



Primary Nitramines Related to Nitroglycerine: 1-Nitramino-2,3-dinitroxypropane and 1,2,3-Trinitraminopropane

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Abstract: The title compounds 1-nitramino-2,3-dinitroxypropane (**NG-N1**) and 1,2,3-trinitraminopropane (**NG-N3**) were formed by multi-step reaction from the corresponding amine. Both compounds were fully characterized by means of multinuclear NMR (^1H , ^{13}C , ^{14}N), vibrational spectroscopy, elemental analysis and mass spectrometry. For prediction of the energetic properties ΔH_c values are determined by oxygen bomb calorimetry and validated by quantum theoretical methods. Both compounds are superior in their performance data to nitroglycerine (NG) and pentaerythritol tetranitrate (PETN). In comparison to nitroglycerine the sensitivities towards mechanical stimuli is greatly reduced. X-ray diffraction elucidated the molecular structure of both compounds. **NG-N1** crystallizes in the monoclinic space group $P2_1$ with a density of 1.799 g/cm^3 , **NG-N3** in the orthorhombic space group $Pnma$ with a density of 1.783 g/cm^3 . The thermal behavior and long term stabilities were checked using differential scanning calorimetry and thermogravimetric measurements. **NG-N1**, shows for primary nitramines, exceptional stability in the molten phase making this compound suitable for melt-cast application (T_{mp} : $65 \text{ }^\circ\text{C}$, T_{dec} : $170 \text{ }^\circ\text{C}$).

Keywords: explosives, primary nitramine, nitroglycerin, structure elucidation, thermostability

Introduction

The synthesis of new energetic materials and their structural and energetic characterization is a constant research topic in our group [1]. In the class of high explosive nitrate esters pentaerythritol tetranitrate (PETN) and nitroglycerine (NG) are the best known compounds. Their application is often limited due to their high sensitivities towards mechanical stimuli (PETN: 3 J, NG: 0.2 J). Several approaches have been made to overcome this problem, e.g. dynamite or several double or triple based propellants with the usage of nitrocellulose.

A new approach to get over this drawback is the chemical substitution of the nitric esters with primary nitramines. Best known examples for this class of high explosives are EDNA (ethylenedinitramine), MDNA (methylenedinitramine) or MNA (methylnitramine) [2a, 2b]. This class of energetic compounds is in many aspects advantageous. Due to the existence of a highly branched hydrogen bonding network, which is a consequence of the acidic proton, sensitivities towards mechanical stimuli are greatly reduced. Furthermore the improved density of the materials results in better performance data, as density is the key feature towards high explosives.

The thermostability of primary nitramines is closely connected to its molecular structure, especially to the acidity of compounds. Increasing the number of nitro groups in the compounds results in lower decomposition temperatures. A suitable decomposition mechanism for primary nitramines has been derived, supporting the decomposition pathway via the tautomeric isonitramine formed in strongly acidic media [3-5].

For nitroglycerine two primary nitramines are known in the literature: 1,3-dinitramino-2-nitroxypropane (**NG-N2**) [6-9] and 1,2,3-trinitraminopropane (**NG-N3**) [10], but only the former compound has been fully characterized in its energetic and structural properties. Here we present 1-nitramino-2,3-dinitroxypropane (**NG-N1**) as a new energetic compound with its full chemical and physical characterization.

Results and Discussion

Synthesis

Both compounds (**NG-N1**, **NG-N3**) were produced via an indirect nitration method starting with the amine. Protection using ethyl chloroformate to urethanes **1** and **3**, followed by nitration in dehydrating media easily yields the nitrated species **2** and **4**, which can be deprotected with ammonia. Finally acidification

furnishes **NG-N1** or **NG-N3** (Figure 1). The yields for each reaction step are given in the experimental part.

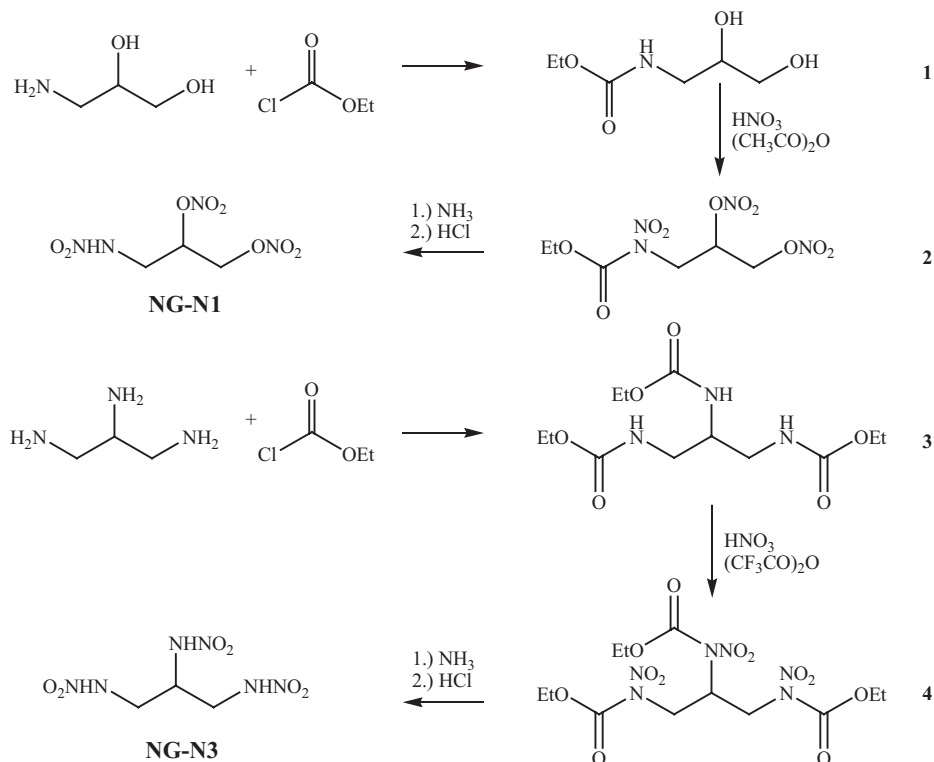


Figure 1. Syntheses of **NG-N1** and **NG-N3**.

Crystallographic Characterization

Suitable crystals for X-ray diffraction were obtained by slow evaporations of dichloromethane (**NG-N1**) or ethyl acetate (**NG-N3**) solutions. **NG-N1** crystallizes in the monoclinic space group $P2_1$ with four molecules in the unit cell and a density of 1.799 g/cm³. The asymmetric unit consists of two independent molecules, in which one molecule is disordered (Figure 2).

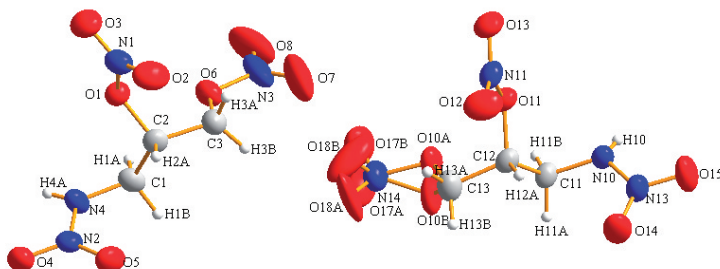


Figure 2. Molecular structure of **NG-N1**, displaced ellipsoids are drawn at the 50% probability level.

The reason for this disorder phenomenon is obvious considering the chemical environment of the nitrate ester groups. Figure 3 shows the neighbouring atoms on a 3 Å surface, indicating that there are no interactions of the nitric ester within this surrounding, which consists of several nitro groups. X-Ray measurements at 100 K supports this theory since the disorder persists.

NG-N3 crystallizes in the orthorhombic space group *Pnma* with a density of 1.783 g/cm³. The N–N bond lengths (1.33 Å) agree well with known nitramines and are significantly shorter than typical N – N single bonds (1.48 Å). A nearly planar amine supports this conjugation effect. The molecular structure of **NG-N3** is shown in Figure 4.

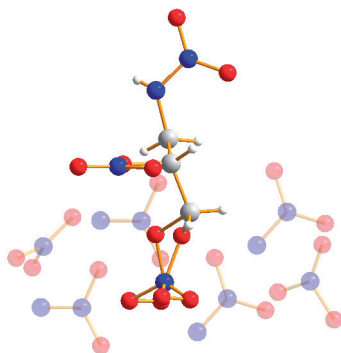


Figure 3. Chemical environment of disordered nitrate ester in **NG-N1**.

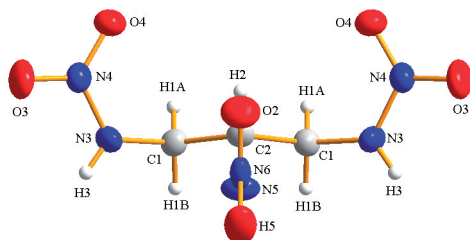


Figure 4. Molecular structure of **NG-N3**, displaced ellipsoids are drawn at the 50% probability level.

Selected bond distances for both compounds are given in Table 1 and the hydrogen bonding geometry is summarized in Table 2. Details of the crystal structure solution and refinement data can be found in Table 3.

Table 1. Selected bond lengths of **NG-N1** and **NG-N3**

Selected bond distances of NG-N1 in Å			
N2 N4 1.330(4)	C1 N4 1.431(5)	C3 O6 1.450(5)	C2 O1 1.445(4)
N1 O1 1.416(4)	N3 O6 1.386(4)	C1 C2 1.506(5)	C2 C3 1.503(5)
N1 O2 1.187(4)	N1 O3 1.203(4)	N2 O5 1.230(3)	N2 O4 1.237(4)
N3 O7 1.170(6)	N3 O8 1.216(6)		
Selected bond distances of NG-N3 in Å:			
N5 N6 1.332(2)	N4 N3 1.330(2)	N5 C2 1.446(3)	C1 N3 1.441(2)
O3 N4 1.226(2)	O4 N4 1.229(2)	O1 N6 1.235(2)	O2 N6 1.205(2)
C1 C2 1.526(2)			

Table 2. Hydrogen bonds present in **NG-N1** and **NG-N3**

Hydrogen bonds of NG-N1 [D-H-A] in Å, [°]				
D-H...A	D-H	H...A	D-A	[°]
N4-H4...O15 ⁱ	0.80(3)	2.36(3)	3.006(4)	138.3(5)
N10-H10...O4 ⁱⁱ	0.68(4)	2.65(3)	3.171(4)	135.0(4)
⁽ⁱ⁾ x+1, y+1, z+1, ⁽ⁱⁱ⁾ x-1, y, z-1				
Hydrogen bonds of NG-N3 [D-H-A] in Å, [°]				
D-H...A	D-H	H...A	D-A	[°]
N3-H3...O4 ⁱⁱⁱ	0.795(2)	2.267(2)	3.040(2)	163.9(2)
N5-H5...O1 ^{iv}	0.930(3)	1.933(3)	2.786(2)	153.0(2)
C1-H1A...O4 ^v	0.945(1)	2.561(2)	3.404(2)	148.8(1)
C2-H2...O2	0.976(2)	2.206(1)	2.737(2)	113.0(1)

⁽ⁱⁱⁱ⁾ 1/2-x, y, 1/2-z; ^(iv) 1/2+x, 1/2-y, 3/2-z; ^(v) 1/2+x, y, 3/2-z

The solid phase arrangement is strongly determined by the interaction of hydrogen bonds (Figure 5). For **NG-N1** a layer like architecture was found, with a minimum gap of 2.71 Å (C11-H11A-O12) between the layers, indicating that there are no interactions between the layers, so only classical hydrogen bonds within the layers are present. For **NG-N3** several classical and non-classical hydrogen bonds [11] are present and result in a three dimensional network arrangement. Due to the high nitration degree these non-classical C–H–O interactions have to be considered making **NG-N3** a very dense but also insensitive compound.

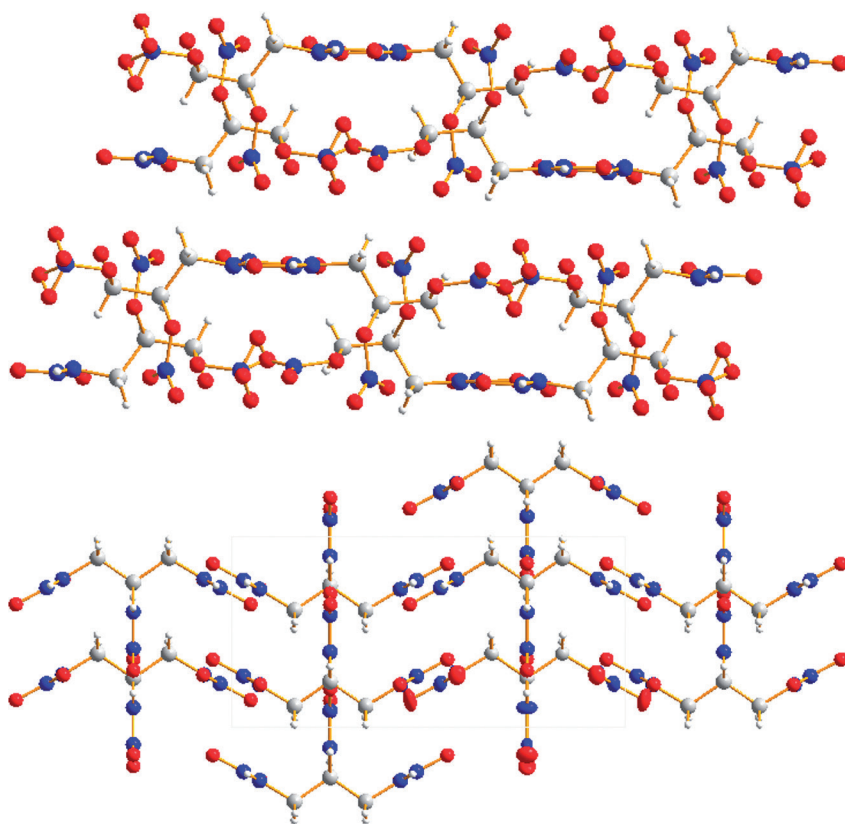


Figure 5. Layer like arrangement of **NG-N1** (top), and 3D arrangement of **NG-N3** (bottom).

Table 3. Crystallographic data

	NG-N1	NG-N3
Formula	C ₃ H ₆ N ₄ O ₈	C ₃ H ₈ N ₆ O ₆
Form. weight [g mol ⁻¹]	226.10	224.13
Crystal system	Monoclinic	Orthorhombic
Space Group	<i>P</i> 2 ₁ (No. 4)	<i>Pnma</i> (No. 62)
Color / Habit	colorless needles	colorless block
Size, mm	0.20 x 0.05 x 0.05	0.20 x 0.10 x 0.10
<i>a</i> [Å]	7.1363(6)	6.7377(3)
<i>b</i> [Å]	8.6355(6)	13.8704(7)
<i>c</i> [Å]	13.7048(12)	8.9341(5)
α [°]	90.0	90.0
β [°]	98.709(9)	90.0
γ [°]	90.0	90.0
<i>V</i> [Å ³]	834.83(12)	834.93(7)
<i>Z</i>	4	4
$\rho_{\text{calc.}}$ [g cm ⁻³]	1.799	1.783
μ [mm ⁻¹]	0.180	0.169
<i>F</i> (000)	464	464
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073
<i>T</i> [K]	200(2)	200(2)
Theta Min-Max [°]	3.7, 32.5	4.6, 33.3
Dataset	-8: 8 ; -10: 10 ; -17: 17	-8: 8 ; -17: 17 ; -9: 11
Reflections collected	8669	4377
Independent reflections	3430	952
Observed reflections	2376	638
No. parameters	348	94
<i>R</i> ₁ (obs)	0.0424	0.0315
<i>wR</i> ₂ (all data)	0.1012	0.0723
<i>S</i>	1.018	0.898
Resd. Dens. [e/ Å ³]	-0.275, 0.294	-0.154, 0.318
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan
CCDC	743398	743399

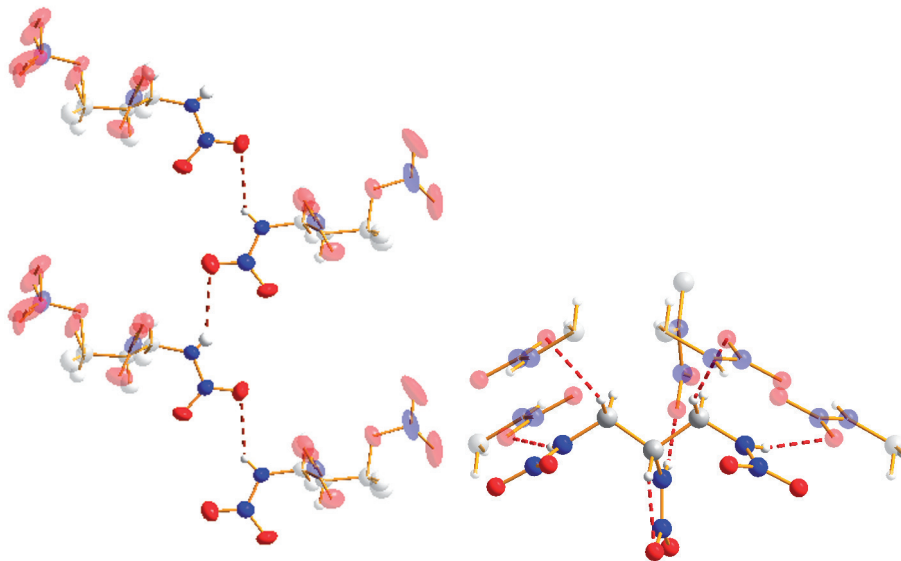


Figure 6. Hydrogen bridge bonds of **NG-N1** (left) and **NG-N3** (right).

Thermal and Energetic Properties

To study the thermal stability of **NG-N1** and **NG-N3** differential scanning calorimetry (DSC) measurements were performed with heating rates of 5 K/min. For safety testing, the impact and friction sensitivities as well as the electrostatic sensitivities were determined [12]. In addition, the constant volume energies of combustion ($\Delta_c U$) were determined experimentally by oxygen bomb calorimetry. Heats and energies of formation were calculated backwards and used subsequently in conjunction with the molecular formula and density from X-Ray measurements to predict the performance parameters, using the EXPLO5 computer code [13]. To confirm the values quantum chemical calculations were performed using the Gaussian G03W (revision B.04) program package [14]. The gas phase enthalpies were calculated according to atomization energy theory with the CBS-4M method following eq. 1 [15-19].

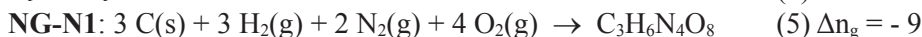
For calculating the solid state enthalpies of formation eq. 2 was used, as the enthalpy of sublimation is approximated by Trouton's law (eq. 3) [20]. Finally the enthalpies of formation are converted to energies of formation according to eqs. (4-6).

$$\Delta_f H^\circ(\text{g, m}) = H(\text{molecule}) - \sum H^\circ(\text{atoms}) + \sum \Delta_f H^\circ(\text{atoms}) \quad (1)$$

$$\Delta_f H^\circ(\text{s}) = \Delta_f H^\circ(\text{g}) - (\Delta_{\text{sub}} H) \quad (2)$$

$$\Delta_{\text{sub}} H. [\text{J mol}^{-1}] = 188 T_m [\text{K}] \quad (3)$$

$$\Delta_f U = \Delta_f H - \Delta nRT \quad (4)$$



$$\Delta_f U^\circ(\text{NG-N1}) = -317 \text{ kcal mol}^{-1} = -1400 \text{ kJ kg}^{-1}$$

$$\Delta_f U^\circ(\text{NG-N3}) = -136 \text{ kcal mol}^{-1} = -609 \text{ kJ kg}^{-1}$$

The physicochemical properties of **NG-N1** and **NG-N3** are listed in Table 4 and compared with the ones of NG (nitroglycerine) and NG-N2 (1,3-dinitramino-2-nitroxypropane).

Table 4. Physicochemical properties of **NG**, **NG-N2**, **NG-N1** and **NG-N3**

	NG	NG-N2	NG-N1	NG-N3
Formula	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9$	$\text{C}_3\text{H}_7\text{N}_5\text{O}_7$	$\text{C}_3\text{H}_6\text{N}_4\text{O}_8$	$\text{C}_3\text{H}_8\text{N}_6\text{O}_6$
Molecular Mass	227.09	225.12	226.10	224.13
Impact sensitivity (J)	0.2	7 ^d	14 ^c	7 ^c
Friction sensitivity (N)	360	96 ^d	96 ^c	144 ^c
Electrical discharge (J)	no value	0.6 ^d	1.1 ^c	0.4 ^c
Ω (%)	+3.5	-17.8	-7.1	-28.6
$T_{\text{melt.}}$ ($^\circ\text{C}$) ^a	14	166	66	127
$T_{\text{dec.}}$ ($^\circ\text{C}$) ^a	143	168	173	134
Density (g cm^{-3})	1.591	1.798 ^b	1.799 ^b	1.783 ^b

^a obtained by DSC measurement ($\beta = 5 \text{ K min}^{-1}$); ^b densities are calculated from X-Ray diffraction; ^c grain sizes 500 μm ; ^d grain size 250 μm .

Due to the presence of hydrogen bonds the impact sensitivity is reduced from the highly sensitive nitroglycerine (0.2 J) to 14 J for **NG-N1** and 7 J for **NG-N3**. Density obtained by single crystal X-ray diffraction increases from 1.591 g/cm^3 to around 1.8 g/cm^3 . Both compounds discussed inside here are solids under standard conditions. For **NG-N1** a low melting point of 65 $^\circ\text{C}$ is the consequence of the layer like arrangement in the solid phase. Decomposition occurs for **NG-N1** at 173 $^\circ\text{C}$, which makes the compound suitable for melt-cast applications. To the best of our knowledge **NG-N1** is unique in its thermal behaviour and so far the only primary nitramine which can be molten without decomposition. DSC plots for **NG-N1** and **NG-N3** are shown in Figure 7.

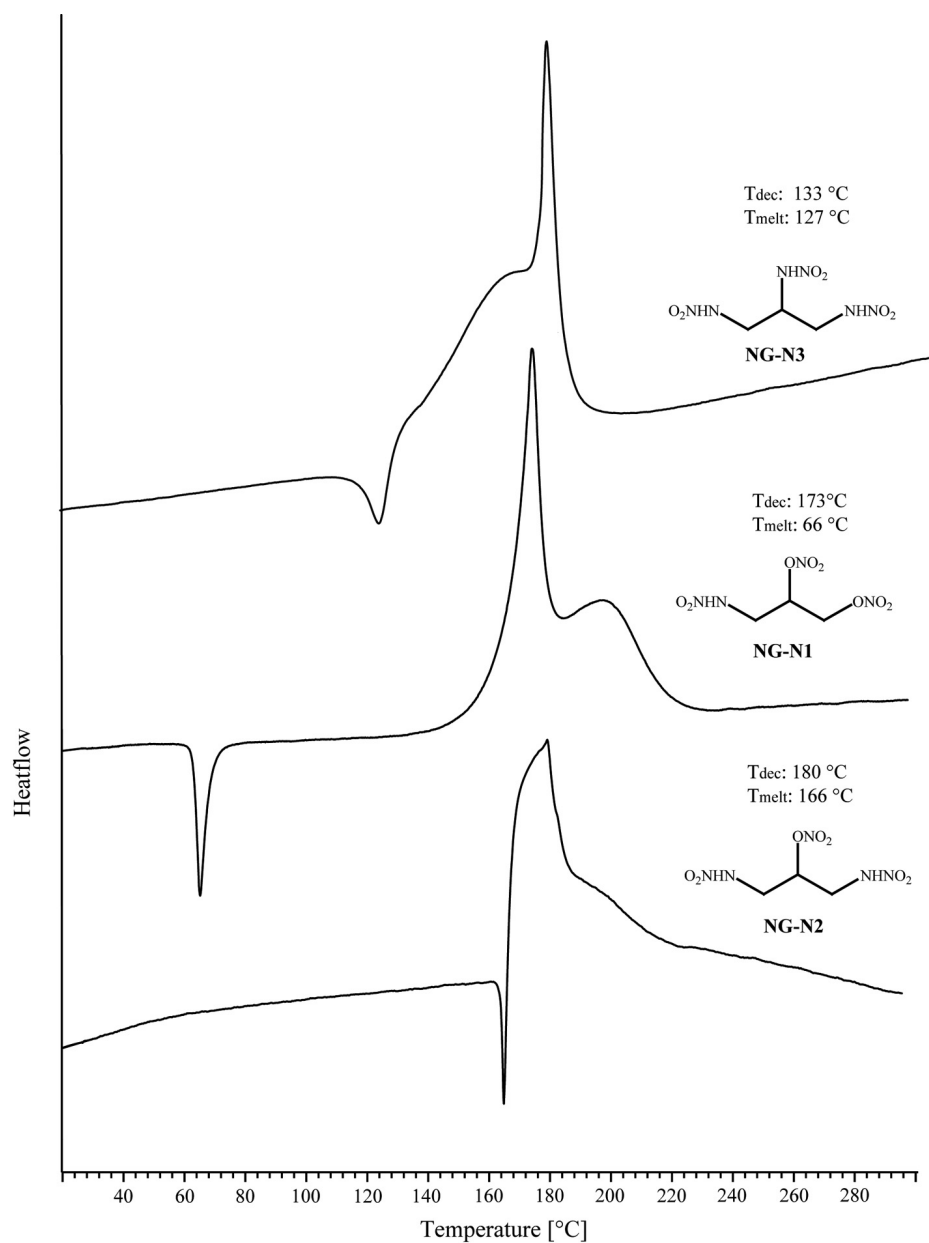


Figure 7. DSC plots of **NG-N2**, **NG-N1** and **NG-N3** with heating rates of 5 K min⁻¹.

For validation we made long term stability measurements at 75 °C in the molten state (Figure 8) and also thermogravimetric analysis (Figure 9) indicating no decomposition at all, which was rechecked by NMR spectroscopy. The commonly assumed decomposition mechanism for primary nitramines via the isonitramine form causes **NG-N3** to decompose immediately with gas evolution, when molten. The presence of more nitramine functionalities increases the acidity enormously and so hydrogen transfer initiates decomposition more easily.

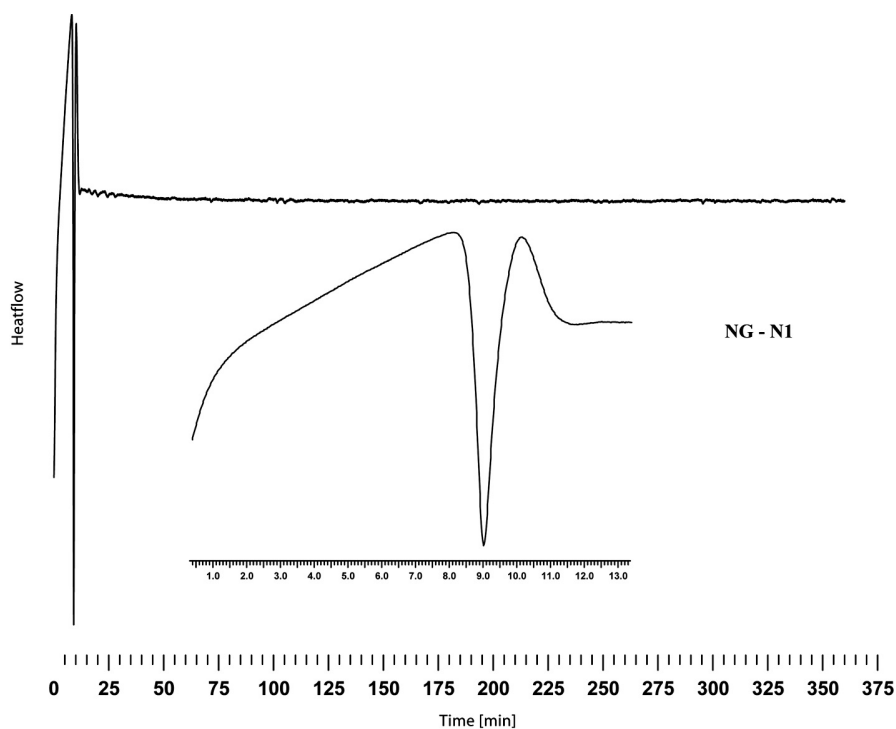


Figure 8. Long-term stability of **NG-N1** in the molten state at 75 °C for 6 hours.

Detonation parameters, calculated with the EXPLO5 program code [13] are compared in Table 5 with the experimentally determined energy of combustion as well as for quantum chemically obtained heats of formations. The relevant parameters (detonation velocity, detonation pressure and heat of explosion) indicate that both compounds are superior to nitroglycerine and comparable to RDX, which is the standard energetic filler in military explosives. For **NG-N3** bomb calorimetric measurements were impossible, due to acid catalyzed decomposition in benzoic acid.

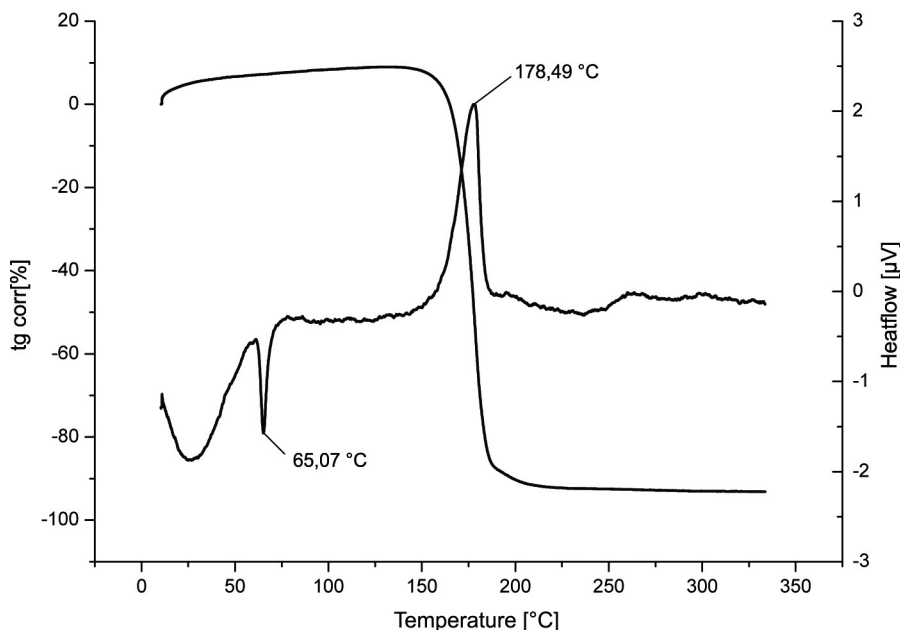


Figure 9. DTG curve of NG-N1 with a heating rate $\beta = 10 \text{ °C/min}$.

Table 5. Computed detonation parameters for NG, NG-N2, NG-N1, NG-N3

	NG _{liquid}		NG-N2		NG-N1		NG-N3
	Theo. ^a	Exp. ^b	Theo. ^a	Exp. ^c	Theo. ^a	Exp. ^c	Theo. ^a
Density (g cm ⁻³)	1.591		1.798		1.799		1.783
ΔH_f (kJ mol ⁻¹)	-335	-370	-137	-98	-338	-310	-161
$\Delta_f U$ (kJ mol ⁻¹)	-314	-345	-114	-74	-317	-288	-136
$\Delta_f U$ (kJ kg ⁻¹)	-1384	-1520	-506	-332	-1400	-1273	-609
Q_v / kJ kg ⁻¹	-6076	-6054	-5968	-6130	-6510	-5879	5246
T_{ex} / K	4598	4639	4249	4331	4659	4316	3729
p / kbar	235	236	342	347	343	326	307
D / m s ⁻¹	7721	7757	8986	8984	8893	8840	8598
V / L kg ⁻¹	722	723	814	815	756	793	825

^a theoretical values obtained from CBS-4M quantum chemical method; ^b NIST database [33];

^c energetic parameters are based on the constant volume energy of combustion derived by oxygen bomb calorimetry.

In order to evaluate the detonation velocity and to prove the initiative properties of **NG-N1** we made detonation velocity measurements with a fibre optic technique using OZM measuring system EXPLOMET-FO-2000. A 14 mm PE tube was filled with 10 g of material and equipped with two optical fibres at a distance of 2 cm. Initiation was achieved by electrical ignition (40V, 5A) PETN-SAcN detonator loaded with 1 g PETN and 0.2 g of silver acetylide nitrate. A detonation velocity of 5405 m/s was measured for a material density of 1.0 g/cm³, which validates the theoretical value of 5941 m/s. High speed pictures of the detonation are shown in Figure 10.



Figure 10. Detonation velocity measurement of **NG-N1** (4000 fps, 4 frames).

Conclusions

From this experimental study the following conclusions can be drawn:

- (i) 1-Nitramino-2,3-dinitroxypropane (**NG-N1**) was prepared in high yield and purity starting from commercially available 1-amino-2,3-propanediol. 1,2,3-Trinitramino-propane (**NG-N3**) was synthesized in the same manner starting from a new, facile and cheap reduction of 1,2,3-triazidopropane by triphenylphosphine.

- (ii) Experimental and theoretical evaluations of the detonation parameters indicate that **NG-N1** has good potential as an energetic filler in high explosive formulations.
- (iii) Thermal characterization of **NG-N1** proved it to be a suitable material for melt cast applications. Long term stability was studied in the molten phase indicating no decomposition at all. For **NG-N3** the thermal stability is lowered significantly proving the acid catalyzed decomposition path way.
- (iv) Due to hydrogen bonding the sensitivities of **NG-N1** and **NG-N3** are greatly reduced in comparison to nitroglycerine, however the performance is significantly higher and comparable with the performance data of RDX.

Experimental

CAUTION! Although we had no problems in synthesis, the investigated compounds are nevertheless energetic materials. Therefore proper protective measures (safety glasses, face shield, leather coat or Kevlar® vest, earthed equipment and shoes, Kevlar® gloves and ear plugs) should be used, especially during the work with NG-N1 and NG-N3. As 1,2,3-triazidopropane is a very explosive substance, the best way to handle it is a ethereal solution.

Single crystal X-ray diffraction was performed on Xcalibur 3 diffractometer equipped with a CCD detector using CrysAlis CCD software [21] for the measurement and CrysAlis RED software for data reduction [22]. All data were collected using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined by means of full-matrix least-squares procedures using WinGX and the available software in the package [23-26]. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were located from difference Fourier electron density maps and refined isotropically. Differential scanning calorimetry measurements were performed in pressed Al-containers, containing a hole (0.1 mm) for gas release, with a nitrogen flow of 20 mL/min on a Linseis PT-10 DSC [27]. Impact Sensitivities were determined according to STANAG 4489 [28] modified according to instruction [29] using a BAM (Bundesanstalt für Material- forschung [30]) drophammer [31]. The friction sensitivity tests were carried out according to STANAG 4487 [32] modified according to instruction [33] using the BAM friction tester. The electrostatic sensitivity tests were carried out using an electric spark tester ESD 2010EN (OZM Research) operating with the “Winspark 1.15 software package” [34]. Constant volume energies of combustion ($\Delta_c U$) were determined experimentally using Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 1108CL oxygen bomb [35]. The reported values are the

average of three separate measurements performed with a probe sample made from approximately 200 mg substance and 800 mg benzoic acid to ensure a residue free burning.

Ethyl-2,3-dihydroxypropylcarbamate (**1**)

3-Aminopropane-1,2-diol (66 mmol, 6.03 g) was dissolved in water (25 mL) and 25 mL of ethyl acetate was added. 3.59 g ethyl chloroformate (33 mmol) was added dropwise under ice cooling. Afterwards 3.59 g ethyl chloroformate (33 mmol) was added simultaneously with a 2 M sodium hydroxide solution (33 mL). The reaction mixture was stirred for 4 h at room temperature, then extracted with ethyl acetate (6 x 100 ml) against a sodium chloride saturated solution and dried over magnesium sulphate. The solvent was evaporated to give a yellow oil as the crude product. Distillation at 120-135 °C and $1 \cdot 10^{-3}$ mbar yielded **1** as a colorless, oily liquid (5.17 g, 48%).

¹H NMR ([d₆]-DMSO) δ /ppm: 6.10 – 5.70 (br, 1H, NH), 4.35 – 4.25 (br, 2H, OH), 3.98 (q, $J = 7.1$ Hz, 2H, CH₃CH₂O), 3.69 – 3.61 (m, 1H, CH), 3.50 (dd, $J_{\text{gem}} = 11.6$ Hz, $J_{\text{cis}} = 3.9$ Hz, 1H, HCHOH), 3.41 (dd, $J_{\text{gem}} = 11.6$ Hz, $J_{\text{trans}} = 5.9$ Hz, 1H, HCHOH), 3.18 (dd, $J_{\text{gem}} = 14.0$ Hz, $J_{\text{cis}} = 4.5$ Hz, 1H, HCHNH), 3.06 (dd, $J_{\text{gem}} = 14.1$ Hz, $J_{\text{trans}} = 6.7$ Hz, 1H, HCHNH), 1.22 (t, $J = 7.0$ Hz, 3H, CH₃CH₂). **¹³C{¹H} NMR** ([d₆]-DMSO) δ /ppm: 157.8 (C=O), 71.2 (CH), 63.9 (CH₂OH), 61.2 (CH₃CH₂), 43.3 (NHCH₂), 14.5 (CH₃). **IR** ν /cm⁻¹: 3317 (m), 2981 (w), 2935 (w), 2873 (w), 1695 (vs), 1682 (vs, 100%), 1532 (s), 1442 (w), 1382 (w), 1333 (w), 1253 (vs), 1173 (m), 1147 (w), 1103 (m), 1028 (vs), 909 (vw), 873 (vw), 778 (w). **Raman** ν /cm⁻¹ (rel. int.): 3259 (7), 2975 (59), 2937 (100), 2879 (15), 1688 (33), 1537 (28), 1455 (63), 1384 (39), 1302 (41), 1274 (47), 1251 (41), 1175 (35), 1116 (63), 1095 (57), 1045 (45), 982 (38), 877 (62), 815 (40), 688 (33), 457 (58), 377 (63), 354 (61). **Elemental analysis**: Calculated: C 44.16%, H 8.03%, N 8.58%; Found: C 43.60%, H 8.27%, N 8.39%.

Ethyl-2,3-bisnitroxypropylnitrocarbamate (**2**)

Nitric acid (169 mmol, 10.64 g) was cooled to -5 °C and **1** (13 mmol, 1.95 g) was added dropwise. The reaction mixture was kept at -5 to 0 °C and stirred for 1 hour. The reaction mixture was poured on crushed ice (70 g) and crude **2** appears as a yellow oily liquid. The aqueous layer was discarded, the yellow oily layer neutralized with saturated sodium bicarbonate solution and extracted with ether (6 x 100 mL). The organic phase was washed with water (2 x 100 mL) and dried over magnesium sulphate. After evaporation of the solvent, **2** remained as a yellow liquid (2.49 g, 64%).

¹H NMR ([d₆]-DMSO) δ /ppm: 5.71 – 5.65 (m, 1H, CH), 4.97 (dd, $J_{\text{gem}} =$

12.8 Hz, $J_{\text{cis}} = 2.8$ Hz, 1H, $\underline{\text{H}}\text{CHNNO}_2$) 4.83 (dd, $J_{\text{gem}} = 12.6$ Hz, $J_{\text{trans}} = 5.8$ Hz, 1H, $\text{HCH}\underline{\text{H}}\text{NNO}_2$), 4.48 (d, $J = 5.5$ Hz, 2H, CH_2ONO_2), 4.28 (q, $J = 7.1$ Hz, 2H, $\text{CH}_3\text{CH}_2\text{O}$), 1.25 (t, $J = 7.2$ Hz, 3H, CH_3CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{d}_6]$ -DMSO) δ/ppm : 150.0 ($\underline{\text{C}}=\text{O}$), 77.4 ($\underline{\text{C}}\text{H}$), 70.6 (CH_2ONO_2), 65.3 (CH_3CH_2), 47.9 ($\text{NNO}_2\underline{\text{C}}\text{H}_2$), 14.1 ($\underline{\text{C}}\text{H}_3\text{CH}_2$). ^{14}N -NMR ($[\text{d}_6]$ -DMSO) δ/ppm : -44 (NNO_2). IR ν/cm^{-1} : 2990 (w), 2472 (w), 2026 (vw), 1973 (vw), 1774 (m), 1718 (m), 1641 (s), 1581 (s), 1429 (m), 1369 (m), 1326 (w), 1270 (s), 1236 (w), 1220 (w), 1177 (s), 1154 (s), 1094 (m), 1054 (w), 988 (s), 832 (vs, 100%), 749 (s), 676 (m). Raman ν/cm^{-1} (rel. int.): 2983 (vs, 100%), 2946 (vs), 2901 (w), 2878 (w), 2781 (w), 2735 (w), 1775 (m), 1742 (m), 1656 (m), 1583 (m), 1500 (w), 1456 (s), 1435 (s), 1398 (w), 1371 (w), 1329 (s), 1294 (vs), 1243 (m), 1214 (m), 1113 (m), 1098 (m), 1055 (vw), 1037 (vw), 865 (vs), 800 (w), 752 (w), 729 (w), 687 (m), 606 (m), 554 (m), 529 (m), 454 (m), 358 (m), 327 (vw), 244 (m). MS (DEI+): m/z (%): 299 (100) [M+H], 245 (30) [M-NO₂], 192 (10) [M-NO₂-ONO₂], 147 (42) [M-NO₂-ONO₂-OCH₂CH₃], 57 (37) [C₃H₇N]. Elemental analysis: Calculated: C 24.17%, H 3.38%, N 18.79%; Found: C 24.32%, H 3.53%, N 18.81%. $T_{\text{dec.}} = 185$ °C.

1-Nitramino-2,3-dinitroxypropane (NG-N1)

2 (3 mmol, 1.1 g) was dissolved in dry ether (20 mL) and cooled to 0 °C. Gaseous ammonia was bubbled through the solution for 5 minutes. The clear solution gets quickly cloudy. At the end of the reaction a white precipitate appears. The reaction mixture was extracted with water (2 x 25 mL) and then poured on ice (20 g). After neutralization with HCl to methyl orange, the mixture was extracted with dichloromethane and dried over magnesium sulphate. After evaporation of the solvent, **NG-N1** remained as a pale yellow solid (0.785 g, 94%).

^1H NMR ($[\text{d}_6]$ -DMSO) δ/ppm : 12.35 – 12.29 (br, 1H, NH), 5.63 – 5.57 (m, 1H, CH), 4.93 (dd, $J_{\text{gem}} = 12.8$ Hz, $J_{\text{cis}} = 3.1$ Hz, 1H, $\underline{\text{H}}\text{CHONO}_2$), 4.78 (dd, $J_{\text{gem}} = 12.8$ Hz, $J_{\text{trans}} = 6.2$ Hz, 1H, $\text{HCH}\underline{\text{H}}\text{ONO}_2$), 3.99 (dd, $J_{\text{gem}} = 15.5$ Hz, $J_{\text{cis}} = 4.2$ Hz, 1H, $\underline{\text{H}}\text{CHNNO}_2$), 3.75 (dd, $J_{\text{gem}} = 15.4$ Hz, $J_{\text{trans}} = 7.5$ Hz, 1H, $\text{HCH}\underline{\text{H}}\text{NNO}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{d}_6]$ -DMSO) δ/ppm : 77.1 ($\underline{\text{C}}\text{H}$), 70.7 (CH_2ONO_2), 44.0 (CH_2NNO_2). ^{14}N -NMR ($[\text{d}_6]$ -DMSO) δ/ppm : -31 (NHNO_2), -48 (ONO_2), -50 (ONO_2) -312 (NHNO_2). IR ν/cm^{-1} : 3309 (s), 3005 (vw), 2904(vw), 1646 (vs), 1628 (vs), 1586 (vs), 1530 (vw), 1435 (s), 1405 (m), 1378 (m), 1334 (s), 1265 (vs, 100%), 1149 (m), 1105 (m), 1075 (s), 1042 (m), 986 (vw), 915 (w), 876 (s), 834 (vs), 775 (w), 748 (m), 724 (w), 686 (w), 653 (w). Raman ν/cm^{-1} (rel. int.): 3295 (w), 2997 (s), 2957 (s), 2976 (s), 2905 (w), 1658 (w), 1630 (w), 1591 (vw), 1464 (w), 1437 (m), 1397 (m), 1364 (m), 1334 (m), 1285 (vs, 100%), 1234 (m), 1153 (m), 1117 (m), 1075 (w), 1045 (m), 986 (m), 931 (w), 914 (vw), 876 (m), 845 (m), 756 (w), 728 (w), 688 (w), 656 (w), 610 (m), 560 (m), 527 (m), 454 (m), 358 (vw),

241 (s). **Elemental analysis:** Calculated: C 15.94%, H 2.67%, N 24.78%; Found: C 16.24%, H 2.55%, N 29.32%. $T_{mp.} = 65\text{ }^{\circ}\text{C}$ $T_{dec.} = 178\text{ }^{\circ}\text{C}$.

1,2,3-Triaminopropane • 3 HCl

A solution of 23.58 g triphenylphosphine (90 mmol) in 230 mL THF was added dropwise under stirring to a solution of 5.0 g 1,2,3-triazidopropane (30 mmol) in 200 mL THF at room temperature. Stirring was continued for 14 hours. The reaction was quenched with 20 mL of water and stirred overnight. The solid was filtered off, washed with water and concentrated in vacuo. The crude oily product was dissolved in ethanol and acidified with HCl to yield 5.60 g (28 mmol, 86%) of 1,2,3-triaminopropane • 3 HCl. The analytical data was identical to the reduction method by Hegetschweiler [36].

Triethyl-propane-1,2,3-triyltricarbamate (**3**)

1,2,3-triaminopropane • 3 HCl (24.5 mmol, 4.84 g) was dissolved in water (40 mL) and 80 ml of ethyl acetate was added. A 2 M sodium hydroxide solution (37 mL) was added dropwise under ice cooling to generate the free base. Then 3.96 g (36.5 mmol) ethyl chloroformate was added dropwise under ice cooling. Afterwards 3.96 g (36.5 mmol) of ethyl chloroformate was added simultaneously with a 2 M sodium hydroxide solution (37 mL) The reaction mixture was stirred for 14 hours, then extracted with ethyl acetate (6 x 100 mL), washed with water (2 x 100 mL) and dried over magnesium sulphate. Ethyl acetate was removed under reduced pressure and **3** remained as a white solid (5.35 g, 71%).

$^1\text{H NMR}$ ($[\text{d}_6]$ -DMSO) δ/ppm : 6.96 (t, $J = 5.4$ Hz, 2H, NH), 6.75 (d, $J = 8.3$ Hz, 1H, NH), 4.00 – 3.91 (m, 6H, OCH_2CH_3), 3.59 – 3.48 (m, 1H, CH), 3.08 – 2.91 (m, 4H, CH_2), 1.13 (t, $J = 7.0$ Hz, 9H, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{d}_6]$ -DMSO) δ/ppm : 157.0 ($\text{C}=\text{O}$), 156.5 ($\text{C}=\text{O}$), 60.3 (OCH_2CH_3), 60.2 (OCH_2CH_3), 51.5 (CH), 42.3 (CH_2), 15.2 (OCH_2CH_3), 15.1 (OCH_2CH_3). **IR** ν/cm^{-1} : 3317 (s), 3069 (vw), 2980 (w), 2937 (w), 1681 (vs), 1537 (vs), 1481 (w), 1440 (w), 1367 (w), 1334 (w), 1287 (ms), 1262 (s), 1242 (s), 1152 (m), 1069 (m), 1031 (m), 917 (vw), 878 (vw), 846 (vw), 779 (w), 657 (m). **MS** (DEI+) m/z (%): 306 (0.37) [M+H], 260 (22) [M-OEt], 203 (100) [M-H₂CNHCO₂Et], 187 (10) [M-OEt-CO₂Et], 157 (87) [M-2-CO₂Et-2H], 115 (24) [-OEt-2CO₂Et], 85 (44) [M-3CO₂Et-H]. **Elemental analysis:** Calculated: C 47.20%, H 7.59%, N 13.76%; Found: C 47.17%, H 6.97%, N 13.66%. $T_{mp.} = 105\text{ }^{\circ}\text{C}$.

Triethyl-propane-1,2,3-triyltrinitrocarbamate (**4**)

A solution containing 10 g (48 mmol) of trifluoroacetic anhydride and 5.36 g (85.5 mmol) of nitric acid was cooled to $-30\text{ }^{\circ}\text{C}$ and **3** was added in small portions

at this temperature. The reaction mixture was allowed to warm up to 0 °C over a period of 2 hours. Then the reaction mixture was quenched by pouring on 100 g of ice water causing the product to precipitate as white oil. To this mixture sodium bicarbonate was added until the gas evolution stopped. The solution was extracted with diethyl ether (6 x 100 mL), washed with sodium bicarbonate and water. After drying over magnesium sulphate and removing the organic solvent in vacuo, **4** remained as a yellow oil (2.75 g, 95%).

¹H NMR ([d₆]-DMSO) δ/ppm: 5.21 – 5.07 (m, 1H, CH), 4.71 (dd, $J_{\text{gem}} = 16.2$ Hz, $J_{\text{trans}} = 9.1$ Hz, 2H, HCH), 4.45 (dd, $J_{\text{gem}} = 16.2$ Hz, $J_{\text{cis}} = 3.9$ Hz, 2H, HCH), 4.31 – 4.20 (m, 6 H, CH₂CH₃), 1.23(t, $J = 7.2$ Hz, 3H, OCH₂CH₃), 1.22 (t, $J = 7.2$ Hz, 6H, OCH₂CH₃). **¹³C{¹H} NMR** ([d₆]-DMSO) δ/ppm: 150.1 (C=O), 149.8 (C=O), 65.9 (OCH₂CH₃), 58.0 (CH), 48.4 (CH₂), 14.0 (OCH₂CH₃). **¹⁴N NMR** ([d₆]-DMSO) δ/ppm: -44 (NNO₂). **IR** ν /cm⁻¹: 2988 (w), 2943 (vw), 2914 (vw), 1772 (vs), 1740 (s), 1574 (vs), 1467 (vw), 1442 (w), 1370 (w), 1333 (vw), 1287 (vw), 1236 (m), 1197 (s), 1172 (vs), 1150 (vs), 1096 (m), 986 (s), 944 (m), 866 (s), 801 (vw), 747 (w), 736 (w). **MS** (DEI+) m/z (%): 441 (0.63) [M+H], 395 (7) [M-OEt, M-NO₂+H], 348 (3) [M-2NO₂], 293 (9) [M-CH₂(NNO₂COOEt)], 230 (5) [M-2NO₂-CO₂Et-OEt], 202 (13) [M-2NO₂-2CO₂Et], 201 (4) [M-3NO₂-CH₂(NNO₂COOEt)], 149 (30) [CH₂(NNO₂COOEt)+2H], 75 (75) [CH₂NHNO₂]. **Elemental analysis:** Calculated: C 32.73%, H 4.58%, N 19.09%; Found: C 32.98%, H 4.58%, N 18.85%.

1,2,3-Trinitraminopropane (NG-N3)

To 30 mL of concentrated ammonia solution (25%) **4** (5.0 mmol, 2.2 g) was added and the temperature was raised up to 70 °C. After 15 minutes the solution was cooled down and acidified with HCl to pH 2. The reaction mixture was extracted with ethyl acetate (5 x 25 mL), washed with water and dried over magnesium sulphate. After removing the organic solvent in vacuo, **NG-N3** remained as a very pale yellow solid (0.84 g, 75%).

¹H NMR ([d₆]-DMSO) δ/ppm: 12.35 – 12.00 (br, 3H, NH), 4.50 – 4.38 (m, 1H, CH), 3.71 (dd, $J_{\text{gem}} = 14.8$ Hz, $J_{\text{cis}} = 4.4$ Hz, 2H, HCH), 3.46 (dd, $J_{\text{gem}} = 14.6$ Hz, $J_{\text{trans}} = 8.3$ Hz, 2H, HCH). **¹³C{¹H} NMR** ([d₆]-DMSO) δ/ppm: 51.9 (CH), 44.9 (CH₂). **¹⁴N-NMR** ([d₆]-DMSO) δ/ppm: -27 (NHNO₂). **IR** ν /cm⁻¹: 3360 (vs), 3275 (vs), 2994 (m), 2957 (m), 1576 (s), 1554 (s), 1422 (s), 1392 (s), 1379 (s), 1337 (vs), 1305 (vs), 1287 (vs), 1241 (s), 1267 (s), 1148 (m), 1121 (m), 1070 (m), 881 (w), 871 (w), 772 (w), 762 (w), 749 (w), 655 (w). **MS** (DEI+) m/z (%): 226 (1) [M+2H], 149 (7) [M-CH₂NHNO₂], 131 (3) [M-2NO₂-H], 105 (27) [M-2NHNO₂+3H], 75 (100) [CH₂NHNO₂], 46 (100) [NO₂], 44 (100) [CH₂CH₂NH+2H]. **Elemental analysis:** Calculated: C 16.08%, H 3.60%,

N 37.80%; Found: C 16.35%, H 3.62%, N 37.07%. $T_{m.p.} = 127\text{ }^{\circ}\text{C}$ $T_{dec.} = 134\text{ }^{\circ}\text{C}$.

Supporting Information

Crystallographic data for the structures **NG-N1** and **NG-N3** reported in this article have been deposited with the Cambridge Crystallographic Data Centre (**NG-N1**: 743398, **NG-N3**: 743399). Copies of the data can be obtained free of charge from CCDC (12 Union Road, Cambridge, CB2 1EZ, UK [fax (internat.) +44(0)1223 /336033; e-mail: deposit@ccdc.cam.ac.uk].

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