts. Complexation of substrate **6** with non-heavy metal salts afforded a series of energetic compounds **20–24** which represent a subclass of coordination polymers (Scheme 7).



Scheme 9. Synthesis and transformations of dipotassium salt of 5,5'-azotetrazolate-1,1'-dioxide 30.<sup>39-41</sup>

Table 5  
Functional properties of HEDMs 30, 32a,b and 33.<sup>39</sup>

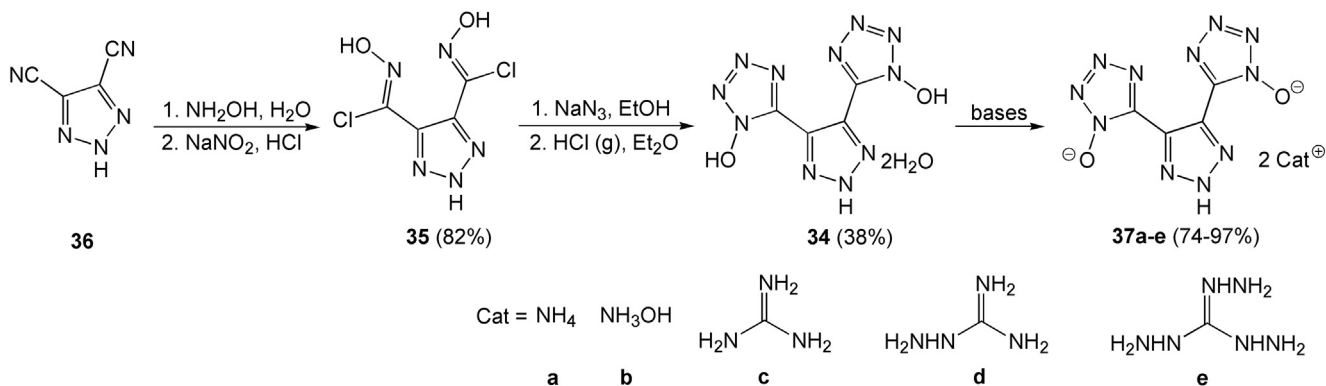
Compound	30	32a	32b	33	RDX	HMX
$T_d/^\circ\text{C}$	285	250	190	120	205	275
$N/\%$	51.1	72.4	63.6	61.7	37.8	37.8
$\Omega_{\text{CO}}/\%$	0	-27.6	-12.1	-16.0	0	0
$\Omega_{\text{CO}_2}/\%$	-17.5	-41.3	-24.2	-32.0	-21.6	-21.6
$\rho/\text{g}\cdot\text{cm}^{-3}$	2.200	1.800	1.778	1.707	1.858	1.944
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1}$	240.2	551.7	730.9	390.1	86.3	116.1
$D/\text{m}\cdot\text{s}^{-1}$	9753	9032	9348	8711	8983	9221
$p/\text{GPa}$	41.0	33.8	37.5	31.2	38.0	41.5
IS/J	20	3	15	1	7.5	7
FS/N	>360	160	54	<5	120	112

All synthesized materials 20–24 showed good thermal stability (>270 °C), high densities and zero oxygen balance (to CO). In addition, these compounds demonstrated good detonation performance and acceptable mechanical sensitivities (Table 3).<sup>31</sup> Coordination polymers 20–22 and 24 exhibited the fast deflagration-to-detonation transition ability enabling their potential application as lead-free primary explosives. For comparison, lead complex of 5,5'-bitetrazole-1,1'-diolate was also recently prepared.<sup>32</sup>

A wide series of nitrogen-rich organic salts incorporating mono- or bitetrazole-1,1'-diolate was synthesized by a direct neutralization of the parent compound 6, although a cation metathesis route was also employed (Scheme 8).<sup>29,33-38</sup> All prepared compounds 25a-k, 26a,b and 27 have high nitrogen content and good detonation velocities (7.0–8.2 km·s<sup>-1</sup>). In addition, synthesized HEDMs were found to be completely insensitive to impact which enables their potential application as secondary explosives (Table 4).

Table 6  
Physicochemical properties and detonation performance of 34, 37a-c.<sup>42</sup>

Compound	34	37a	37b	37c	RDX	HMX
$T_d/^\circ\text{C}$	246	241	182	244	205	275
$N/\%$	65.0	67.1	60.1	67.0	37.8	37.8
$\Omega_{\text{CO}}/\%$	-23.6	-38.4	-23.8	-47.3	0	0
$\Omega_{\text{CO}_2}/\%$	-50.6	-62.0	-44.9	-74.4	-21.6	-21.6
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.67	1.736	1.63	1.56	1.858	1.944
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1}$	823	682	722	331	86.3	116.1
$D/\text{m}\cdot\text{s}^{-1}$	8277	8991	8561	7659	8983	9221
$p/\text{GPa}$	26.0	28.8	27.0	18.6	38.0	41.5
IS/J	1	10	7	>40	7.5	7
FS/N	240	>360	>360	>360	120	112



Scheme 10. Synthesis of 4,5-bis(1-hydroxytetrazolyl)-2H-1,2,3-triazole 34 and salts thereof.<sup>42</sup>



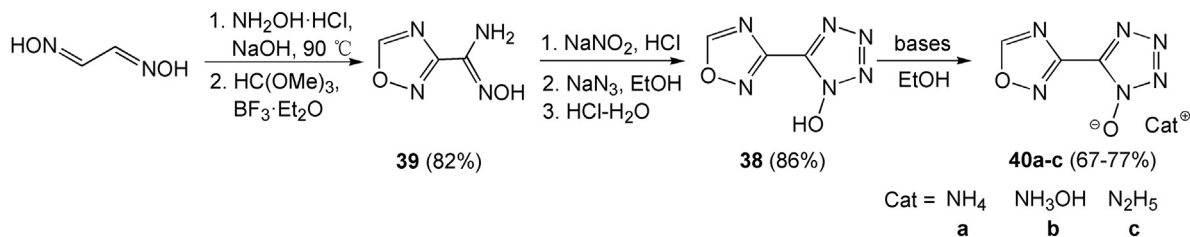
Scheme 11. Preparation of energetic salts of 5-(1,2,4-oxadiazolyl)-1-hydroxytetrazole.<sup>43</sup>

Table 7

Physicochemical properties and detonation performance of energetic salts 40a-c.<sup>43</sup>

Compound	40a	40b	40c	RDX	HMX	TNT
$T_d/^\circ\text{C}$	174	152	141	210	279	290
$N/\%$	57.3	60.2	52.4	37.8	37.8	18.5
$\Omega_{\text{CO}}/\%$	-32.8	-21.4	-34.4	0	0	-24.7
$\Omega_{\text{CO}_2}/\%$	-63.1	-68.8	-47.0	-21.6	-21.6	-74.0
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.72	1.71	1.79	1.858	1.944	1.648
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1}$	322	478	372	86.3	116.1	-55.5
$D/\text{m}\cdot\text{s}^{-1}$	8576	8929	8913	8983	9221	7459
$p/\text{GPa}$	28.0	30.4	32.7	34.1	41.5	19.5
IS/J	10	8	8	7.5	7	15
FS/N	120	108	96	120	112	353

An assembly of hydroxylammonium 5-aminotetrazole-1-olate **28** was accomplished through a cascade transformation of cyanogen bromide. This reaction sequence involved nucleophilic substitution of the bromide

anion in BrCN with azide one generating highly toxic and explosive cyanogen azide ( $\text{N}_3\text{CN}$ ) which cannot be isolated. The subsequent treatment of a solution of  $\text{N}_3\text{CN}$  with hydroxylamine resulted in a one-pot formation of target salt **28** through a condensation-cyclization-neutralization route. Upon acid-base treatment compound **28** can be easily converted to the corresponding ammonium salt **29**. Oxidation of amine **28** with  $\text{KMnO}_4$  in basic media afforded dipotassium salt of 5,5'-azotetrazolate-1,1'-dioxide **30**.<sup>39</sup> An acid-base work-up of compound **30** afforded a series of non-heavy metal (**31a-e**).<sup>40,41</sup> and metal-free (**32a-c**)<sup>39</sup> energetic salts. In addition, azo group in azotetrazolate **30** was chemoselectively reduced to the hydrazo moiety providing 1, 1'-dihydroxy-5,5'-bistetrazolylhydrazine **33** in a good yield (Scheme 9).<sup>39</sup>

Dipotassium 5,5'-azotetrazolate-1,1'-dioxide **30** showed excellent thermal stability and outstanding detonation performance ( $D = 9753 \text{ m}\cdot\text{s}^{-1}$ ;  $p = 41.0 \text{ GPa}$ ) far exceeding those of RDX and HMX. Furthermore, compound **30** is less sensitive to impact and completely insensitive to friction. Energetic salts **32a,b** have higher nitrogen content, but their

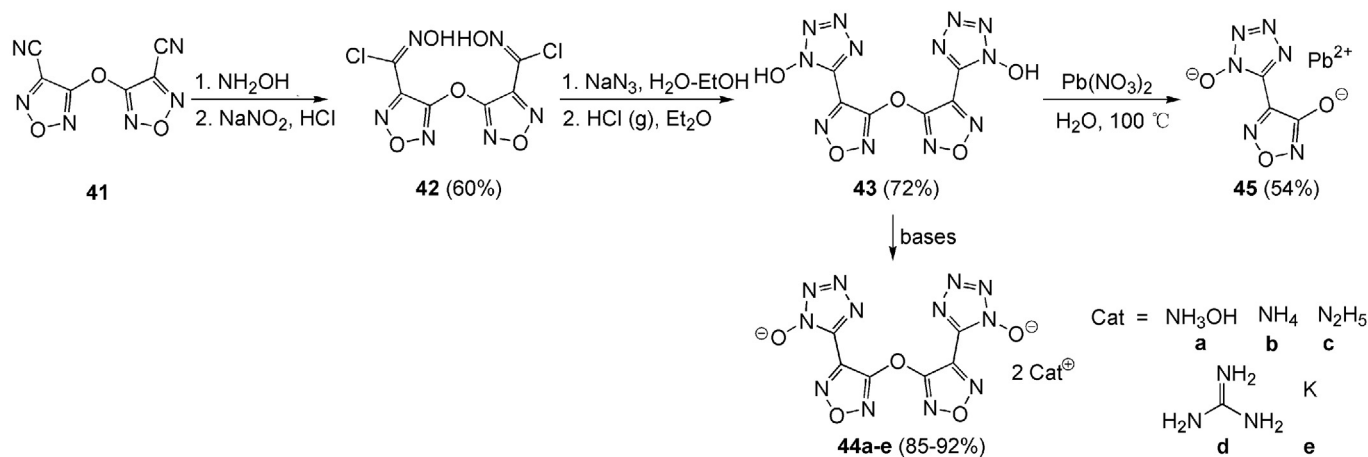
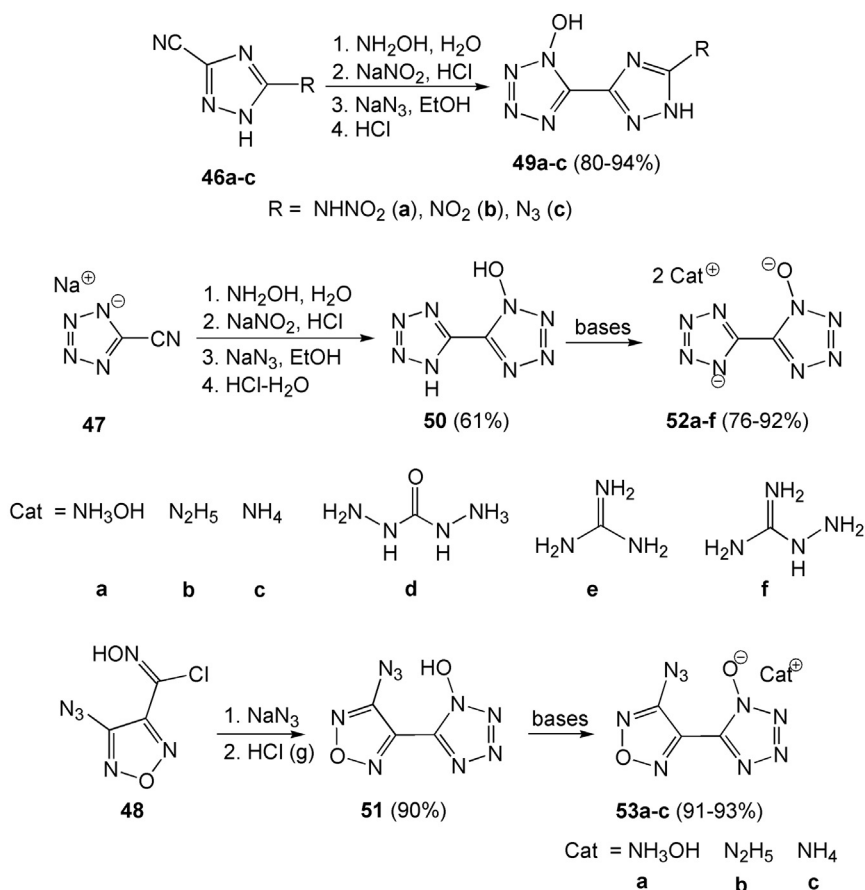
Scheme 12. Synthesis of 4,4'-oxybis[3,3'-(1-hydroxytetrazolyl)]furazan **43** and salts thereof.<sup>44,45</sup>

Table 8

Physicochemical properties and detonation performance of 44a-e, 45.<sup>44,45</sup>

Compound	44a	44b	44c	44d	44e-H <sub>2</sub> O	45	RDX	CL-20
$T_d/^\circ\text{C}$	198	250	219	215	236	258	210	211
$N/\%$	50.5	55.1	58.0	57.3	40.4	20.4	37.8	38.4
$\Omega_{\text{CO}}/\%$	-12.4	-22.5	-24.9	-32.7	-3.9	-3.0	0	11.0
$\Omega_{\text{CO}_2}/\%$	-37.1	-49.4	-49.7	-61.8	-26.9	-21.2	-21.6	-11.0
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.802	1.705	1.772	1.631	1.856	3.38	1.81	2.04
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1}$	853.7	753.1	1060.0	767.7	293.7	-	86.3	403.0
$D/\text{m}\cdot\text{s}^{-1}$	8898	8319	8913	7818	7063	9210	8.80	9.73
$p/\text{GPa}$	34.2	27.2	32.1	22.4	20.3	50.9	33.92	44.40
IS/J	6	10	5	12	3	25	7.5	4
FS/N	240	>360	240	>360	120	>360	120	48

Scheme 13. Synthesis of hetaryl substituted 1-hydroxytetrazoles.<sup>46–49</sup>Table 9  
Physicochemical properties and detonation performance of 49a,c, 50, 51, 52a, 53c.<sup>46–49</sup>

Compound	49a	49c	50	51	52a	53c	RDX	TKX-50
$T_d/^\circ\text{C}$	116	144	192	154	200	208	186	170
$N/\%$	59.2	72.2	72.3	64.6	63.6	66.0	37.8	59.3
$\Omega_{\text{CO}}/\%$	-11.3	-24.7	-20.8	-12.3	-21.8	-22.6	0	-13.6
$\Omega_{\text{CO}_2}/\%$	-33.8	-49.4	-41.5	-36.9	-36.3	-45.3	-21.6	-27.1
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.850	1.690	1.762	1.751	1.731	1.712	1.800	1.877
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1}$	515.0	795.0	636.6	820.9	469.0	779.9	70.3	458.7
$D/\text{m}\cdot\text{s}^{-1}$	8776	8239	8843	8784	9117	8687	8787	9781
$p/\text{GPa}$	34.2	27.5	31.4	31.8	32.3	29.9	35.3	40.1
IS/J	<1	4	40	3	12	15	7.5	20
FS/N	60	120	240	20	216	120	120	120

sensitivity is also higher.<sup>39</sup> Hydrazo derivative **33** is very sensitive both to impact and friction which restrict its potential application in practice (Table 5).

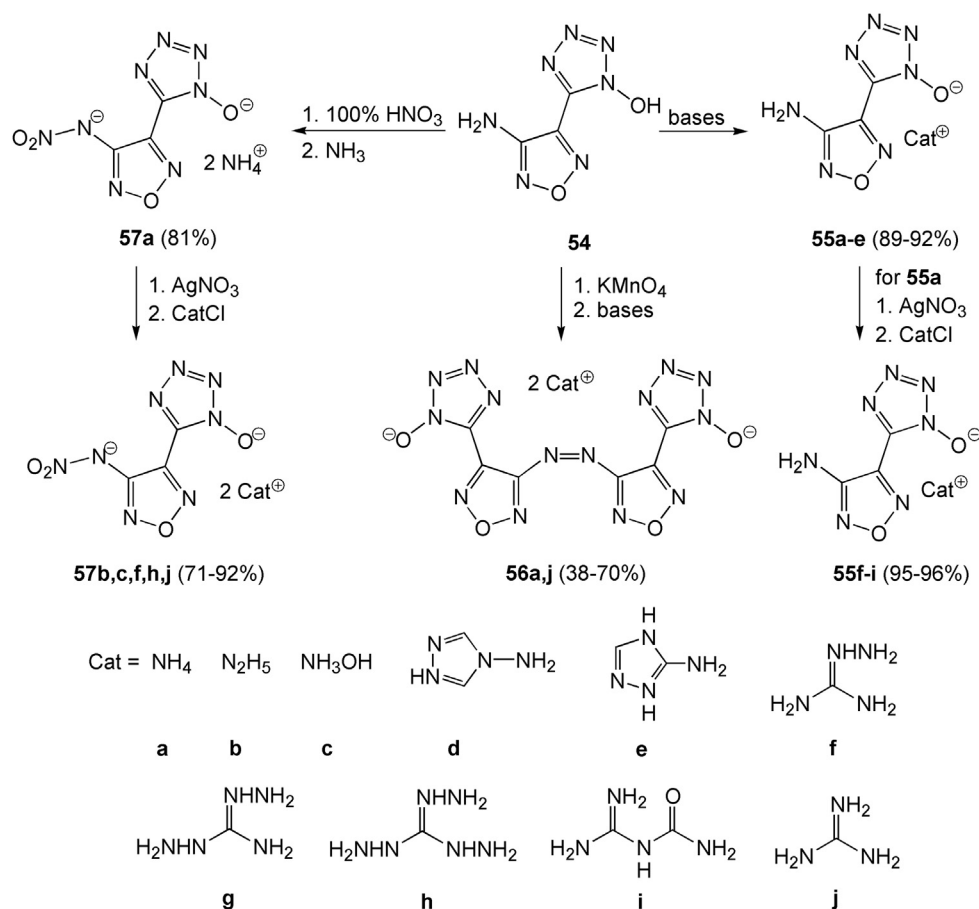
The hydroxytetrazole motif was also successfully incorporated in a number of HEDMs comprising of structurally diverse heterocyclic subunits. 4,5-Bis(1-hydroxytetrazolyl)-2H-1,2,3-triazole **34** was synthesized through a standard two-step procedure from the corresponding bis(chloroxime) **35** which was in turn prepared from 4,5-dicyano-2H-1,2,3-triazole **36**. Neutralization of compound **34** with free bases or their carbonate (bicarbonate) salts afforded a series of nitrogen-rich organic salts **37a-e** (Scheme 10).<sup>42</sup> Investigation of the functional properties of the synthesized HEDMs revealed that parent heterocyclic scaffold **34** is highly sensitive to impact, while salts **37a-c** are much less sensitive to impact and completely insensitive to friction. Ammonium and hydroxylammonium salts **37a,b** have good thermal stability and high

detonation performance which allows to consider them as a potential replacement to RDX (Table 6).

5-(1,2,4-Oxadiazolyl)-1-hydroxytetrazole **38** was prepared by a three-step conversion of the corresponding amidoxime **39**. Compound **39** was synthesized via a double condensation procedure of the commercially available unsubstituted glyoxime. Direct neutralization of the hydroxytetrazole **38** afforded a series of organic salts **40a-c** bearing small nitrogen-based cations (Scheme 11).<sup>43</sup> Although salts **40a-c** showed lower thermal stability than RDX and HMX, their nitrogen content is much higher which indicates their eco-friendliness. In addition, salts **40b,c** have the same detonation performance and mechanical sensitivity as RDX (Table 7).

Interaction of dicyanodifurazanyl ether **41** with hydroxylamine followed by nitrosation of formed bis(amidoxime) resulted in a formation of bis(chloroxime) **42**. A treatment of compound **42** with NaN<sub>3</sub> followed by



Scheme 14. Synthesis of (1-hydroxytetrazolyl)furazans.<sup>50,51</sup>Table 10  
Physicochemical properties and detonation performance of 54, 55c, h, 56a, 57c, f.<sup>50,51</sup>

Compound	54	55c	55h	56a	57c	57f	RDX	TATB
$T_d/^\circ\text{C}$	–	–	–	266	204	251	204	324
$N/\%$	58.0	55.5	66.7	60.9	50.0	61.9	37.8	32.5
$\Omega_{\text{CO}}/\%$	–23.7	–23.8	–44.0	–26.1	–5.7	–35.4	0	–18.6
$\Omega_{\text{CO}_2}/\%$	–52.1	–47.5	–67.4	–52.2	–22.9	–57.5	–21.6	–55.8
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.790	1.803	1.710	1.710	1.840	1.740	1.820	1.930
$\Delta H_f^\circ/\text{kJ}\cdot\text{mol}^{-1}$	441.0	454.5	712.5	1026.1	398.9	570.6	80.0	–139.3
$D/\text{m}\cdot\text{s}^{-1}$	8601	9100	8859	8456	9323	8755	8748	8144
$p/\text{GPa}$	30.0	33.4	29.0	27.7	38.3	28.8	34.9	31.2
IS/J	37	>50	45	17	14	>40	7.4	50
FS/N	>360	>360	>360	160	160	360	120	360

bubbling of gaseous HCl through an ethereal solution of intermediate bis(azidooxime) afforded 4,4'-oxybis[3,3'-(1-hydroxytetrazolyl)]furazan **43** which was converted to a series of nitrogen-cation salts **44a-d** and potassium salt **44e**. Treatment of compound **43** with lead(II) nitrate resulted in a destructive cleavage of initial ether **43** to form the corresponding salt **45** (Scheme 12).<sup>44,45</sup> All synthesized HEDMs **44a-e**, **45** have high thermal stability (>200 °C) and high enthalpies of formation. Compounds **44a-c** have excellent detonation performance ( $D = 8300\text{--}8900 \text{ m}\cdot\text{s}^{-1}$ ) on the level of RDX,<sup>44</sup> while lead-based derivative **45** has even higher detonation parameters ( $D = 9210 \text{ m}\cdot\text{s}^{-1}$ ;  $p = 50.9 \text{ GPa}$ ) and surprisingly low sensitivity to impact and friction (Table 8).<sup>45</sup>

Available 3-cyano-1,2,4-triazoles **46a-c**, 5-cyanotetrazolyl sodium salt **47** and (azidofurazanyl)chloroxime **48** may also serve as suitable substrates for the construction of biheteroaryl energetic materials incorporating the 1-hydroxytetrazole subunit. 5-(1,2,4-Triazolyl)-1-

hydroxytetrazoles **49a-c** were studied as is,<sup>46</sup> while hydroxytetrazoles **50** and **51** were converted to the corresponding nitrogen-rich energetic salts **52a-f** and **53a-c**, respectively (Scheme 13).<sup>47,48</sup> A similar synthetic approach was also employed for the preparation of bis(1-hydroxytetrazolyl)-1,2,5-oxadiazoles and a series of salts thereof.<sup>49</sup> Synthesized compounds have very high nitrogen content (up to 72%) and high enthalpies of formation (470–820 kJ·mol<sup>–1</sup>). 1-Hydroxytetrazoles **49a** and **51** bearing nitramine and azidofurazanyl motifs, respectively, showed very high sensitivity to impact and friction which restrict their application potential. At the same time, HEDMs **50** and **52a** comprising of a bitetrazole core have acceptable mechanical sensitivities and very good detonation performance exceeding those of RDX, which allows to consider them as environmentally benign secondary explosives (Table 9).

(4-Aminofurazanyl)-1-hydroxytetrazole **54** was found to be a valuable scaffold for the construction of a variety of low-sensitive highly

energetic HEDMs. It was used as an anion source for the synthesis of energetic salts **55a-i** either by direct neutralization or through a double metathesis procedure.<sup>50</sup> Oxidation of the amino group in compound **54** to the azo moiety with subsequent base treatment afforded nitrogen-rich derivatives **56a,j**. Amino group was also nitrated to the corresponding nitramine which was in situ neutralized to form the dianionic salt **57a**. Subsequent double cation metathesis provided a series of dianionic salts **57b,c,f,h,j** (Scheme 14).<sup>51</sup> All synthesized HEDMs have very high nitrogen content (>50%) and high enthalpies of formation (>400 kJ·mol<sup>-1</sup>). Furthermore, prepared materials have excellent detonation velocities (>8500 m·s<sup>-1</sup>) and very low sensitivity toward impact and friction (Table 10). These advantages enable the strong potential of the presented HEDMs as a promising replacement for various secondary explosives (RDX, HMX, TATB).

#### 4. Conclusion

In conclusion, the main achievements in the design and synthesis of hydroxytetrazole-based HEDMs were summarized. Various routes to the regioselective formation of both 1- and 2-hydroxytetrazole subunits and their energetic derivatives were discussed. Hydroxytetrazole was found to be a valuable heterocyclic scaffold for the preparation of various energy-rich materials. Due to the highly acidic nature of the hydroxy moiety, hydroxytetrazoles may serve as a synthetic platform for the construction of wide arrays of structurally diverse ionic energy-rich derivatives. Variation of explosophoric motifs at the tetrazole ring as well as of cationic counterparts resulted in a formation of multipurpose energetic materials which have high potential as environmentally benign primary and secondary explosives.

Taking into account the emerging development of heterocyclic chemistry, there is no doubt that hydroxytetrazole-based HEDMs will retain their leading position in the framework of materials science. In our opinion, a search of powerful HEDMs in a hydroxytetrazole series is far from being exhausted. A combined multidisciplinary investigation will gain deep insights in structure-property relationships and will also provide new industrial applications. A high level of environmental compatibility of hydroxytetrazole-based energetic materials will guarantee the sustainability of chemical processes. Finally, the authors of this review hope that it will stimulate researchers for further work in this field.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant #19-03-00069).

#### References

- O'Sullivan OT, Zdilla MJ. Properties and promise of catenated nitrogen systems as high-energy-density materials. *Chem Rev.* 2020;120(12):5682–5744.
- Ma X, Li Y, Hussain I, Shen R, Yang G, Zhang K. Core-shell structured nanoenergetic materials: Preparation and fundamental properties. *Adv Mater.* 2020;32(30):2001291.
- Klapötke TM. *Energetic Materials Encyclopedia*. Berlin: De Gruyter; 2018.
- Klapötke TM. *Chemistry of High-Energy Materials*. 3rd ed. Berlin: De Gruyter; 2015.
- Bernstein A, Ronen Z. Biodegradation of the explosives TNT, RDX and HMX. In: *Microbial Degradation of Xenobiotics*. Berlin, Heidelberg: Springer; 2012:135–176.
- Kuchurov IV, Zharkov MN, Fershtat LL, Makhova NN, Zlotin SG. Prospective symbiosis of green chemistry and energetic materials. *ChemSusChem.* 2017;10(20):3914–3946.
- Matyás R, Pachman J. *Primary Explosives*. Berlin: Springer-Verlag; 2013:2–6.
- Fershtat LL, Makhova NN. 1,2,5-Oxadiazole-based high-energy-density materials: Synthesis and performance. *ChemPlusChem.* 2020;85(1):13–42.
- Yin P, Shreeve JM. Nitrogen-rich azoles as high density energy materials: Reviewing the energetic footprints of heterocycles. *Adv Heterocycl Chem.* 2017;121:89–131.
- Gao H, Zhang Q, Shreeve JM. Fused heterocycle-based energetic materials (2012–2019). *J Mater Chem.* 2020;8(8):4193–4216.
- Larin AA, Shaferov AV, Epishina MA, Melnikov IN, Muravyev NV, Ananyev IV, Fershtat LL, Makhova NN. Pushing the energy-sensitivity balance with high-performance bifuroxans. *ACS Appl Energy Mater.* 2020;3(8):7764–7771.
- Qian L, Yang H, Xiong H, Gu H, Tang J, Xue Y, Cheng G. Low sensitive energetic material based on the combination of furoxan and 1,3,4-oxadiazole structures. *Energ Mater Front.* 2020;1(2):74–82.
- Voronin AA, Fedyanin IV, Churakov AM, Pivkina AN, Muravyev NV, Strelenko YuA, Klenov MS, Lempert DB, Tartakovskiy VA. 4H-[1,2,3]Triazolo[4,5-c][1,2,5]oxadiazole 5-oxide and its salts: Promising multipurpose energetic materials. *ACS Appl Energy Mater.* 2020;3(9):9401–9407.
- Leonov NE, Klenov MS, Anikin OV, Churakov AM, Strelenko YuA, Monogarov KA, Tartakovskiy VA. First synthesis of aliphatic nitro-NNO-azoxy compounds. *Eur J Org Chem.* 2019;2019(1):91–94.
- Fershtat LL, Ovchinnikov IV, Epishina MA, Romanova AA, Lempert DB, Muravyev NV, Makhova NN. Assembly of nitrofurazan and nitrofurazan frameworks for high-performance energetic materials. *ChemPlusChem.* 2017;82(11):1315–1319.
- Wurzenberger MH, Endrass SMJ, Lommel M, Klapötke TM, Stierstorfer J. Comparison of 1-propyl-5H-tetrazole and 1-azidopropyl-5H-tetrazole as ligands for laser ignitable energetic materials. *ACS Appl Energy Mater.* 2020;3(4):3798–3806.
- Zheng Y, Zhao X, Qi X, Wang K, Liu T. Synthesis of 5-(1H-pyrazol-1-yl)-2H-tetrazole-derived energetic salts with high thermal stability and low sensitivity. *Energ Mater Front.* 2020;1(2):83–89.
- Wurzenberger MH, Lommel M, Grubbe MS, Szimhardt N, Stierstorfer J. Refinement of copper(II) azide with 1-alkyl-5H-tetrazoles: Adaptable energetic complexes. *Angew Chem Int Ed.* 2020;59(30):12367–12370.
- Gorn MV, Gritsan NP, Goldsmith F, Kiselev VG. Thermal stability of bis-tetrazole and bis-triazole derivatives with long catenated nitrogen chains: Quantitative insights from high-level quantum chemical calculations. *J Phys Chem.* 2020;124(38):7665–7677.
- He P, Zhang J-G, Yin X, Wu J-T, Wu L, Zhou Z-N, Zhang T-L. Energetic salts based on tetrazole N-oxide. *Chem Eur J.* 2016;22(23):7670–7685.
- Göbel M, Karaghiosoff K, Klapötke TM, Piercey DG, Stierstorfer J. Nitrotetrazolate-2N-oxides and the strategy of N-oxide introduction. *J Am Chem Soc.* 2010;132(48):17216–17226.
- Klapötke TM, Piercey DG, Stierstorfer J. The taming of CN<sup>-</sup>: The azidotetrazolate 2-oxide anion. *Chem Eur J.* 2011;17(46):13068–13077.
- Boneberg F, Kirchner A, Klapötke TM, Piercey DG, Poller MJ, Stierstorfer J. A study of cyanotetrazole oxides and derivatives thereof. *Chem Asian J.* 2013;8(1):148–159.
- Fischer N, Fischer D, Klapötke TM, Piercey DG, Stierstorfer J. Pushing the limits of energetic materials – The synthesis and characterization of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate. *J Mater Chem.* 2012;22(38):20418–20422.
- Fischer N, Gao L, Klapötke TM, Stierstorfer J. Energetic salts of 5,5'-bis(tetrazole-2-oxide) in a comparison to 5,5'-bis(tetrazole-1-oxide) derivatives. *Polyhedron.* 2013;51:201–210.
- Muravyev NV, Monogarov KA, Asachenko AF, Nechaev MS, Ananyev IV, Fomenkov IV, Kiselev VG, Pivkina AN. Pursuing reliable thermal analysis techniques for energetic materials: decomposition kinetics and thermal stability of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50). *Phys Chem Chem Phys.* 2017;19(1):436–449.
- Xiao L, Guo S, Su H, Gou B, Liu Q, Hao G, Hu Y, Wang X, Jiang W. Preparation and characteristics of a novel PETN/TKX-50 co-crystal by a solvent/non-solvent method. *RSC Adv.* 2019;9(16):9204–9210.
- Pang W-Q, Wang K, Zhang W, DeLuca LT, Fan X-Z, Li J-Q. CL-20-Based cocrystal energetic materials: Simulation, preparation and performance. *Molecules.* 2020;25(18):4311.
- Zhang J, Jin B, Peng R, Niu C, Xiao L, Guo Z, Zhang Q. Novel strategies for synthesizing energetic materials based on BTO with improved performances. *Dalton Trans.* 2019;48(31):11848–11854.
- Zhao G, He C, Yin P, Imler GH, Parrish DA, Shreeve JM. Efficient construction of energetic materials via nonmetallic catalytic Carbon–Carbon cleavage/oxime-release-coupling reactions. *J Am Chem Soc.* 2018;140(10):3560–3563.
- Zhang Q, Chen D, Jing D, Fan G, He L, Li H, Wang W, Nie F. Access to green primary explosives via constructing coordination polymers based on bis-tetrazole oxide and non-lead metals. *Green Chem.* 2019;21(8):1947–1955.
- Su Q, Wang XJ, Shu QH, Chen SS, Jin SH, Li LJ. Synthesis, crystal structure, and properties of energetic complexes constructed from transition metal cations (Fe, Co, Cu, and Pb) and BTO<sup>2-</sup>. *J Heterocycl Chem.* 2017;54(6):3227–3234.
- Shang Y, Jin B, Peng R, Guo Z, Liu Q, Zhao J, Zhang Q. Nitrogen-rich energetic salts of 1H,1'H-5,5'-bistetrazole-1,1'-diolate: Synthesis, characterization, and thermal behaviors. *RSC Adv.* 2016;6(54):48590–48598.
- Niu C, Jin B, Shang Y, Liu Q, Peng R. Synthesis, characterization, and thermal analysis of a new energetic salt based on 1'-hydroxy-1H,1'H-5,5'-bitetrazole-1-olate. *J Energetic Mater.* 2018;36(2):236–246.
- Shang Y, Jin B, Liu Q, Peng R, Guo Z, Zhang Q. Synthesis, thermal behavior, and energetic properties of diuronium 1H,1'H-5,5'-bistetrazole-1,1'-diolate salt. *J Mol Struct.* 2017;1133:519–525.
- Yang T, Zhang Z-B, Zhang J-G. Two energetic salts based on 5,5'-Bitetrazole-1,1'-diolate: Syntheses, characterization, and properties. *Z Anorg Allg Chem.* 2017;643(6):413–419.
- Tao J, Jin B, Chu S, Peng R, Shang Y, Tan B. Novel insensitive energetic-cocrystal-based BTO with good comprehensive properties. *RSC Adv.* 2018;8(4):1784–1790.

38. Luo L, Jin B, Peng R, Shang Y, Xiao L, Chu S. Preparation and characterization of nitrogen-rich bis-1-methylimidazole 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate energetic salt. *J Therm Anal Calorim*. 2019;135(6):3005–3013.
39. Fischer D, Klapötke TM, Piercey DG, Stierstorfer J. Synthesis of 5-aminotetrazole-1*N*-oxide and its azo derivative: A key step in the development of new energetic materials. *Chem Eur J*. 2013;19(14):4602–4613.
40. He P, Zhang J-G, Wu L, Wu J-T, Zhang T-L. Magnesium azotetrazole-1,1'-dioxide: Synthesis and promising properties of green insensitive energetic materials. *Z Anorg Allg Chem*. 2017;643(6):432–436.
41. Zhang J, Jin B, Li X, Hao W, Huang T, Lei B, Guo Z, Shen J, Peng R. Study of H<sub>2</sub>AzTO-based energetic metal-organic frameworks for catalyzing the thermal decomposition of ammonium perchlorate. *Chem Eng J*. 2021;404:126287.
42. Dippold AA, Izsak D, Klapötke TM, Pflüger C. Combining the advantages of tetrazoles and 1,2,3-triazoles: 4,5-Bis(tetrazol-5-yl)-1,2,3-triazole, 4,5-Bis(1-hydroxytetrazol-5-yl)-1,2,3-triazole, and their energetic derivatives. *Chem Eur J*. 2016;22(5):1768–1778.
43. Yan C, Wang K, Liu T, Yang H, Cheng G, Zhang Q. Exploiting the energetic potential of 1,2,4-oxadiazole derivatives: combining the benefits of a 1,2,4-oxadiazole framework with various energetic functionalities. *Dalton Trans*. 2017;46(41):14210–14218.
44. Tang Y, He C, Imler GH, Parrish DA, Shreeve JM. Energetic 4,4'-Oxybis[3,3'-(1-hydroxytetrazolyl)]furan and its salts. *Chem Asian J*. 2016;11(21):3113–3117.
45. Hao W, Jin B, Zhang J, Li X, Huang T, Shen J, Peng R. Novel energetic metal-organic frameworks assembled from the energetic combination of furazan and tetrazole. *Dalton Trans*. 2020;49(19):6295–6301.
46. Dippold AA, Izsak D, Klapötke TM. A study of 5-(1,2,4-triazol-C-yl)tetrazol-1-ols: Combining the benefits of different heterocycles for the design of energetic materials. *Chem Eur J*. 2013;19(36):12042–12051.
47. Fischer D, Klapötke TM, Reymann M, Schmid PC, Stierstorfer J, Suceška M. Synthesis of 5-(1*H*-tetrazolyl)-1-hydroxy-tetrazole and energetically relevant nitrogen-rich ionic derivatives. *Propellants Explos Pyrotech*. 2014;39(4):550–557.
48. Zhang J, Yin P, Pan G, Wang Z, Zhang J, Mitchell LA, Parrish DA, Shreeve JM. 5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole and its derivatives: from green primary to secondary explosives. *New J Chem*. 2019;43(32):12684–12689.
49. Fischer D, Klapötke TM, Reymann M, Stierstorfer J, Völkl MBR. Energetic alliance of tetrazole-1-oxides and 1,2,5-oxadiazoles. *New J Chem*. 2015;39(3):1619–1627.
50. Zhang J, Mitchell LA, Parrish DA, Shreeve JM. Enforced layer-by-layer stacking of energetic salts towards high-performance insensitive energetic materials. *J Am Chem Soc*. 2015;137(33):10532–10535.
51. Wei H, Zhang J, He C, Shreeve JM. Energetic salts based on furazan-functionalized tetrazoles: routes to boost energy. *Chem Eur J*. 2015;21(23):8607–8612.



**Alexander Larin** graduated from the Lomonosov Moscow State University in 2015 (Department of Chemistry). He received his Ph.D. degree from the N. D. Zelinsky Institute of Organic Chemistry in 2019 under the supervision of Prof. N. N. Makhova. Currently, he is a researcher in the same institute. His scientific interests include development of novel synthetic methodologies in the field of nitrogen-containing heterocycles, especially, high-energy 1,2,5-oxadiazoles 2-oxides (furoxans).



**Leonid Fershtat** graduated from the D. I. Mendeleev University of Chemical Technology in 2012 (faculty Higher Chemical College of the Russian Academy of Sciences). He received his Ph.D. degree from the N. D. Zelinsky Institute of Organic Chemistry in 2015 under the supervision of Prof. N. N. Makhova. In 2020, he finished his habilitation studies in the same institute. His scientific interests include a creation of novel methodologies in the synthesis and transformations of nitrogen-containing heterocycles, and search for pharmacologically active and high energy heterocyclic derivatives.