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Novel energetic oxadiazole assemblies

Alexander A. Larin,[a] Alexander V. Shaferov,[a] Konstantin A. Monogarov,[b] Dmitry B. Meerov,[b] Alla N. Pivkina[b] and Leonid L. Fershtat*[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: fershtat@bk.ru*
[b] *N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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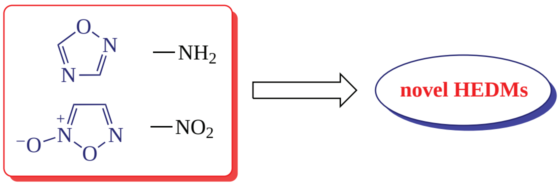
A series of novel, structurally diverse 1,2,4- and 1,2,5-oxadiazole assemblies was synthesized from readily available furoxanyl precursors. Experimentally determined physicochemical properties and calculated detonation parameters showed an application potential of the prepared nitrogen-oxygen molecular systems as promising energetic materials.



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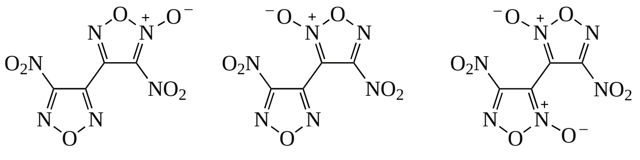
Design and synthesis of novel energetic materials became an emergent topic in recent years.[1] Significant interest in this fundamental and applied area is focused on the incorporation of high-energy density materials (HEDMs) in dual-use technologies for military and civilian purposes. Traditional energetic materials such as trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), pentaerythritol tetranitrate (PETN) suffer from harsh methods for their synthesis and a lack of environmental compatibility.[2] Last generation caged HEDMs, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)[3] and octanitrocubane (ONC),[4] have much higher energy level, however, their wide application is restricted due to the low cost efficiency of their synthesis along with an increased sensitivity to mechanical stimulation and a low level of their eco-friendliness. Therefore, a search for novel powerful materials with superior performance, whilst adhering to strict demands regarding safe preparation, isolation and handling, especially in a more environmentally focused society, remains highly urgent.

Over the last few decades, considerable interest has been focused on the design and synthesis of new energetic compounds comprising of aromatic nitrogen-oxygen heterocycles and energy-rich functional groups.[5] 1,2,5-Oxadiazole 2-oxide (furoxan) is an important energetic unit which has been widely investigated in the synthesis of HEDMs.[6] Furoxan ring has high positive enthalpy of formation (198.5 kJ mol^{-1}) and high nitrogen-oxygen content (69.7%). In recent years, a series of energetic bi- and ter-1,2,5-oxadiazole assemblies was synthesized. For example, regioisomeric dinitro(furazanyl)furoxans DNFF-1 and DNFF-2 represent highly dense compounds with slightly different detonation velocities[7] (Figure 1). Recently, our team developed a scalable route to the preparation of one of the lead compounds in this series, namely, 4,4′-dinitro-3,3′-bifuroxan (DNBFO) possessing zero oxygen balance to CO_2 and high density of 1.97 g cm^{-3} (at 298 K).[8]

In continuation of our studies on energy-rich 1,2,5-oxadiazoles, herein, we report on a preparation of some novel oxadiazole assemblies incorporating a nitrobifuroxan core or comprising 1,2,4-oxadiazole and furoxan rings linked *via* C–C bonds along with an evaluation of functional properties of the synthesized

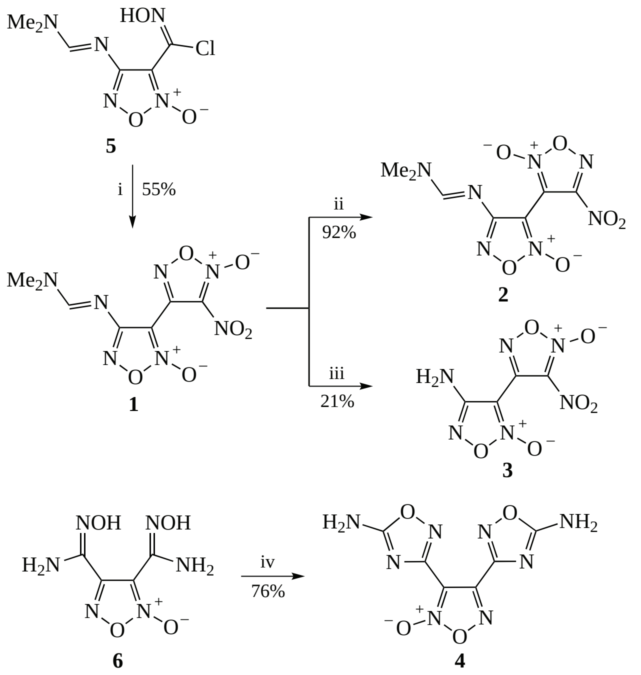


DNFF-1
ρ = 1.92 g cm^{-3}
Ω_{CO_2} = –6.6%
V_D = 9.18 km s^{-1}

DNFF-2
ρ = 1.93 g cm^{-3}
Ω_{CO_2} = –6.6%
V_D = 9.23 km s^{-1}

DNBFO
ρ = 1.97 g cm^{-3}
Ω_{CO_2} = 0
V_D = 9.75 km s^{-1}

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



Scheme 1 *Reagents and conditions*: i, $NaCH(NO_2)_2$, DMF, 0–5 °C, then AcONa, AcOH and $NaNO_2$; ii, CCl_4, reflux, 5 h; iii, $MeSO_3H$, MeCN, H_2O, room temperature, 2 h; iv, BrCN, $KHCO_3$, EtOH, H_2O, 20 °C, 10 h.

HEDMs. Synthesis of target HEDMs **1–4** is presented in Scheme 1. 3-Nitrobifuroxan **1** was synthesized from a known (furoxanyl)chloroxime **5**[9] *via* a previously developed approach based on an acylation of sodium dinitromethanide followed by one-pot nitrosation.[10] Thermal isomerization of compound **1** proceeds chemoselectively upon refluxing in CCl_4 and results in a migration of *N*-oxide moiety to afford product **2**. For the synthesis of amine **3**, deprotection of formamidine protective group was performed. It is known, that such deprotection is usually conducted under acidic conditions.[9] However, a brief screening of reaction conditions for the preparation of **3** showed that both weak and strong Brønsted acids (AcOH, HCl, TFA, CF_3SO_3H) promoted not only hydrolysis of the formamidine functionality, but also resulted in a significant decomposition of starting material. The best conditions for this transformation included application of $MeSO_3H$ in MeCN–H_2O mixture, which resulted in a 21% yield of amine **3**. The synthesis of bis(5-amino-1,2,4-oxadiazol-3-yl)furoxan **4** was accomplished upon cyclization of bis(amidoxime) **6** with BrCN. Although the preparation of compound **4** was reported previously,[11] we improved its yield upon using $KHCO_3$ instead of NaOH. All compounds were characterized by IR and multinuclear (^{1}H, ^{13}C, ^{14}N) NMR spectroscopy and elemental analysis. The conclusive data on the structure of 4-amino-3′-nitro-3,4′-bifuroxan **3** were obtained by the single-crystal X-ray diffraction study (Figure 2, for details, see Online Supplementary Materials).[†]

Experimental densities of compounds **1**, **2**, **4** were measured with a gas pycnometer and were found in a range of 1.54–1.71 g cm^{-3}. All synthesized compounds possess high nitrogen-oxygen content (>68%), while compound **3** has even positive oxygen balance to CO (Table 1). Enthalpies of formation of oxadiazole assemblies **1–4** were calculated by the additive method.[12] With the experimentally obtained densities and calculated enthalpy of formation values, the energetic performance of the synthesized furoxans was computed.[13] Among the studied compounds, the highest detonation performance offers **3**, reaching the level of RDX and BTF (see Table 1). Other three species **1**, **2**, **4** in terms of energetic potential could be compared to TNT explosive. However, with the exception of **4**, the thermal stability of investigated compounds is inferior to the above benchmark energetic materials. More specifically, **1** and **2** melt at 127 and 133 °C, respectively, with immediate thermal decomposition. Thermolysis of **3** is so vigorous, that even with mass as low as 0.13 mg, self-heating of the sample takes place (see Online Supplementary Materials, Figures S1–S4). Only compound **4** has high thermal stability, showing the exotherm of decomposition after 269 °C. Additionally, thanks to the amino(1,2,4-oxadiazolyl) substituents, it is insensitive to impact and friction stimuli. Friction sensitivity of **1** is on the nitramine's level (see RDX, Table 1), while its isomer **2** is more sensitive.

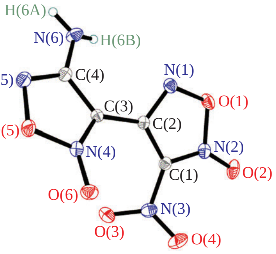


Figure 2 Molecular structure of **3** with atoms shown as thermal ellipsoids at 50% probability level.

In conclusion, a series of novel energetic oxadiazole assemblies was synthesized from readily available furoxanyl precursors. Prepared regioisomeric nitrobifuroxans incorporating an additional dimethylformamidine moiety possess moderate physicochemical and detonation properties, while bis[amino(1,2,4-oxadiazolyl)]furoxan has high thermal stability and is completely insensitive to mechanical stimuli. Overall, synthesized high-energy compounds are of interest for future insights in the development of energetic materials and formulations thereof.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.036.

Table 1 Physical properties and detonation parameters.

Compound	T_d[a]/°C	ρ[b]/g cm^{-3}	Ω_{CO}[c] (%)	N + O[d] (%)	$\Delta H^\circ_{f,solid}$[e]/kJ mol^{-1}	IS[f]/J	FS[g]/N	V_D[h]/km s^{-1}	P[i]/GPa
1	127	1.55	–80.2	68.1	434	4	100	7.27	21.4
2	133	1.54	–80.2	68.1	434	3	85	7.24	21.5
3	125	1.81[j]	+14.4	78.3	198	–	–	8.83	37.5
4	269	1.71	–63.0	69.8	178	>100	>360	7.28	23.7
TNT	275[k]	1.64	–24.7	60.8	–62[l]	30[k]	>360[k]	6.86	20.4
RDX	204[k]	1.80	0	81.1	68[l]	8[k]	140[k]	8.87	35.5
BTF	253[k]	1.90	0	71.4	624[l]	3[k]	140[k]	8.83	37.0

[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] Nitrogen-oxygen content. [e] Calculated enthalpy of formation *via* the additive method. [f] Experimental impact sensitivity obtained in the present study. [g] Experimental friction sensitivity obtained in the present study. [h] Detonation velocity. [i] Detonation pressure. [j] X-ray density extrapolated to 298 K. [k] Ref. 18. [l] Ref. 19.

[†] *Crystal data for* **3**. $C_4H_2N_6O_6$ (M_r = 230.12), monoclinic, space group $P2_1/c$, a = 7.2485(4), b = 11.9618(5) and c = 9.3932(5) Å, V = 794.18(7) Å^3, Z = 4, d_x = 1.925 g cm^{-3}, absorption coefficient: 0.181 mm^{-1}, F(000) = 464, the final R = 0.0454, wR = 0.0892 for 1933 observed reflections with $I > 2\sigma(I)$.

X-ray diffraction data were collected at 100 K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using MoKα-radiation (0.71073 Å). The intensity data were integrated by the SAINT program[14] and were corrected for absorption and decay using SADABS.[15] The structure was solved by direct methods using SHELXS-2013[16] and refined on F^2 using SHELXL-2018.[17] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Positions of hydrogen atoms H(6A) and H(6B) were found from the electron density-difference map, these atoms were refined with individual isotropic displacement parameters. The SHELXTL program suite[14] was used for molecular graphics.

CCDC 2113370 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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