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Alexander Larin, Alexander Shaferov, Margarita Epishina, Igor Melnikov,
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Pushing the energy-sensitivity balance with high-performance bifuroxans

*Alexander A. Larin,^a Alexander V. Shaferov,^a Margarita A. Epishina,^a Igor Melnikov,^b Nikita V. Muravyev,^{*b} Ivan V. Ananyev,^{c,d} Leonid L. Fershtat,^{*a} Nina N. Makhova^a*

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

^b N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences,
4 Kosygin Str., Moscow 119991 (Russian Federation)

^c A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
Vavilova str., 28, Moscow, 119991 (Russian Federation)

^d National Research University Higher School of Economics, Moscow, 101000 (Russian Federation)

KEYWORDS: energetic materials, furoxan, 1,2,5-oxadiazole, nitrogen heterocycles, detonation performance.

ABSTRACT: Several energy-rich bifuroxans incorporating nitro and azido functionalities have been synthesized and thoroughly characterized by IR and multinuclear NMR spectroscopy, elemental analysis, single-crystal X-ray diffraction and differential scanning calorimetry. *N*-oxide

regiochemistry was employed to design the tunable azido(nitro)bifuroxans with different physicochemical and energetic properties. All synthesized compounds have high enthalpies of formation (449-777 kJ mol⁻¹) and attractive performance evidenced by high detonation velocity (8.95-9.75 km s⁻¹) and Champan-Jouguet pressure (35-45 GPa). The most powerful energetic material in this series is 4,4'-dinitro-3,3'-bifuroxan. This hydrogen-free molecule (C₄N₆O₈) exhibits an outstanding heat of explosion value of 15.3 kJ cm⁻¹ far exceeding the top energetic material hexanitrohexaazaisowurtzitane CL-20. At the same time, the impact and friction sensitivities of 4,4'-dinitro-3,3'-bifuroxan deemed acceptable for practical use. Overall, 4,4'-dinitro-3,3'-bifuroxan breaks a general trend called “energy-sensitivity rule” representing a linear increase of mechanical sensitivity with a growth of energetic content of the molecule and, thus, offers a great promise for future applications.

INTRODUCTION

Design and synthesis of novel organic functional materials became an emergent topic in recent years with significant focus on high-energy density materials (HEDMs).^{1,2} The development of energetic materials can be illustrated by the following row of common explosives: trinitrotoluene (TNT), hexogen (RDX), octogen (HMX). Unfortunately, these substances suffer from harsh methods for their synthesis and a lack of environmental compatibility that leaves much room for a possible improvement.^{3,4} From the application prospective, an increase of energetic performance of novel HEDMs along with their balanced physicochemical properties are constantly required. However, it has been realized that for a wide range of substances there is a strict linear relationship between mechanical sensitivity and energy content, which is called an “energy-sensitivity rule”.⁵ Although a less deterministic compilation has been reported, a wide applicability of the discussed

rule was verified many times.⁶ Latest generation of HEDMs represented by the caged structures, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)^{7,8} and octanitrocubane (ONC)⁹ falls in the above pattern by delivering more energy along with increased hazards. Moreover, the low cost efficiency of their synthesis and low level of their eco-friendliness restrict their widespread use. Therefore, a search of novel energetic materials with superior performance and acceptable sensitivity, whilst adhering to strict demands regarding safe preparation, isolation and handling, remains highly urgent.

Over the last few decades considerable interest has been focused on the design and synthesis of new energetic compounds representing a combination of aromatic nitrogen-oxygen heterocycles and energetic functional groups such as NO₂, N₃, NHNO₂, N=N, and N=N(O) as substituents.^{10,11} In this sense, 1,2,5-oxadiazole (furazan) and its *N*-oxide (furoxan) attract significant attention due to high positive enthalpies of formation (196.8 and 198.5 kJ mol⁻¹, respectively) and a huge nitrogen-oxygen content presented within the core. Moreover, functionalization of the 1,2,5-oxadiazole backbone enables a preparation of energetic materials with high density and improved properties.¹²⁻¹⁵

Synthetic design of 1,2,5-oxadiazole ring assemblies linked directly *via* a C-C bond emerged recently. In this regard, the non-hydrogen HEDMs incorporating a ter-1,2,5-oxadiazole (either furazan or furoxan) framework have been synthesized.¹⁶⁻¹⁹ Meanwhile, the covalent bi-1,2,5-oxadiazole derivatives are far less explored, although they are expected to be more energetic due to a higher nitrogen-oxygen content and an increased density.²⁰ For example, 4,4'-dinitro-3,3'-bifurazan (DNBF) revealed a high detonation velocity (9.2 km s⁻¹) and good thermal stability.²¹ Recently, our group synthesized two regioisomeric dinitro(furazanyl)furoxans DNFF-1 and DNFF-2 which were more dense compared to DNBF and revealed comparable performance.²²

Also, there is an example of 4,4'-dinitro-3,3'-bifuroxan **1** – a highly energetic compound with zero oxygen balance to CO₂ and high density of 1.97 g cm⁻³ (at 298 K). However, this promising energetic compound **1** was isolated only as a few crystals suitable for X-ray study, while its properties including spectral characteristics, thermal stability and mechanical sensitivity have not been determined because of irreproducible synthesis and insufficient amount of material.²³

Herein, we report an improved scalable procedure for the preparation of 4,4'-dinitro-3,3'-bifuroxan **1** along with the synthesis of 3- and 4-nitrobifuroxans **2** and **3** (Fig. 1) incorporating an azide moiety that aims to enhance the energetic properties. Since it is known that both density and thermal stability of 3- and 4-nitrofuroxan isomers are usually different,^{17,22} this type of *N*-oxide regioisomerism is considered as a possible strategy to manage the performance of furoxan-based energetic materials.

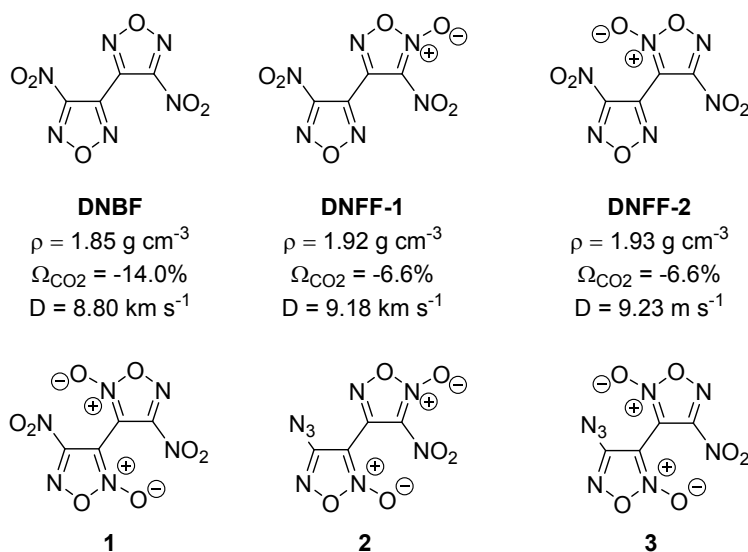
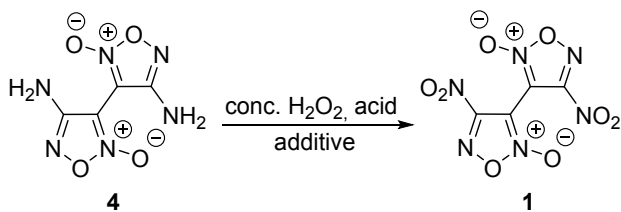


Figure 1. Previously reported and newly synthesized bi-1,2,5-oxadiazole HEDMs.

RESULTS AND DISCUSSION

Previously, T.M. Klapötke et al. conducted an oxidation of 4,4'-diamino-3,3'-bifuroxan **4**, however the target dinitro compound **1** was isolated only in trace amounts.²³ To establish a reliable and reproducible method for the preparation of the target HEDM, an optimization of oxidation conditions was performed. Initial diamine **4** was synthesized according to a previously described scalable procedure.²³ Our attempt to reproduce known oxidation conditions resulted in target 4,4'-dinitro-3,3'-bifuroxan **1**, albeit in a low yield (Table 1, entry 1). Arguably, such reaction outcome is attributed to the extremely low basicity and nucleophilicity of the amino group due to the exceptionally strong electron-withdrawing effect of the bifuroxan framework. Therefore, we performed an oxidation using highly concentrated H₂O₂ (93%) and a reduced amount of an additive. To our delight, a utilization of 93% H₂O₂ and 1 equiv. of (NH₄)₂S₂O₈ or Na₂WO₄ afforded compound **1** in 35-38% yield (entries 2,3). A replacement of H₂SO₄ with MeSO₃H provided higher yields of the target product **1** (entries 4-7) and an optimal additive was found to be 2 equiv. of Na₂WO₄ (entry 5). Therefore, under these conditions 4,4'-dinitro-3,3'-bifuroxan **1** was synthesized in a 64% yield.

Table 1. Optimization of the reaction conditions for the synthesis of compound **1**.^[a]

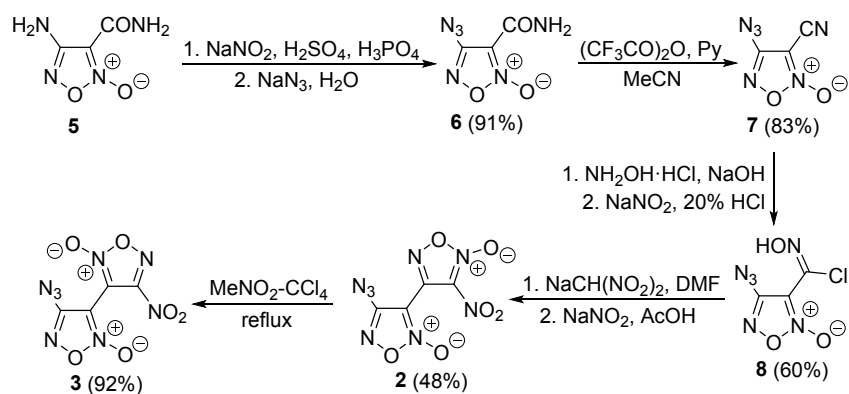


Entry	Concentration of H ₂ O ₂ , %	Acid	Additive (equiv.)	Time, h	Yield, % ^[b]
1 ^[c]	50	98% H ₂ SO ₄	(NH ₄) ₂ S ₂ O ₈ (12)	5	Trace ^[d]
2	93	98% H ₂ SO ₄	(NH ₄) ₂ S ₂ O ₈ (1)	4	38
3	93	98% H ₂ SO ₄	Na ₂ WO ₄ ·2H ₂ O (1)	4	35
4	93	MeSO ₃ H	Na ₂ WO ₄ ·2H ₂ O (1)	4	58

5	93	MeSO ₃ H	Na ₂ WO ₄ ·2H ₂ O (2)	4	64
6	93	MeSO ₃ H	Na ₂ WO ₄ ·2H ₂ O (3)	4	55
7	93	MeSO ₃ H	(NH ₄) ₂ S ₂ O ₈ (2)	4	41

[a] Reaction conditions: conc. H₂O₂ (10 mL), acid (3 mL), additive, 5-10 °C, then diamine **4** (1 mmol), 20 °C. [b] Isolated yields. [c] Reaction conditions used are described in.^[9] [d] Determined by TLC and ¹⁴N NMR spectroscopy.

Synthetic route to the energetic azido derivatives **2** and **3** involves the use of 4-aminofuroxan-3-carboxamide **5** easily synthesized according to a previously established procedure.²⁴ Tandem diazotization/azo coupling reaction of compound **5** resulted in a formation of azidofuroxan **6**, which upon dehydration was transformed into nitrile **7**. Two-step post-modification of a nitrile functionality provided (furoxanyl)chloroxime **8** which was involved in a one-pot cascade acylation/nitrosation/cyclization process to afford target 3-nitrobifuroxan **2** (Scheme 1; for mechanism for the formation of **2**, see SI). Although energetic derivative **2** has previously been reported,²⁵ its physical and energetic properties have not been studied. To estimate the influence of a position of the *N*-oxide motif in regioisomeric pairs on properties and performance, 3-nitrofuroxanyl moiety in compound **2** was isomerized thermally to the corresponding 4-nitrobifuroxan **3**. This unimolecular reaction was found to proceed almost quantitatively under reflux in a mixture of MeNO₂-CCl₄ (binary azeotrope 34:66, mol/mol, bp 71.3 °C), while at heating in other solvents (THF, CCl₄, PhH, dioxane) a fast decomposition of starting material was observed.



Scheme 1. Synthesis of azido derivatives **2** and **3**.

All compounds were characterized by IR and multinuclear (^{13}C , ^{14}N) NMR spectroscopy and elemental analysis. ^{14}N NMR spectrum of dinitrobifuroxan **1** indicated a presence of a single peak for both nitro groups (-37.0 ppm) due to the symmetry of the molecule. For each of two isomers **2** and **3** two signals in ^{14}N NMR spectra were observed, assigned to nitro (-42.7 and -38.7 ppm, respectively) and azido (-149.6 and -148.3 ppm, respectively) groups (Fig. 2). Since 3- NO_2 group is located more upfield than 4- NO_2 group in regioisomeric nitrofuroxans,^{22,26} ^{14}N NMR spectroscopy reliably distinguishes 3- and 4-nitrofuroxan regioisomers. 4,4'-Dinitro-3,3'-bifuroxan **1** was additionally characterized by ^{15}N NMR spectroscopy (Fig. 3). The chemical shift of *N*-oxide nitrogen atoms occurred more downfield (-7.7 ppm) in comparison with N(5) atoms (-21.6 ppm) of the furoxan rings. This assignment was accomplished according to the literature values of resonance peaks in similar compounds.¹⁴ Both nitro groups nitrogen atoms resonate at -37.4 ppm which is similar to ^{14}N NMR spectroscopy data.

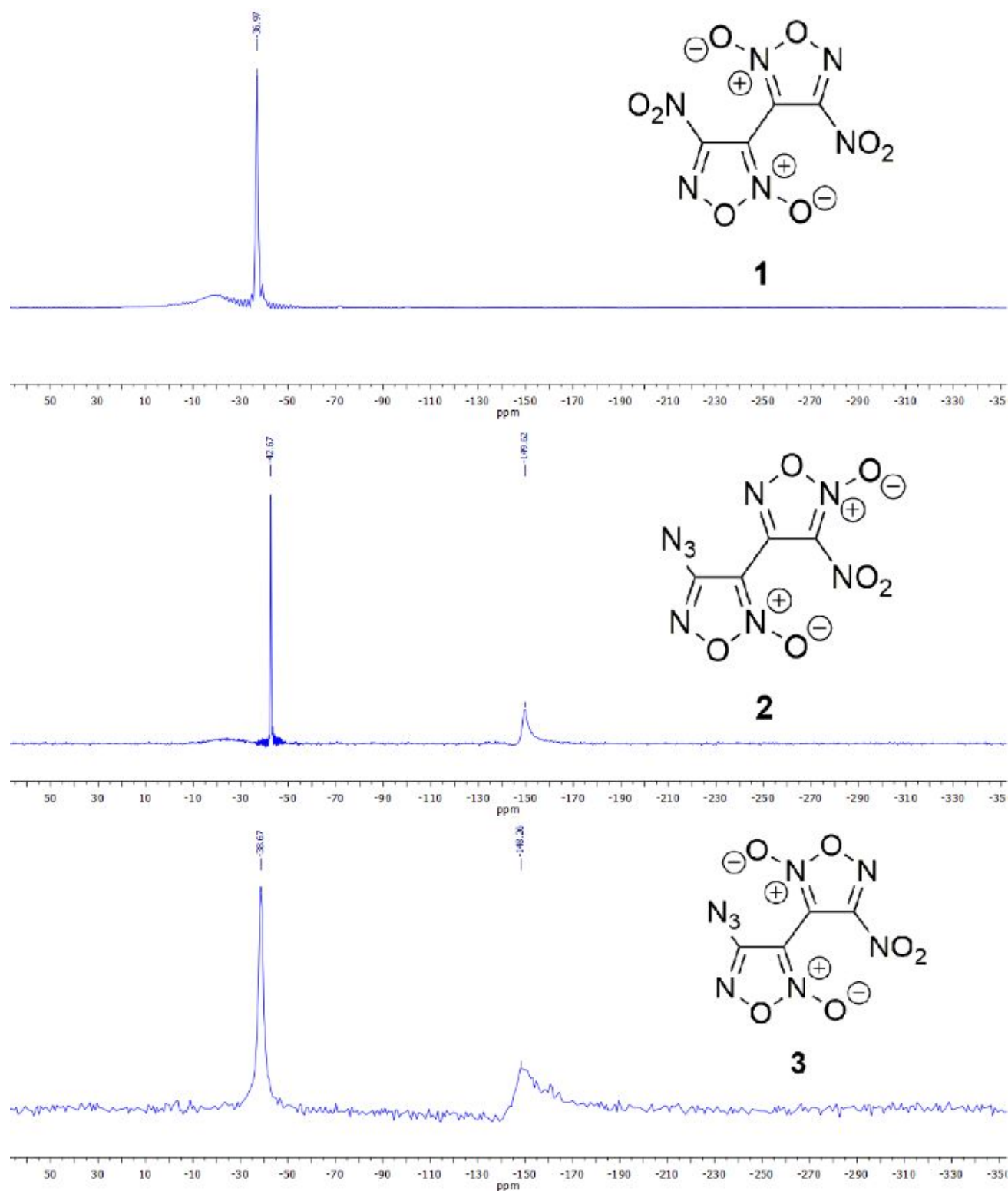


Figure 2. ^{14}N NMR spectra for compounds 1-3.

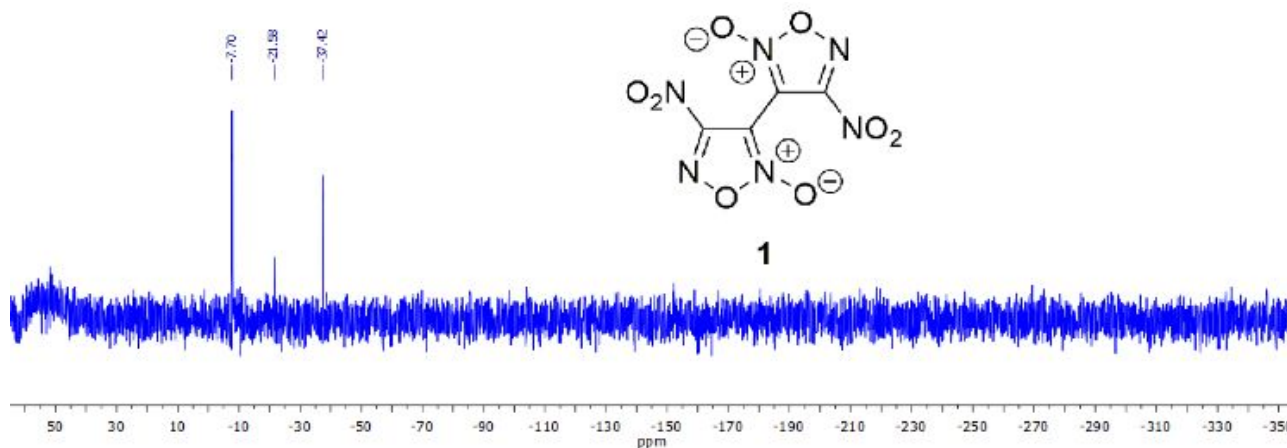


Figure 3. ^{15}N NMR spectrum for compound **1**.

The conclusive data on the structure of azidofuroxan **3** were obtained by the single-crystal X-ray diffraction study (Fig. 4). The comparison of **3** with the previously published²³ structure of **1** (Figure S1, see SI) was made to explore the influence of furoxan substituents on density and other relevant crystal properties. The more compact, Z-like configuration of **1** results in the formation of the short intramolecular contacts between NO_2 groups and between N-oxide fragments ($\text{O}\cdots\text{O}$ 3.001 and 2.951 Å, respectively). The absence of noncovalent interactions determines the only difference between molecular structures of bifuroxans **1** and **3** – the mutual orientation of the furoxan rings defined by the C-C-C-C torsion angle (54° and $114.7(2)^\circ$ for **1** and **3**, respectively).

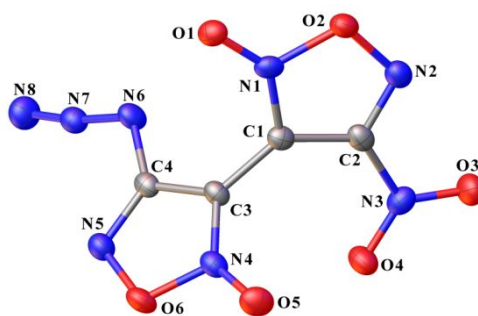


Figure 4. The structure of azidofuroxan **3** according to the X-ray diffraction study. Atoms are given as probability ellipsoids of atomic displacements ($p=0.5$).

According to the PBE0-D3/6-311++G(d,p) calculations, the qualitative difference between **1** and **3** holds in the isolated state (Fig. 5). The molecule of **1** was found to be significantly more rigid with respect to environment effects: the corresponding torsion angle in a gas phase is close to that in crystal (53°) and the r.m.s deviation between crystal and isolated structures is small (ca. 0.07 \AA). In contrast, molecule of **3** is more flexible and increases the C-C-C-C torsion angle up to 128° upon the crystal-to-gas transition. Along with the rotation of N_3 group against adjacent furoxan plane (on 10°) this feature results in the large r.m.s. deviation between crystal and gas structures of **3** (ca. 0.27 \AA).

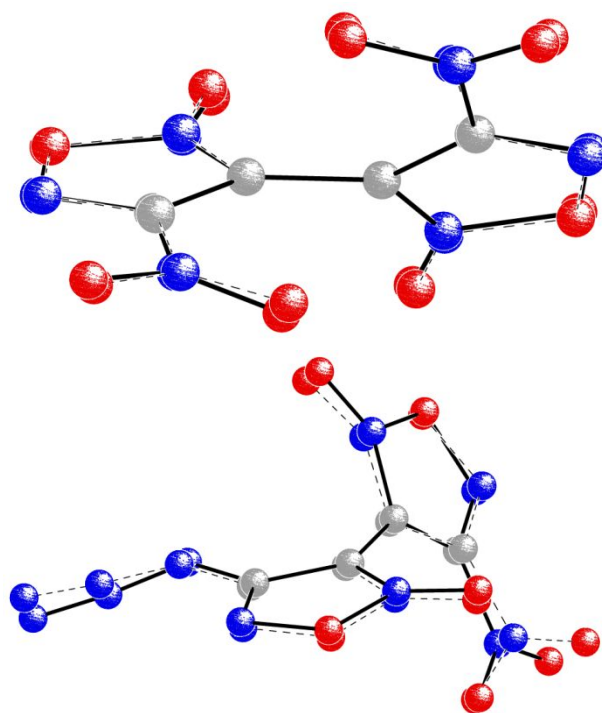


Figure 5. The overlap of crystal (solid lines) and equilibrium gas (dashed lines) structures of molecules **1** (left) and **3** (right).

It is interesting to note, that in contrast to 4,4'-dinitro-3,3'-bifuroxan **1** strong intermolecular interactions in azidobifuroxan **3** are nearly absent. The crystal packing of **3** is defined only by shortened intramolecular contacts between functional groups. At the same time, a replacement of

an azide moiety with a nitro group results in strong intermolecular O...O contacts in the structure of 4,4'-dinitro-3,3'-bifuroxan **1**, which results in a density increase (Fig. 6).

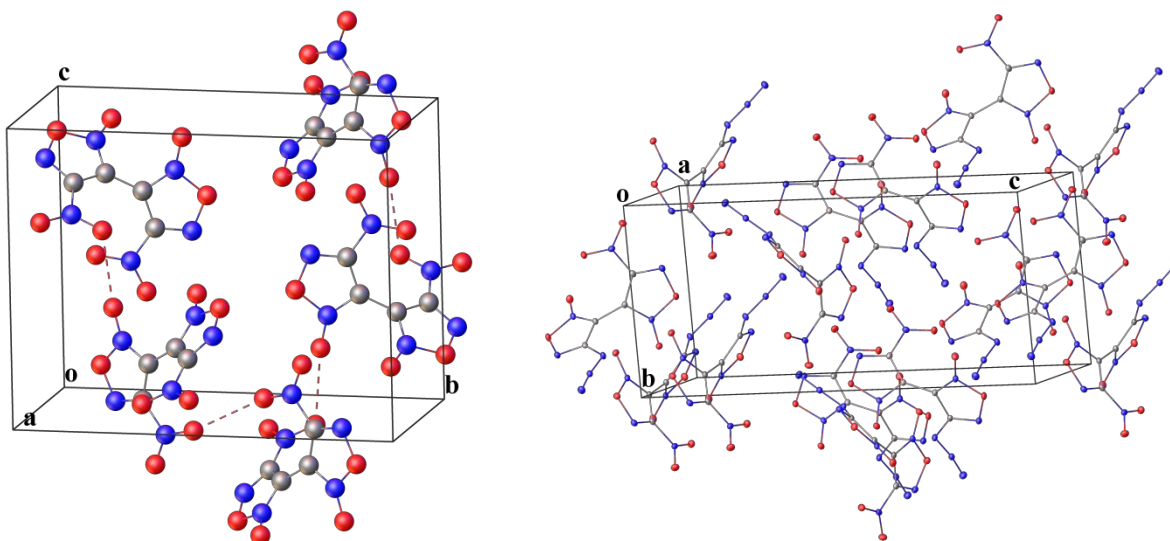


Figure 6. A fragment of crystal packing of **1** and **3**.

Notably, the more rigid and compact molecule of **1** produces crystals of the larger density: d_{cryst} is $2.007 \text{ g}\cdot\text{cm}^{-3}$ at 173K for **1**²³ and $1.883 \text{ g}\cdot\text{cm}^{-3}$ at 120K for **3** ($1.876 \text{ g}\cdot\text{cm}^{-3}$ according to additional measurements at 173K). Overall, experimental densities at 298 K for both azidobifuroxans **2** and **3** ($1.75\text{-}1.83 \text{ g cm}^{-3}$) are lower than that of dinitrobifuroxan **1** (1.97 g cm^{-3}). The formalism proposed by Prof. Suponitsky^{27,28} was then invoked to elucidate differences in intra- and intermolecular contributions into density of the crystals. This method is based on the separate consideration of density of a molecule itself (isolated molecule, d_{mol}) and its increase upon formation of a crystal structure (Δ_{OED}) (details can be found in SI). As theoretical analysis show, an incorporation of the azide fragment slightly decreases crystal density mainly due to the relative supramolecular inactivity of an azide moiety in comparison to the nitro and furoxan fragments. The presence of a higher number of *N*-oxide fragments in compound **1** increases its density

comparing with the corresponding difurazan or (furazanyl)furoxan analogues, i.e., DNTF, DNFF-1, DNFF-2 (Fig. S3, see SI).

Thermal behavior was studied with differential scanning calorimetry (DSC) as shown in Figure 7. Two regioisomeric azidobifuroxans **2** and **3** revealed the similar decomposition behavior illustrated by a marked exothermic peak starting at 110 °C and later weak heat evolution around 220 °C. The only difference between two isomers was in a melting peak present at 87 °C for **3**, and absent for **2** (the sample represents a viscous liquid). 4,4'-Dinitro-3,3'-bifuroxan **1** is the most thermally stable among considered bifuroxans with the decomposition starting just after melting at 135 °C. Caloric signal measured under atmospheric pressure shows some spikes characteristic for boiling behavior (Fig. S4, see SI), while the application of elevated pressure of 2 MPa reveals smooth trace as presented on Figure 7 and resolves a short region between melting and decomposition events.

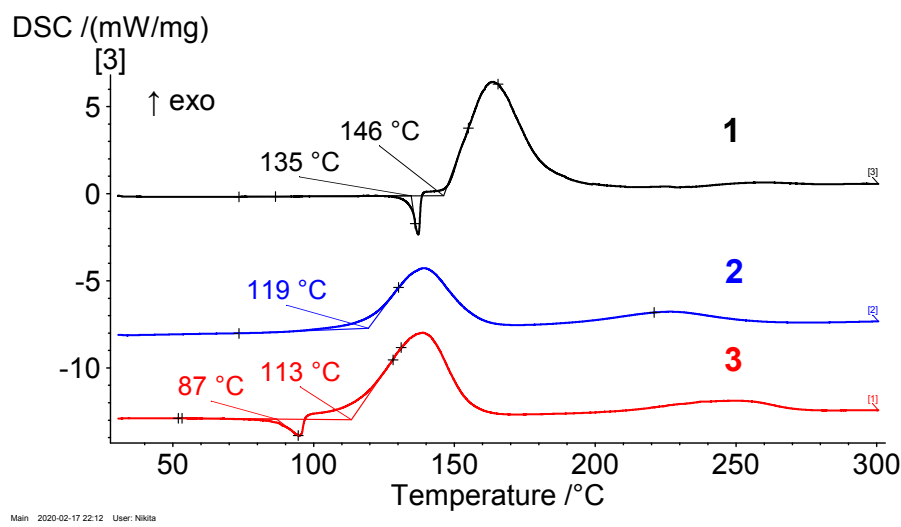


Figure 7. Differential scanning calorimetry for bifuroxans **1-3** taken at heating rate of 5 K min⁻¹.

Impact and friction sensitivities for solids **1**, **3** and several reference compounds were determined using standard procedures,^{29,30} whereas for a liquid sample **2** the impact sensitivity was obtained

with an assembly with free volume according to recommendations.³¹ Bifuroxan **1** has the same impact sensitivity (3.9 ± 0.2 J) as the high-energy hexanitroisowurtzitane CL-20, while the solid azide **3** is more sensitive (2.0 ± 0.7 J). The liquid **2** has a high sensitivity (0.7 ± 0.2 J), but it is more safe than a benchmark liquid explosive nitroglycerin (NG showed 100% probability of explosions at the lower limit in our experiments). Friction sensitivity for both HEDMs **1**, **3** is near 30 N indicating their higher sensitivity than that of nitroesters.

All synthesized bifuroxans **1-3** have high nitrogen content (32.3-43.8%) and attractive oxygen balance being close to zero. Along with the chemical balance and the crystal density, thermochemistry plays a crucial role in performance of the energetic material. The enthalpy of formation $\Delta H_{f, \text{solid}}^0$ for species was computed with the Gaussian09 software package (see SI for details).³² It was found that compounds **1-3** have high positive enthalpies of formation, exceeding that of commonly used explosives (Table 2). Regioisomers **2** and **3** revealed the higher enthalpies of formation ($762\text{--}777$ kJ mol⁻¹) than 4,4'-dinitro-3,3'-bifuroxan **1** (449 kJ mol⁻¹) due to the presence of an azide functional group.

Calculation of the detonation velocities (D) and pressures (P) was performed using the several literature methods.³³⁻³⁵ The output of these computational approaches has been verified over a wide set of experimental data from compilations,^{36,37} and method by Pepekina and Lebedev³⁸ was shown to give a minimal error on the subset of CNO compounds (see SI for details). Overall, the detonation performance for newly synthesized and reference energetic materials is listed in Table 2. It was found that liquid 3-nitrofuroxan **2** exhibits the high detonation parameters (8.95 km s⁻¹, 35.2 GPa) which are superior to the benchmark nitroglycerin explosive (7.80 km s⁻¹, 25.6 GPa) and comparable to RDX (8.87 km s⁻¹, 35.5 GPa). Due to its larger density, the detonation velocity (9.28 km s⁻¹) and pressure (38.1 GPa) of the regioisomeric 4-nitrofuroxan **3** are even higher and

approach those for a high explosive HMX (9.31 km s⁻¹, 40.6 GPa). Importantly, 4,4'-dinitro-3,3'-bifuroxan **1** possess an excellent detonation performance (9.75 km s⁻¹, 45.0 GPa) reaching the level of one of the most powerful explosives used today, CL-20 (9.77 km s⁻¹, 46.6 GPa). Another crucial detonation parameter for energetic materials is a heat of explosion (Q) which represents a total energy content within the chemical substance and its ability to produce work.³⁹ The heat of explosion of bifuroxan **1** is 15.3 kJ cm⁻³ which exceeds significantly CL-20 (13.5 kJ cm⁻³) and is slightly higher than for landmark octanitrocubane (15.2 kJ cm⁻³).

Table 2. Physical properties and detonation parameters.

Compound	T _d ^[a] [°C]	ρ ^[b] [g cm ⁻³]	Ω _{CO} ^[c] [%]	Ω _{CO₂} ^[d] [%]	N ^[e] [%]	ΔH _{f,solid} ^[f] [kJ mol ⁻¹ (kJ g ⁻¹)]	IS ^[g] [J]	FS ^[h] [N]	D ^[i] [km s ⁻¹]	P ^[j] [GPa]	Q ^[k] [kJ cm ⁻³]
1	146	1.97 ^[l]	+12.3	0	32.3	449 (1.7)	3.9	26	9.75	45.0	15.3
3	113	1.83 ^[l]	+6.25	-6.25	43.8	762 (3.0)	2.0	32	9.28	38.1	13.9
RDX	204	1.80	0	-21.6	37.8	70.3 (0.3)	8	140	8.87	35.5	11.2
HMX	280	1.91	0	-21.6	37.8	75 (0.3)	7	150	9.31	40.6	11.8
CL-20	229	2.04	+11.0	-11.0	38.4	403 (0.9)	4	110	9.77	46.6	13.5
BTF	253	1.90	0	-38.1	33.3	581 (2.3)	3	140	8.77	36.6	13.3
2	119	1.75	+6.25	-6.25	43.8	777 (3.0)	0.7	-	8.95	35.2	13.9
NG	143	1.60	+24.7	+3.5	18.5	-380(-1.7)	<0.2	-	7.78	25.5	9.9

[a] Decomposition temperature (DSC, 5 K min⁻¹). [b] Density measured by gas pycnometer (298 K). [c] Oxygen balance (based on CO) for C_aH_bO_cN_d, 1600(c-a-b/2)/MW. [d] Oxygen balance (based on CO₂) for C_aH_bO_cN_d, 1600(c-2a-b/2)/MW. [e] Nitrogen content. [f] Calculated enthalpy of formation. [g] Experimental impact sensitivity obtained in present study. [h] Experimental friction sensitivity obtained in present study. [i] Detonation velocity. [j] Detonation pressure. [k] Heat of detonation. [l] X-ray density.

It is instructive to analyze the results for solid bifuroxans **1** and **3** in frame of “energy-sensitivity rule”, a general trend iteratively found within data for novel energetic materials. Indeed, along

with an increase of the energy content, the mechanical sensitivity continuously increases as well (initiation stimulus becomes lower), which is outlined on Fig. 8. Azide **3** agrees well with this common trend. However, bifuroxan **1** bends the rule: it offers the highest heat of explosion at much lower sensitivity than can be expected for such an energetic molecule.

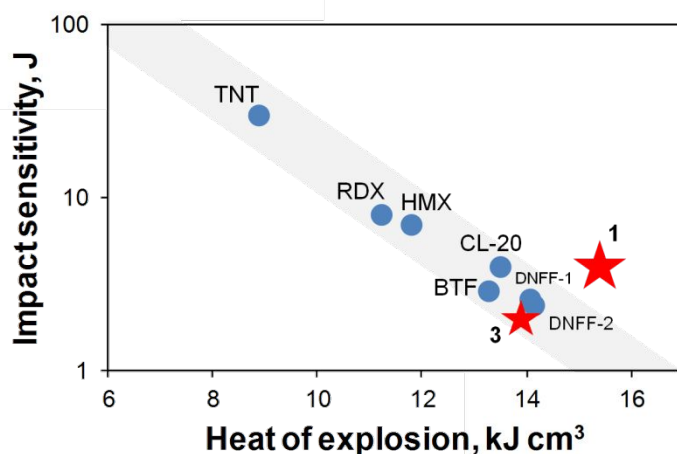


Figure 8. “Energy-sensitivity rule” for synthesized species (red stars) compared to the reference energetic materials (blue circles).

CONCLUSION

A series of high-energy non-hydrogen bifuroxan structures incorporating additional nitro and azido explosophoric functionalities was designed and synthesized through convenient and reproducible synthetic routes. All energetic materials were fully characterized by IR and ^{13}C , ^{14}N , ^{15}N NMR spectroscopy, elemental analysis, and differential scanning calorimetry. The molecular structure of 4-azido-4'-nitro-3,3'-bifuroxan was additionally confirmed by single-crystal X-ray diffraction. Using crystallographic data analysis and quantum-chemical calculations, it was shown that the crystal density of energetic materials incorporating an azide moiety is lower due to the relative supramolecular inactivity of azido group with respect to nitro and furoxan fragments. Tunability of the synthesized regioisomeric azidobifuroxans demonstrated their potential

relevance to various energetic formulations. 4-Azido-3'-nitro-3,4'-bifuroxan **2** has good oxygen balance (+6.25% to CO) and detonation performance (8.95 km s⁻¹, 35.2 GPa) superior to nitroglycerine (7.80 km s⁻¹, 25.6 GPa) which along with its lower sensitivity to impact make this material a promising component of smokeless powder. Possessing the same oxygen balance, regioisomeric 4-azido-4'-nitro-3,3'-bifuroxan **3** has lower mechanical sensitivity, better detonation properties (9.28 km s⁻¹, 38.9 GPa) and may be recommended as a promising replacement of PETN (8.40 km s⁻¹, 31.9 GPa). The most energetic compound in the synthesized series, 4,4'-dinitro-3,3-bifuroxan **1** has a zero oxygen balance to CO₂ with detonation performance (9.75 km s⁻¹, 45.0 GPa) and impact sensitivity similar to CL-20. Moreover, bifuroxan **1** reveals the highest heat of explosion of 15.3 kJ cm⁻³ value among considered high-energy materials. Taking into account its extremely high energy content and exceptionally moderate mechanical sensitivity, its potential application as an oxidizer or solid rocket propellant additive is highly desirable.

ASSOCIATED CONTENT

Supporting Information.

Experimental part and general methods, crystallographic data, thermal behavior and DSC plots, theoretical study, references and copies of NMR spectra.

This data is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* muravyev.nikita@ya.ru (N.V. Muravyev)

* fershtat@bk.ru (L.L. Fershtat)

Notes

The authors declare no competing financial interest.

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TOC Graphic

