Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2018, **28**, 135–137

Mendeleev Communications

1-Amino-1-hydroxyamino-2,2-dinitroethene: novel insights in chemistry of FOX-7

Aleksandr E. Frumkin,[a] Nikolai V. Yudin,[b] Kyrill Yu. Suponitsky[c] and Aleksei B. Sheremetev*[a]

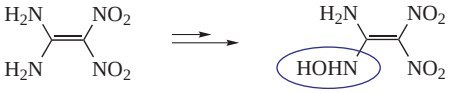
[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: sab@ioc.ac.ru*

[b] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation*

[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2018.03.007

Structurally unique conjugated *N*-hydroxy nitro enamine, namely, 1-amino-1-hydroxyamino-2,2-dinitroethene, has been synthesized by transamination of 1,1-diamino-2,2-dinitroethene (FOX-7) with hydroxylamine. The compound is a highly energetic material, its structure being confirmed by X-ray crystallography.

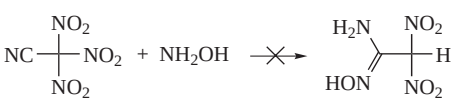


There is an increasing need for green energetic compounds to develop novel explosive materials and propellant formulations.[1] These compounds might offer advantages in terms of either performance, safety, or cost over the currently available energetic components. Oxygen- and nitrogen-rich dense organic compounds are very useful to the purpose.[2] The incorporation of conjugated nitroenamine structural motif into energetic molecules has had a significant impact on the discovery and development of insensitive energetic materials. 1,1-Diamino-2,2-dinitroethene **1** (FOX-7) is the most widely investigating enamine of this type.[3] However, despite favorable insensitivity, energetic properties (detonation velocity, *D*; detonation pressure, P_{CJ}) of the compound is inferior to those of high explosive benchmark 1,3,5-trinitrohexahydro-*s*-triazine (RDX).

As part of a continuing effort focused on the design of insensitive energetic materials, it was of interest to explore the effect of replacing one amino group of enamine **1** with a hydroxyamino group. Based on computational predictions, the product, 1-amino-1-hydroxyamino-2,2-dinitroethene **2**, would possess more powerful energetic properties. Herein we report our efforts to synthesize and characterize compound **2**.

Two synthetic protocols to compound **2** were considered. As shown in Scheme 1, the first was based on a reaction of trinitroacetonitrile **3** with hydroxylamine. It is known that nitriles can be condensed with hydroxylamine with formation of amidoximes.[4] On the other hand, when treated with hydroxylamine, the trinitromethyl group is reduced to a dinitromethyl one.[5] We hoped that trinitroacetonitrile would be transformed into the desired product **2** when both reactions were implemented.

The reaction between hydroxylamine and trinitroacetonitrile was tried under a variety of conditions. However, none of the reactions led to identifiable products. Typically, copious gas

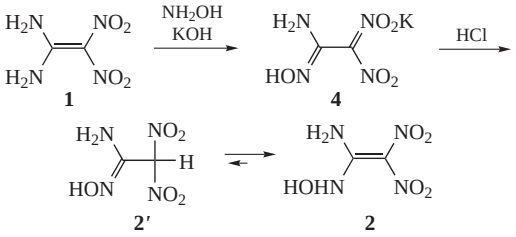


3 **1**

Scheme 1

evolution occurred indicating that the polynitro compound was undergoing decomposition.

The second protocol for the synthesis of compound **2** was transamination of diamine **1** (Scheme 2). Enamine **1** is a reactive compound used for the construction of diverse high-energy molecules.[6] In particular, the route presented in Scheme 2 is based on analogy to the synthesis of 1-amino-1-alkylamino-2,2-dinitroethylene and 1-amino-1-hydrazino-2,2-dinitroethylene (NH_2-FOX) from enamine **1** and primary alkylamines and hydrazine.[7] To our surprise, transamination of compound **1** with hydroxylamine has not been explored.



1 **4** **2′** **2**

Scheme 2

Several literature procedures were tried, with the best being one developed by Shreeve[8] for the conversion of enamine **1** to hydrazine analogue; this procedure involves adding hydrazine hydrate (4 equiv.) to a slurry of compound **1** (1 equiv.) and KOH (2 equiv.) in absolute ethanol and refluxing for 10 h. In our first attempts, even with the best Shreeve's conditions, only a low yield (3–8%) of the desired potassium salt **4** was obtained utilizing hydroxylamine instead of hydrazine.

However, we were pleased to discover that using an aqueous solution of compound **1** and KOH and solution of hydroxylamine in 50% MeOH at short reaction time (3 h), the amino group underwent efficient replacement with hydroxyamino group (see Scheme 2), to give salt **4** in 67% yield. Acidification of the salt with anhydrous HCl in THF at 0 to 5 °C afforded the hydroxyamino derivative **2** in 78% isolated yield as a solid. The solid was essentially pure (NMR data). Its further crystallization from diethyl ether furnished

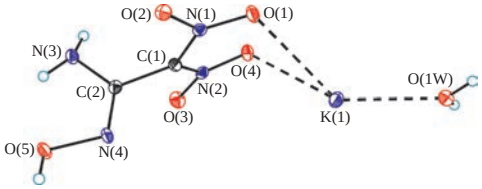


Figure 1 General view of monohydrate of K-salt **4**. Thermal ellipsoids set at 50% probability.

2 as a light yellow crystalline material. *N*-Hydroxy derivative **2** is stable in solid state and in a diethyl ether solution, however, it decomposes when treated with water. Only gas evolution was observed in unsuccessful attempts to synthesize salts of **2** with hydroxylamine, hydrazine, and triaminoguanidine. Meantime, by treating **2** with guanidine in anhydrous ethanol solution, its guanidinium salt can be synthesized.

The new compounds were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy (see Online Supplementary Materials). To confirm the proposed structure of *N*-hydroxy derivative **2** and K-salt **4**, an X-ray diffraction study was carried out.† As expected, the amidoxime moiety of salt **4** possesses a typical geometry, and potassium atom is bonded to oxygen atoms of nitro groups and a water molecule (Figure 1). Similar bonding pattern was also observed for K-salt FOX-7.[8] In both K-salts, the C(1)–C(2) bond is elongated and the C(2)–N(3) bond is shortened due to the localization of the positive charge on the C(1) atom. As a result both anions adopt perpendicular structure.

The *N*-hydroxy derivative **2** represents an amidoxime which can exist in multiple tautomeric forms, two of which (most possible **2** and **2′**) are shown in Scheme 1. For typical amidoximes, however, the equilibrium favors the oxime tautomer (likewise **2′**) exclusively over the enamine, regardless of the nature of functional group bound to the moiety. Surprisingly, the X-ray crystal structure demonstrates that compound **2** exists in the enamine form (Figure 2). That is, compound **2** is a unique example of a 'push-pull' alkene of the nitroenamine type with hydroxyamino group at the C=C double bond. The same tautomeric form was also observed for NH_2-FOX,‡ and it has non-planar geometry.[9] In contrast, both FOX-7[10] and compound **2** adopt nearly planar geometries. Moreover, the C=C bonds of these compounds are somewhat shorter than that of NH_2-FOX (for details, see Online Supplementary Materials).

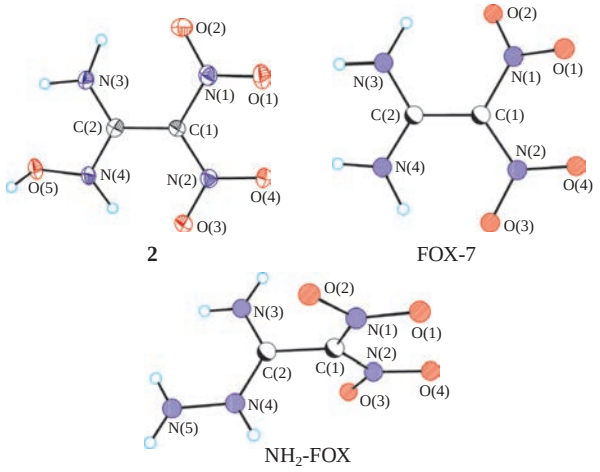


Figure 2 General view of compound **2**, FOX-7 and NH_2-FOX. For **2**, only one independent molecule is shown with thermal ellipsoids set at 50% probability.

In the solid state, all three compounds form dense crystal packings. In this nitroenamine series, compound **2** has the highest packing density (Table 1) that can be rationalized based on combination of geometric and energetic approaches.[11] The difference in packing motifs for FOX-7, NH_2-FOX and compound **2** is clearly illustrated in Figure 3. As can be seen, compound **2** forms a 3-D H-bonded network. On the other hand, for FOX and NH_2-FOX packing motifs are characterized by the formation of a 2-D H-bonded network, while in the third direction only $NO_2\cdots NO_2$ or van-der-Waals interactions are observed (for details, see Online Supplementary Materials).

As can be seen from Table 1, the total percentage of nitrogen and oxygen of compound **2** is much higher than that of its

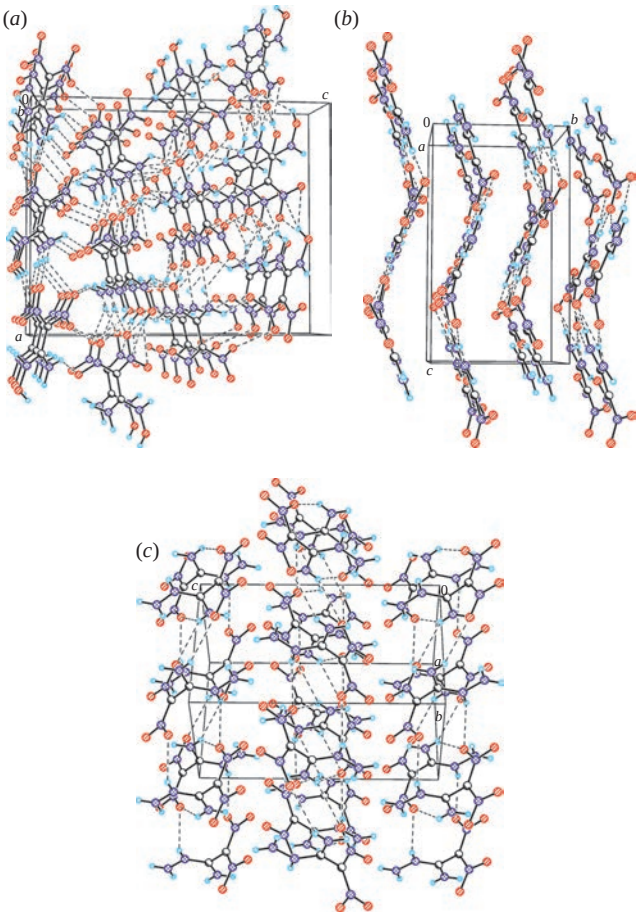


Figure 3 Crystal packing patterns of compound (*a*) **2**, (*b*) FOX-7 and (*c*) NH_2-FOX.

† *Crystal data for compound* **2**: $C_2H_4N_4O_5$, orthorhombic, space group $Pca2_1$, a = 13.330(3), b = 4.8713(10) and c = 17.141(4) Å, V = 1113.0(4)Å^3, Z = 8, M = 164.09, d_{calc} = 1.959 g cm^{-3}, wR_2 = 0.0778 calculated on F^2_{hkl} for all 2432 independent reflections with 2θ < 54.0° [GOF = 1.049, R = 0.0441 calculated on F_{hkl} for 1864 reflections with $I > 2\sigma(I)$].

Crystal data for salt **4**: $C_2H_4N_4O_5^-K^+\cdot H_2O$ (M = 220.20), triclinic, space group $P\bar{1}$, a = 4.905(2), b = 7.711(4) and c = 10.591(4) Å, α = = 69.924(7)°, β = 81.709(7)°, γ = 79.035(7)°, V = 368.0(2) Å^3, Z = 2, d_{calc} = = 1.987 g cm^{-3}, wR_2 = 0.0842 calculated on F^2_{hkl} for all 3456 independent reflections with 2θ < 56.03° [GOF = 1.109, R = 0.0317 calculated on F_{hkl} for 3077 reflections with $I > 2\sigma(I)$].

CCDC 1586048 and 1586049 contain 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.

‡ The quality of first reported X-ray experiment of NH_2-FOX is low and its molecular conformation given is probably incorrect.[9(a)] Recently, this compound was correctly reinvestigated[9(b)] but the cif-file is not yet available in CSD (see details in Online Supplementary Materials). Note that according to the literature and our recent data, planar NHR–NHR structure is rather unfavorable.[13]

Table 1 Physical and calculated energetic properties of compound **2** compared with some analogues.

Compound	Formula	T_{decomp} [a]/°C	α [b]	N + O [c] (%)	d [d]/g cm^{-3}	ΔH_f^0 [e]/kJ mol^{-1} (kJ g^{-1})	D [f]/m s^{-1}	P_{CJ} [g]/GPa	I_{sp} [h]/s	T_{ad} [i]/K
2	$C_2H_4N_4O_5$	75	0.83	82.90	1.900	–175 (–1.07)	8974	37.7	254	3168
FOX-7 **1**	$C_2H_4N_4O_4$	238	0.67	81.06	1.883	–134 (–0.91)	8795	35.6	240	2788
NH_2-FOX	$C_2H_5N_5O_4$	124	0.62	82.18	1.820	–21 (–0.13)	8865	35.5	249	2864
RDX	$C_3H_6N_6O_6$	204	0.67	81.06	1.82	67 (0.30)	8951	35.5	266	3287

[a] Extrapolated onset temperature (DSC, 5 K min^{-1}). [b] The oxygen coefficient is an index of the deficiency or excess amount of oxygen in a compound that is required to convert all carbon atoms into CO_2 and all hydrogen atoms into H_2O. For a compound with the molecular formula of $C_xH_yN_wO_z$, $\alpha = z/(2x + y/2)$. A compound with $\alpha > 1$ is an oxidizer. [c] Combined nitrogen and oxygen content. [d] Density recalculated for the transition from 100 to 298 K, $d_{298\,K} = d_{100\,K}/1.035$.[14] [e] Calculated enthalpy of the formation for solid state. [f] Calculated detonation velocity. [g] Calculated detonation (Chapman–Jouguet) pressure. [h] Calculated specific impulse and adiabatic temperature for isobaric combustion at 7 MPa with equilibrium expansion to 0.1 MPa. [i] Adiabatic flame temperature for combustion at 7 MPa.

analogues and RDX. Wherein, the oxygen coefficient of **2** is 0.83, which is significantly better than that of the other compounds listed in Table 1. The enthalpy of formation of **2** calculated using the additive method is lower than that of FOX-7.

Using the calculated enthalpy of formation and the experimental room temperature densities, detonation and combustion properties for *N*-hydroxy derivative **2** and its analogues were predicted with the Smirnov's[12] method and are given in Table 1. As can be seen compound **2** has higher detonation pressure (P_{CJ} = 37.7 GPa) and detonation velocity (D = 8974 m s^{-1}) than those of its analogues and its detonation performance is compared to RDX. The specific impulse (I_{sp}) that characterize the performance of rocket propellant ingredients (as a monopropellant) for compound **2** has the highest value in the family of nitro enamines. The impact sensitivities of **2** are measured to be 17 J, which is lower than that of TNT (15 J). According to differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) measurements (scanning at 5 K min^{-1}), compound **2** begins to decompose at 75 °C. Thus, this compound is thermally less stable than FOX-7.

In conclusion, we have synthesized a conjugated *N*-hydroxy nitro enamine **2** starting from FOX-7. There is no literature precedence for high-nitrogen energetic materials containing enhydroxyamine backbone. Compound **2** displays good oxygen balance and density, it is insensitive to impact, and predicted to have performance properties similar to RDX, but has low thermal stability. The simple and effective synthesis of amino hydroxyamino-functionalized compound **2** makes it an attractive building block worthy of further investigation.

This work was supported by the Russian Science Foundation (grant nos. 14-13-01153 to A.B.S. and 16-13-10404 to K.Y.S., structural investigation).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.007.

References

1 (*a*) *Green Energetic Materials*, ed. T. Brinck, Wiley, 2014; (*b*) I. V. Kuchurov, M. N. Zharkov, L. L. Fershtat, N. N. Makhova and S. G. Zlotin, *ChemSusChem*, 2017, **10**, 3914.

2 (*a*) P. Yin and J. M. Shreeve, *Adv. Heterocycl. Chem*., 2017, **121**, 89; (*b*) S. G. Zlotin, A. M. Churakov, I. L. Dalinger, O. A. Luk'yanov, N. N. Makhova, A. Yu. Sukhorukov and V. A. Tartakovsky, *Mendeleev Commun*., 2017, **27**, 535; (*c*) V. P. Ananikov, D. B. Eremin, S. A. Yakukhnov, A. D. Dilman, V. V. Levin, M. P. Egorov, S. S. Karlov, L. M. Kustov, A. L. Tarasov, A. A. Greish, A. A. Shesterkina, A. M. Sakharov, Z. N. Nysenko, A. B. Sheremetev, A. Yu. Stakheev, I. S. Mashkovsky, A. Yu. Sukhorukov, S. L. Ioffe, A. O. Terent'ev, V. A. Vil', Yu. V. Tomilov, R. A. Novikov, S. G. Zlotin, A. S. Kucherenko, N. E. Ustyuzhanina, V. B. Krylov, Yu. E. Tsvetkov, M. L. Gening and N. E. Nifantiev, *Meneleev Commun*., 2017, **27**, 425.

3 W. A. Trzciński and A. Belaada, *Cent. Eur. J. Energ. Mater*., 2016, **13**, 527.

4 (*a*) F. Eloy and R. Lenaers, *Chem. Rev*., 1962, **62**, 155; (*b*) I. A. Poplavskaya and R. G. Kurmangalieva, *Khimiya amidoksimov (Chemistry of Amidoximes)*, Nauka, Alma-Ata, 1988 (in Russian).

5 V. V. Bakharev, A. A. Gidaspov and V. E. Parfenov, *Chem. Heterocycl. Compd*., 2017, **53**, 659 (*Khim. Geterotsikl. Soedin*., 2017, **53**, 659).

6 (*a*) L. Simková, F. Liska and J. Ludvík, *Curr. Org. Chem*., 2011, **15**, 2983; (*b*) Y. Zhang, Q. Sun, K. Xu, J. Song and F. Zhao, *Propellants Explos. Pyrotech*., 2016, **41**, 35; (*c*) H. Gao and J. M. Shreeve, *RSC Adv*., 2016, **6**, 56271.

7 (*a*) A. J. Bellamy, N. V. Latypov and P. Goede, *J. Chem. Res. (S)*, 2003, 529; (*b*) A. V. Shastin, B. L. Korsunskii, T. I. Godovikova and V. P. Lodygina, *Russ. J. Appl. Chem*., 2009, **82**, 1802 (*Zh. Prikl. Khim*., 2009, **82**, 1650).

8 H. Gao, Y.-H. Joo, D. A. Parrish, T. Vo and J. M. Shreeve, *Chem. Eur. J*., 2011, **17**, 4613.

9 (*a*) C.-R. Chang, K.-Z. Xu, J.-R. Song, B. Yan, H.-X. Ma, H.-X. Gao and F.-Q. Zhao, *Acta Chim. Sinica (Huaxue Xuebao)*, 2008, **66**, 1399; (*b*) Q. J. Axthammer, B. Krumm and T. M. Klapötke, *J. Phys. Chem. A*, 2017, **121**, 3567.

10 A. Meents, B. Dittrich, S. K. J. Johnas, V. Thome and E. F. Weckert, *Acta Crystallogr*., 2008, **B64**, 42.

11 (*a*) I. L. Dalinger, A. Kh. Shakhnes, K. A. Monogarov, K. Yu. Suponitsky and A. B. Sheremetev, *Mendeleev Commun*., 2015, **25**, 429; (*b*) A. O. Dmitrienko, V. A. Karnoukhova, A. A. Potemkin, M. I. Struchkova, I. A. Kryazhevskikh and K. Yu. Suponitsky, *Chem. Heterocycl. Compd*., 2017, **53**, 532 (*Khim. Geterotsikl. Soedin*., 2017, **53**, 532); (*c*) A. B. Sheremetev, B. V. Lyalin, A. M. Kozeev, N. V. Palysaeva, M. I. Struchkova, K. Yu. Suponitsky, *RSC Adv*., 2015, **5**, 37617.

12 A. S. Smirnov, S. P. Smirnov, T. S. Pivina, D. B. Lempert and L. K. Maslova, *Russ. Chem. Bull., Int. Ed*., 2016, **65**, 2315 (*Izv. Akad. Nauk, Ser. Khim*., 2016, 2315).

13 (*a*) A. F. Pozharskii, V. V. Kuz'menko, C. Foces-Foces, A. L. Llamas-Saiz, R. M. Claramunt, D. Sanz and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1994, 841; (*b*) A. B. Sheremetev, N. V. Palysaeva, M. I. Struchkova and K. Yu. Suponitsky, *Mendeleev Commun*., 2012, **22**, 302.

14 (*a*) A. A. Gidaspov, V. A. Zalomlenkov, V. V. Bakharev, V. E. Parfenov, E. V. Yurtaev, M. I. Struchkova, N. V. Palysaeva, K. Yu. Suponitsky, D. B. Lempert and A. B. Sheremetev, *RSC Adv*., 2016, **6**, 34921; (*b*) A. A. Gidaspov, V. V. Bakharev, K. Yu. Suponitsky, V. G. Nikitin and A. B. Sheremetev, *RSC Adv*., 2016, **6**, 104325.

Received: 17th November 2017; Com. 17/5411