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Short Note

Potassium (3-Methyl-2-oxido-1,2,5-oxadiazol-4-yl)dinitromethanide

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Abstract: Furoxan derivatives enriched with explosophoric functionalities are promising compounds in the preparation of novel energetic materials. Herein, a previously unknown potassium (3-methyl-2-oxido-1,2,5-oxadiazol-4-yl)dinitromethanide (also referred to as potassium 4-dinitromethyl-3-methylfuroxanate) was synthesized via tandem nitration-reduction reactions of an available (furoxanyl)chloroxime. The structure of the synthesized compound was established by elemental analysis, IR, ^{1}H, ^{13}C and ^{14}N NMR spectroscopy. Thermal stability and mechanical sensitivity of the prepared compound toward impact and friction were experimentally determined.

Keywords: nitrogen heterocycles; oxadiazoles; energetic materials; furoxans; nitration; thermal stability; polynitro compounds

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1. Introduction

High-energy materials (HEMs) are among the most important functional materials and occupy a dominant position in the development of dual-use technologies [1–9]. Commonly used cyclic nitramines-1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) synthesized over a century ago are still considered the "golden standard" in the field of energetic materials due to their high detonation performance and facile synthesis. By the end of the 20th century, next-generation HEMs were obtained: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) [10,11] and octanitrocubane (ONC) [12]. Their functional properties are significantly higher than those of RDX and HMX; however, their sensitivity to mechanical stress is also much higher. Therefore, the search for new and effective, but less sensitive to mechanical stimuli, HEMs among polynitrogen–oxygen and nitrogen–oxygen heterocyclic compounds remain especially relevant. The use of heterocyclic scaffolds as a synthetic platform for the construction of high-energy structures has a number of advantages: such compounds usually have high enthalpies of formation, higher densities, and high nitrogen content, which allows for reducing the amount of oxidant used in energetic formulations. In a recent decade, new synthetic methodologies for the construction of heterocycle-based energetic materials were developed, and nowadays, a search of new HEMs is mainly performed in the field of heterocyclic chemistry [13–17]. A special interest in the energetic materials' chemistry is focused on energy-rich substances containing the furoxan (1,2,5-oxadiazole 2-oxide) ring. Compared with other azoles, furoxan derivatives have a number of advantages, including high density, high enthalpy of formation and low volatility (Figure 1) [18,19]. Due to these properties, the furoxan ring became a key structural fragment in the synthesis of a number of high-energy substances [20–23].

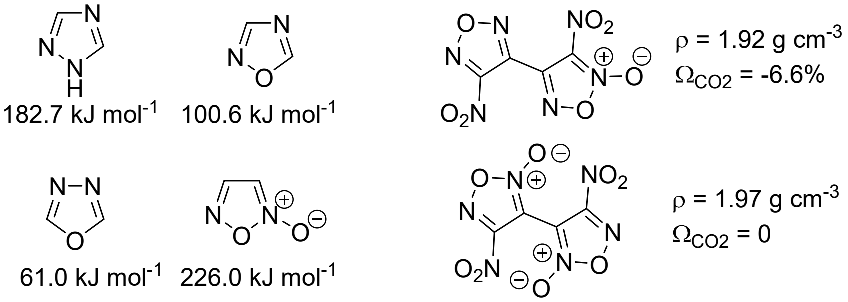
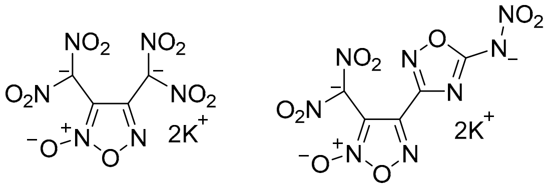


Figure 1. Enthalpies of formation of various azoles and representative furoxan-based HEMs.

Keeping in mind the desired synthesis of high-energy materials with an increased oxygen content, it seems promising to combine the furoxan cycle and the dinitromethyl functionality in one molecule. Recently, energetic dinitromethylfuroxan potassium salts **1** [24] and **2** [25] exhibiting high densities and thermal stability, as well as a positive oxygen balance to CO, were synthesized (Figure 2). However, both of these substances are highly sensitive to mechanical stress. Therefore, the goal of this work includes the synthesis of energy-rich potassium 4-dinitromethyl-3-methylfuroxanate **3**, which will also have a high oxygen content, but due to the presence of a methyl group, it may turn out to be less sensitive to impact and friction.



1

ρ = 2.13 g cm^{-3}
T_d = 218 °C
Ω_{CO} = +21.3%

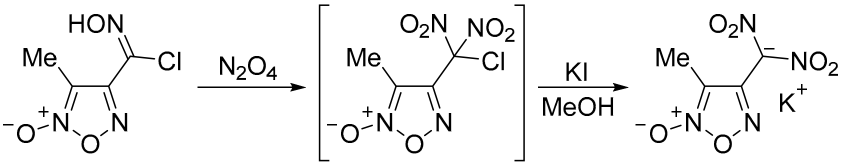
2

ρ = 2.14 g cm^{-3}
T_d = 186 °C
Ω_{CO} = +12.2%

Figure 2. Structures and some physicochemical properties of dinitromethylfuroxanates.

2. Results and Discussion

A synthetic route to the target compound **3** is based on one-pot transformations of the readily available (furoxanyl)chloroxime **4**, which was previously synthesized by our research group from ethyl acetoacetate [26]. We found that nitration of substrate **4** using an excess of N_2O_4 followed by a one-pot reduction in the intermediate *gem*-chlorodinitrofuroxan **5** upon its treatment with KI afforded potassium salt **3** in an overall yield of 58% (Scheme 1). The structure of the furoxanate **3** was confirmed by elemental analysis, IR, ^{1}H, ^{13}C and ^{14}N NMR spectroscopy. The ^{13}C NMR spectrum showed four signals of carbon atoms: Me group (8.0 ppm), characteristic signals of C-3 and C-4 carbons of the furoxan ring (113.7 and 152.6 ppm, respectively) and a broadened signal of the $C(NO_2)_2$ functionality (123.3 ppm). The presence of the $C(NO_2)_2$ moiety was additionally confirmed by ^{14}N NMR spectroscopy (characteristic signal at −23.5 ppm).



4 **5** **3** (58%)

Scheme 1. Synthesis of potassium 4-dinitromethyl-3-methylfuroxanate **3**.

A set of important physicochemical properties of the potassium salt **3** was also established (Table 1). It was found that compound **3** has a remarkably high density (1.91 g cm^{-3}), zero oxygen balance (to CO) and quite high combined nitrogen-oxygen content (62.8%). Under linear heating at 5 K min^{-1} rate, sample **3** first shows a phase transition at 133 °C with the following thermal decomposition after 207 °C (Figure 3). Hence, with this preliminary estimate of thermal stability, compound **3** could be placed in between known dinitromethylfuroxan derivatives **1** and **2**. At the same time, the mechanical sensitivity of synthesized **3** is beneficially less than for previous synthesized salts **1** and **2** (Table 1). Impact sensitivity of **3** is on the level of nitramines (see RDX, Table 1), whereas the friction sensitivity of **3** approaches the nitroester's level (see PETN, Table 1).

Table 1. Comparison of physicochemical parameters of the compound **3** with known energetic materials.

Compound	T_d [1] [°C]	ρ [2] [g cm^{-3}]	Ω_{CO} [3] [%]	N+O [4] [%]	IS [5] [J]	FS [6] [N]
3	207	1.91	0	62.8	6	90
1	218	2.13	+21.3	65.9	2	5
2	186	2.14	+12.2	65.0	3	60
RDX	204 [7]	1.80	0	81.1	8 [7]	140 [7]
PETN	181 [7]	1.78	+15.2	78.5	3 [7]	70 [7]

[1] Decomposition temperature (DSC, 5 K min^{-1}). [2] Density measured by gas pycnometry (298 K). [3] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, 1600(c-a-b/2)/MW. [4] Combined nitrogen and oxygen content. [5] Impact sensitivity. [6] Friction sensitivity. [7] Ref. [27].

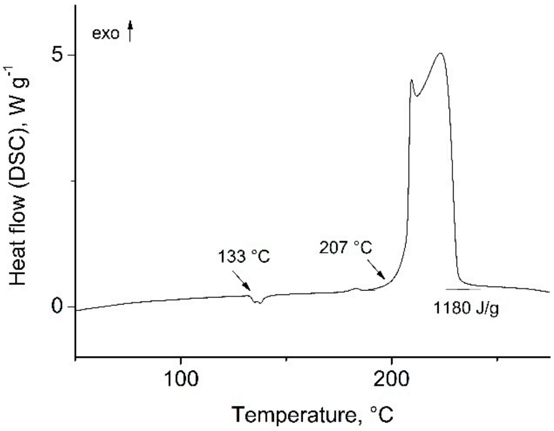


Figure 3. DSC curve for compound **3**.

In conclusion, a new high-energy potassium 4-dinitromethyl-3-methylfuroxanate was synthesized through tandem nitration-reduction reactions of the readily available 3-methyl-4- (chloroximino)furoxan. Thermal stability and mechanical sensitivity of the synthesized compound were experimentally determined. It was found that thus-prepared potassium salt has a high decomposition temperature (207 °C), high density (1.91 g cm^{-3}) and moderate sensitivity to mechanical stress, which enable its potential application in energetic materials science.

3. Materials and Methods

CAUTION! Although we have encountered no difficulties during preparation and handling of compounds described in this paper, they are potentially explosive energetic materials which are sensitive to impact and friction. Mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Any manipulations must be carried out by using appropriate standard safety precautions.

All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (Billerica, MA, USA) AM-300

(300 and 75.5 MHz, respectively) spectrometer and referenced to residual solvent peak. The ^{14}N NMR spectrum was measured on a Bruker AM-300 (21.7 MHz) spectrometer using $MeNO_2$ (δ_{14N} = 0.0 ppm) as an external standard. The chemical shifts are reported in ppm (δ). The IR spectrum was recorded on a Bruker "Alpha" spectrometer in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}). Elemental analysis was performed by the CHN analyzer EuroVector EA (Pavia, Italy). All solvents were purified and dried using standard methods prior to use. All standard reagents were purchased from Aldrich(Burlington, MA, USA) or Acros Organics (Geel, Belgium) and used without further purification. Thermal analysis was performed using Netzsch DSC 204 HP (Selb, Germany) apparatus. Sample weighting 1.1 mg was poured in an aluminum pan, covered with a pierced lid and heated at 5 K min^{-1} rate up to 300 °C under nitrogen flow (50 mL min^{-1}). Impact and friction sensitivity were determined with standard procedures; the details can be found elsewhere [27]. IR, ^{1}H, ^{13}C and ^{14}N NMR spectra are available in Supplementary Materials.

Synthesis of potassium (3-methyl-2-oxido-1,2,5-oxadiazol-4-yl)dinitromethanide **3**. Chloroxime **4** (355 mg, 2 mmol) was placed in a 10 mL round-bottom flask and then N_2O_4 (2.6 mL, 40 mmol) was added in one portion at 20 °C. The resulting mixture was stirred until the complete dissolution of initial compound **4** and then for additional 24 h at 20 °C;. The thus-formed dark green solution was concentrated on a rotary evaporator and the residue was passed through a short pad of SiO_2 (eluent–CH_2Cl_2). Then, the solvent was evaporated and thus obtained chlorodinitrofuroxan **5** (340 mg) was dissolved in MeOH (4.5 mL) followed by an addition of KI (522 mg, 3.15 mmol) in one portion. The reaction mixture was cooled to 0 °C, stirred for 4 h and left in a refrigerator at 4 °C; for 12 h to initiate crystallization. The solid formed was filtered off, washed with cold MeOH (1 × 1 mL) and hexanes (2 × 5 mL) and dried in air. Yield 280 mg (58%), pale yellow solid. IR spectrum (KBr), ν, cm^{-1}: 2937, 2836, 1618, 1537, 1475, 1373, 1233, 1143, 1021, 818, 749. ^{1}H NMR (300 MHz, DMSO-d_6, 300K), δ, ppm: 2.00 (3H, s, Me). ^{13}C NMR (75.5 MHz, DMSO-d_6, 300K), δ, ppm: 8.0 (Me), 113.7 (C-3 furoxan), 123.3 (br, $C(NO_2)_2$), 152.6 (C-4 furoxan). ^{14}N NMR (21.7 MHz, DMSO-d_6, 300K), δ, ppm: −23.5 ($C(NO_2)_2$). Anal. calcd for $C_4H_3KN_4O_6$: C, 19.84; H, 1.25; N, 23.13; found: C, 20.12; H, 1.43; N, 22.79%.

Supplementary Materials: The following are available online: copies of IR, ^{1}H, ^{13}C and ^{14}N NMR spectra.

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References

1. O'Sullivan, O.T.; Zdilla, M.J. Properties and Promise of Catenated Nitrogen Systems as High-Energy—Density Materials. *Chem. Rev.* **2020**, *120*, 5682–5744. [CrossRef] [PubMed]
2. Li, G.; Zhang, C. Review of the Molecular and Crystal Correlations on Sensitivities of Energetic Materials. *J. Hazard. Mater.* **2020**, *398*, 122910. [CrossRef] [PubMed]
3. Sabatini, J.J.; Johnson, E.C. A Short Review of Nitric Esters and Their Role in Energetic Materials. *ACS Omega* **2021**, *6*, 11813–11821. [CrossRef] [PubMed]
4. Das, J.; Shem-Tov, D.; Wang, S.; Zhang, L.; Flaxer, E.; Zhang, S.; Stierstorfer, J.; Wang, K.; Yan, Q.-L.; Dobrovetsky, R.; et al. Hydride- and boron-free solid hypergolic H_2O_2-ignitophores. *Chem. Eng. J.* **2021**, *426*, 131806. [CrossRef]
5. Luo, S.-N.; Gozin, M. Energetic Materials: Novel Syntheses and Diagnostics. *Engineering* **2020**, *6*, 974–975. [CrossRef]
6. Larin, A.A.; Fershtat, L.L. High-Energy Hydroxytetrazoles: Design, Synthesis and Performance. *Energ. Mater. Front.* **2021**, *2*, 3–13. [CrossRef]

7. Tarchoun, A.F.; Trache, D.; Klapötke, T.M.; Khimeche, K. Tetrazole-Functionalized Microcrystalline Cellulose: A Promising Biopolymer for Advanced Energetic Materials. *Chem. Eng. J.* **2020**, *400*, 125960. [CrossRef]
8. Snyder, C.J.; Imler, G.H.; Chavez, D.E.; Parrish, D.A. Synergetic Explosive Performance through Cocrystallization. *Cryst. Growth Des.* **2021**, *21*, 1401–1405. [CrossRef]
9. Kuchurov, I.V.; Zharkov, M.N.; Fershtat, L.L.; Makhova, N.N.; Zlotin, S.G. Prospective Symbiosis of Green Chemistry and Energetic Materials. *ChemSusChem* **2017**, *10*, 3914–3946. [CrossRef]
10. Simpson, R.L.; Urtiew, P.A.; Ornellas, D.L.; Moody, G.L.; Scribner, K.J.; Hoffman, D.M. CL-20 performance exceeds that of HMX and its sensitivity is moderate. *Propellants Explos. Pyrotech.* **1997**, *22*, 249–255. [CrossRef]
11. Fedyanin, I.V.; Lyssenko, K.A.; Fershtat, L.L.; Muravyev, N.V.; Makhova, N.N. Crystal Solvates of Energetic 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane Molecule with [bmim]—Based Ionic Liquids. *Cryst. Growth Des.* **2019**, *19*, 3660–3669. [CrossRef]
12. Zhang, M.; Eaton, P.E.; Gilardi, R. Hepta-and octanitrocubanes. *Angew. Chem. Int. Ed.* **2000**, *39*, 401–404. [CrossRef]
13. Zhou, J.; Zhang, J.; Wang, B.; Qiu, L.; Xu, R.; Sheremetev, A.B. Recent Synthetic Efforts towards High Energy Density Materials: How to Design High-Performance Energetic Structures? *FirePhysChem* **2021**, in press. [CrossRef]
14. Wozniak, D.R.; Salfer, B.; Zeller, M.; Byrd, E.F.C.; Piercey, D.G. Tailoring Energetic Sensitivity and Classification through Regioisomerism. *Org. Lett.* **2020**, *22*, 9114–9117. [CrossRef] [PubMed]
15. Yount, J.R.; Zeller, M.; Byrd, E.F.C.; Piercey, D.G. 4,4′,5,5′-Tetraamino-3,3′-azo-bis-1,2,4-triazole and the electrosynthesis of high-performing insensitive energetic materials. *J. Mater. Chem. A* **2020**, *8*, 19337–19347. [CrossRef]
16. Wurzenberger, M.H.; Gruhne, M.S.; Lommel, M.; Braun, V.; Szimhardt, N.; Stierstorfer, J. Taming the Dragon: Complexation of Silver Fulminate with Nitrogen-Rich Azole Ligands. *Inorg. Chem.* **2020**, *59*, 17875–17879. [CrossRef] [PubMed]
17. Voronin, A.A.; Fedyanin, I.V.; Churakov, A.M.; Pivkina, A.N.; Muravyev, N.V.; Strelenko, Y.A.; Klenov, M.S.; Lempert, D.B.; Tartakovsky, V.A. 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*, 9401–9407. [CrossRef]
18. Fershtat, L.L.; Makhova, N.N. 1,2,5-Oxadiazole-Based High-Energy-Density Materials: Synthesis and Performance. *ChemPlusChem* **2020**, *85*, 13–42. [CrossRef]
19. Bystrov, D.M.; Fershtat, L.L.; Makhova, N.N. Synthesis and reactivity of aminofuroxans. *Chem. Heterocycl. Compd.* **2019**, *55*, 1143–1164. [CrossRef]
20. Larin, A.A.; Bystrov, D.M.; Fershtat, L.L.; Konnov, A.A.; Makhova, N.N.; Monogarov, K.A.; Meerov, D.B.; Melnikov, I.N.; Pivkina, A.N.; Kiselev, V.G.; et al. Nitro-, Cyano-, and Methylfuroxans, and Their Bis-Derivatives: From Green Primary to Melt-Cast Explosives. *Molecules* **2020**, *25*, 5836. [CrossRef]
21. Larin, A.A.; Shaferov, A.V.; Epishina, M.A.; Melnikov, I.N.; Muravyev, N.V.; Ananyev, I.V.; Fershtat, L.L.; Makhova, N.N. Pushing the Energy-Sensitivity Balance with High-Performance Bifuroxans. *ACS Appl. Energy Mater.* **2020**, *3*, 7764–7771. [CrossRef]
22. Larin, A.A.; Fershtat, L.L.; Makhova, N.N. Tandem Reactions of Thermolysis and [3+2] Cycloaddition in the Synthesis of 3-Hetaryl-4-Nitrofuroxans from 4-Nitrofuroxannitrolic Acid. *Chem. Heterocycl. Compd.* **2020**, *56*, 607–610. [CrossRef]
23. Larin, A.A.; Muravyev, N.V.; Pivkina, A.N.; Suponitsky, K.Y.; Ananyev, I.V.; Khakimov, D.V.; Fershtat, L.L.; Makhova, N.N. Assembly of Tetrazolylfuroxan Organic Salts: Multipurpose Green Energetic Materials with High Enthalpies of Formation and Excellent Detonation Performance. *Chem. Eur. J.* **2019**, *25*, 4225–4233. [CrossRef] [PubMed]
24. He, C.; Shreeve, J.M. Potassium 4,5-Bis (dinitromethyl) furoxanate: A Green Primary Explosive with a Positive Oxygen Balance. *Angew. Chem. Int. Ed.* **2016**, *55*, 772–775. [CrossRef]
25. Liu, Y.; He, C.; Tang, Y.; Imler, G.H.; Parrish, D.A.; Shreeve, J.M. Asymmetric nitrogen-rich energetic materials resulting from the combination of tetrazolyl, dinitromethyl and (1,2,4-oxadiazol-5-yl)nitroamino groups with furoxan. *Dalton Trans.* **2018**, *47*, 16558–16566. [CrossRef] [PubMed]
26. Fershtat, L.L.; Larin, A.A.; Epishina, M.A.; Kulikov, A.S.; Ovchinnikov, I.V.; Ananyev, I.V.; Makhova, N.N. Regioselective synthesis of bifuroxanyl systems with the 3-nitrobifuroxanyl core via a one-pot acylation/nitrosation/cyclization cascade. *Tetrahedron Lett.* **2016**, *57*, 4268–4272. [CrossRef]
27. Muravyev, N.V.; Meerov, D.B.; Monogarov, K.A.; Melnikov, I.N.; Kosareva, E.K.; Fershtat, L.L.; Sheremetev, A.B.; Dalinger, I.L.; Fomenkov, I.V.; Pivkina, A.N. Sensitivity of Energetic Materials: Evidence of Thermodynamic Factor on a Large Array of CHNOFCl Compounds. *Chem. Eng. J.* **2021**, *421 Pt 1*, 129804. [CrossRef]