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ARTICLE

The Pyridazine Scaffold as a Building Block for Energetic Materials: Synthesis, Characterization, and Properties

Ivan Gospodinov,[a] Johannes Singer,[a] Thomas M. Klapötke,*[a] and Jörg Stierstorfer[a]

Abstract. In the present studies, the synthesis of new energetic materials based on the pyridazine scaffold and their characterization is the main subject. For this purpose, desired 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide (**7**) was synthesized in the first instance. The persubstituted pyridazine precursor laid the groundwork for further preparative modification. The targeted functionalization through the regioselective introduction of various smaller amine nucleophiles such as methylamine or 2-aminoethanol gave several new energetic materials. Among them are 3,5-bis(methylamino)-4,6-dinitropyridazine-1-oxide (**8**), 3,5-bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (**9**), 3,5-bis(dimethylamino)-4,6-dinitropyridazine-1-oxide (**10**), and 3,5-bis((2-hydroxyethyl)amino)-4,6-dinitropyridazine-1-oxide (**11**). With the aim of increasing the detonation performance, compound **8** was additionally nitrated and 3,5-bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (**9**) was obtained. These new energetic materials were characterized and identified by multinuclear NMR (^{1}H, ^{13}C, ^{14}N, ^{15}N) and IR spectroscopy, elemental analysis and mass spectrometry. In addition, their sensitivities toward impact, friction and electrostatic discharge were thoroughly examined. Furthermore, obtained single-crystals of the substances were characterized by low-temperature single-crystal X-ray diffraction.

Introduction

During the last decades, extensive work and efforts have been made to discover highly efficient and performing new energetic materials with high thermal stability and good sensitivities toward accidental stimuli.[1] In addition, the production of new environmental benign energetic materials is desired process, due to the fact that mostly of the nowadays synthesized HEDM (RDX, TATB and TNT) are either carcinogenic or toxic.[2] For this purpose scientists worldwide have been developing modern approaches for the synthesis of new energetic materials. An emerging approach is the use of polyfunctionalized nitrogen-rich heterocycles as a building block for new materials. In several instances, azole and diazine based energetic materials have been found to have promising physico-chemical properties e.g. 3,4,5-trinitropyrazole,[3] bis(4-amino-3,5-dinitropyrazolyl)-methane[4] and 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105).[5] It appears that the combination of nitrogen-rich heterocycles with an alternating C–NH_2/C–NO_2 and N^+–O^- moiety results in the formation of thermally stable, insensitive materials with good detonation parameters. This can be explained with the formation of intra- and intermolecular hydrogen bonding throughout the explosive material, which on other hand results in the stabilization of the molecular structure (e.g. LLM-105, TANPyO and DADNP). The introduction of a N^+–O^- moiety into the energetic materials results in an increase of the density,[6] improves the oxygen balance,[7] increases the stability in the molecular structure[8] and in addition improves the detonation properties.[9] Good examples for this class of *N*-oxidized energetic materials are dihydroxylammonium 5,5′-bistetrazole-1,1′-dioxide (TKX-50) and 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105). In comparison to its O-free analogue, dihydroxylammonium 5,5′-bistetrazolate, the density of TKX-50 increases from 1.74 to 1.88 $g\cdot cm^{-3}$, and its calculated detonation velocity increases from 8854 $m\cdot s^{-1}$ to 9698 $m\cdot s^{-1}$.[10,11] The same effect is observed for LLM-105 (ρ = 1.92 $g\cdot cm^{-3}$, D_{C-J} = 8516 $m\cdot s^{-1}$) and its precursor 2,6-diamino-3,5-dinitropyrazine (ANPZ, ρ = 1.84 $g\cdot cm^{-3}$, D_{C-J} = 7892 $m\cdot s^{-1}$).[7,12] (Figure 1)

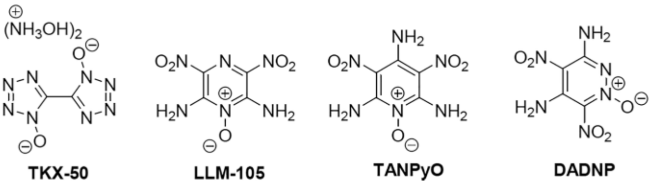

Figure 1. Literature known *N*-oxidized energetic materials.

Recently, in our research group we managed to functionalize the 1,2-diazine scaffold by synthesizing 3,5-diamino-4,6-dinitropyridazine-1-oxide and its precursor 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide.[13] For this purpose, a selective functionalization of the pyridazine scaffold was carried out by introducing explosophore NO_2 groups and selectively introducing a N^+–O^- moiety. In this present work we reacted 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide (**7**) with different amines and investigated the physico-chemical properties of the newly synthesized derivatives **8**–**11**. The detonation properties

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* Prof. Dr. T. M. Klapötke
Fax: +49-89-2180-77492
E-Mail: tmk@cup.uni-muenchen.de
Homepage: http://www.hedm.cup.uni-muenchen.de
[a] Department of Chemistry
Ludwig-Maximilian University Munich
Butenandtstr. 5–13 (D)
81377 München, Germany

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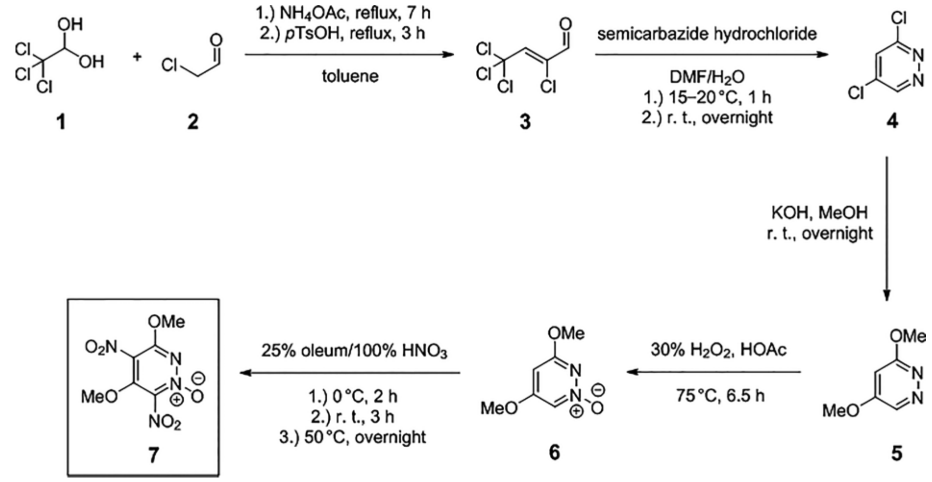
and the sensitivities of the energetic pyridazines can be adjusted depending on the used amine for the reaction.

Results and Discussion

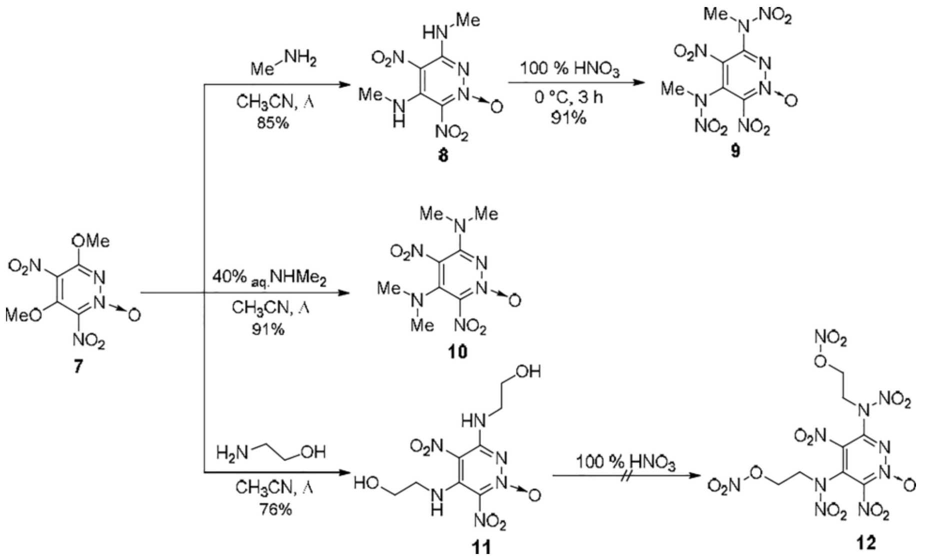
Synthesis

Herein, we report the synthesis of new pyridazine based energetic materials. The target molecules 3,5-bis(methylamino)-4,6-dinitropyridazine-1-oxide (**8**), 3,5-bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (**9**) 3,5-bis(dimethylamino)-4,6-dinitroypridazine-1-oxide (**10**), and 3,5-bis((2-(hydroxyethyl)amino)-4,6-dinitropyridazine-1-oxide (**11**) were synthesized by using 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide (**7**) as starting material. Compound **7** was prepared according the literature known five step procedure and will not be discussed in this work.[13] The exact synthetic path for **7** is shown in Scheme 1.

Compound **7** was used as the starting material for further functionalization of the pyridazine scaffold. Further nucleophilic substitution of the methoxy groups allows regioselectiv functionalization of compound **7**. As appropriate nucleophiles various smaller amines e.g. methylamine, dimethylamine and 2-aminoethanol were reacted with compound **7**. Compounds **8**–**11** were obtained in good yields 76–91 %. To enhance the performance of the newly synthesized pyridazine based energetic materials compounds **8** and **11** were further nitrated. Nitration of compound **8** resulted in the formation of 3,5-bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (**9**) in 91 % yield. Nitration of compound **11** resulted in decomposition of the starting material and the polynitrated compound **12** was not obtained. All obtained energetic materials were thoroughly characterized and further examined regarding their sensitivities toward mechanical and electrostatic stimuli. All reactions are displayed in Scheme 2.



Scheme 1. Literature known synthesis for 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide.



Scheme 2. Synthesis of new energetic pyridazine derivatives by functionalizing the 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide scaffold (**7**).

Crystal Structures

During this work the crystal structures of all four synthesized compounds (**8**–**11**) were obtained. Selected data and parameters from the low-temperature X-ray data collection are given in the Supporting Information (Tables S1 and S2, Supporting Information). Single-crystals of compound **8** were obtained by evaporating a solution of **8** in acetone and water. Compound **8** crystallizes in the orthorhombic space group *Pbca* (no. 61) with eight formula units per cell and has a cell volume of 1941.40(7) Å^3. The cell constants are a = 9.7734(2) Å, b = 13.5583(3) Å and c = 14.6509(3) Å. The calculated density at 143(2) K is 1.67 g·cm^{-3}.

Looking at the determined bond lengths 1.3276(18) Å (N1–N2), 1.3506(19) Å (C4–N1), 1.352(2) Å (N2–C1), 1.432(2) Å (C1–C2), 1.433(2) Å (C2–C3) and 1.412(2) Å (C3–C4), the existing aromaticity inside the ring structure can be comprehended (Figure 2). They are all between the typical values for single and double bonds concerning these involved elements.[14,15,16] The interatomic distances of N3–C1 (1.329 Å) and N5–C3 [1.332(2) Å] also display a participation of these bonds in aromatic resonance. The bond in the N$^+$–O$^-$ moiety is 1.2635(17) Å and herewith slightly shorter than that of its precursor 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide (**7**) with 1.268(2) Å.[13] The slight deformation of the planar ring structure can be recognized by the observed divergent dihedral angles 4.5(2)° (N1–N2–C1–C2) and –6.6(2)° (N2–C1–C2–C3). The C4-connected nitro group is twisted against the ring plane according to the O5–N6–C4–N1 torsions angle of –74.69(18)°. Its significant rotation can be understood by both the high spatial demand of the voluminous methylamine neighbor, which even shows only a moderate displacement regarding the ring plane, and especially the high electrostatic repulsion between the vicinal-located N$^+$–O$^-$ moiety and the nitro-oxygens. As a result of its noticeable turn, the C4–N6 bond length of 1.4637(19) Å is elongated compared that of the other intramolecular nitro group with 1.4157(19) Å.

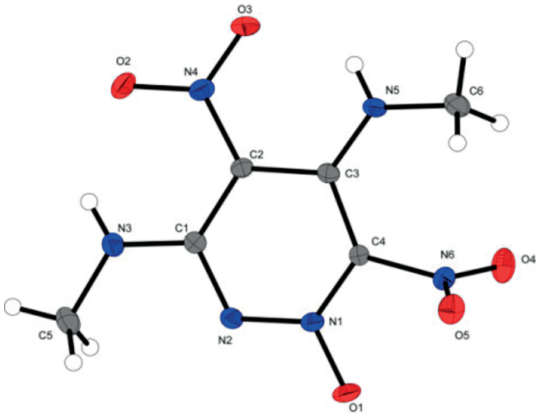


Figure 2. Molecular unit of compound **8** in the crystalline state. Ellipsoids correspond to 50 % probability levels. Hydrogen radii are arbitrary. Selected bond lengths reported in Å and angles reported in °: N1–N2 1.3276(18), C4–N1 1.3506(19), N2–C1 1.352(2), C1–C2 1.432(2), C2–C3 1.433(2), C3–C4 1.412(2), O1–N1 1.2635(17), N3–C1 1.329(2), N5–C3 1.332(2), N4–C2 1.4157(19), O2–N4 1.2401(19), N6–C4 1.4637(19), O4–N6 1.2229(18), N2–N1–C4 123.90(13), N1–C4–N6 111.94(13), O1–N1–N2–C1 –177.94(14) N1–N2–C1–C2 4.5(2), N2–C1–C2–C3 –6.6(2), C2–C3–C4–N1 2.7(2), C5–N3–C1–N2 –2.6(2), C6–N5–C3–C4 –9.1(3), O2–N4–C2–C1 12.6(2), N5–C3–C4–N6 –0.2(2), O5–N6–C4–N1 –74.69(18).

Single-crystals of **9** were obtained by evaporating a solution of compound **9** in a mixture of acetone and water. Compound **9** crystallizes in the orthorhombic space group $P222$ (no. 16) with four formula units per cell and has a cell volume of 1287.01(10) Å^3. The calculated density at 143(2) K is 1.73 g·cm^{-3}, which is higher than the density of its precursor **8** with 1.67 g·cm^{-3}.

The N–O distance 1.2561(17) Å in the N$^+$–O$^-$ moiety is distinctly shortened compared to those values found in precursor **8** [1.2635(17) Å] and related 3,5-diamino-4,6-dinitropyridazine-1-oxide [DADNP, 1.2681(19) Å].[13] These differences in length can be understood by comparing the mesomeric impacts of the different amino substituents to the aromatic system in each compound. With increasing the degree of substitution regarding the amino substituents their +M character is diminished. In consequence, the less electron density inside the aromatic ring causes the observed bond contractions. In molecule **9** this effect attains an extra dimension due to the nitration of the respective amino substituents because of the strong electron-withdrawing nitro groups. In contrast, the N–N distances in the pyridazine ring structure show an opposing trend. The N–N bond lengths in DADNP with 1.323(2) Å and compound **8** 1.3276(18) Å are shorter than that found in pyridazine **9** with 1.335(2) Å (N1–N2).[13] All remaining N–C and C–C bonds in the ring are with slightly divergence to each other in the aromatic range.[14,15,16]

The ring-internal dihedral angles such as C1–C2–C3–C4 with 3.4(2)° and N2–C1–C2–C3 with –2.7(3)° show only slight aberration. This reflects the high planarity of the aromatic backbone. The nitro groups connected to the backbone exhibit different amounts of rotation against the ring plane according to the torsions angles O4–N5–C2–C1 with –40.3(2)° and C3–C4–N8–O8 with even 81.8(2)°. The eminently twist of latter substituent, which is surprisingly near to 90°, restricts the p_z-orbital of the N8-nitrogen to participate in aromaticity because of the slim π-overlap. In further consequence, the considerable elongation of the interatomic distance between N8 and C4 results. In its precursor **8** the bond length of the analogous nitro group is 1.4157(19) Å with a twist of –74.69(18)°. In comparison, this bond in pyridazine derivative **9** is 1.459(2) Å and thus slightly elongated. The dihedral angles for the tertiary amino substituents are –58.0(2)° (N7–N6–C3–C2) und –26.0(2)° (C5–N3–C1–N2). The distances of the N3–N4 and N5–N6 bonds in the nitramine moieties are 1.408(3) Å and 1.385(2) Å, respectively. The bond angle 123.21(17)° included from C2–C1–N3 is somewhat widened, while the adjacent N2–C1–N3 bond angle with 112.77(16)° is noticeably compressed (Figure 3).

Single-crystals from compound **10** were obtained by evaporating a solution of **10** in acetone and water. Compound **10** crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with four formula units per cell and has a cell volume of 1144.00(8) Å^3. The cell constants are a = 9.7162(4) Å, b = 13.6057(5) Å

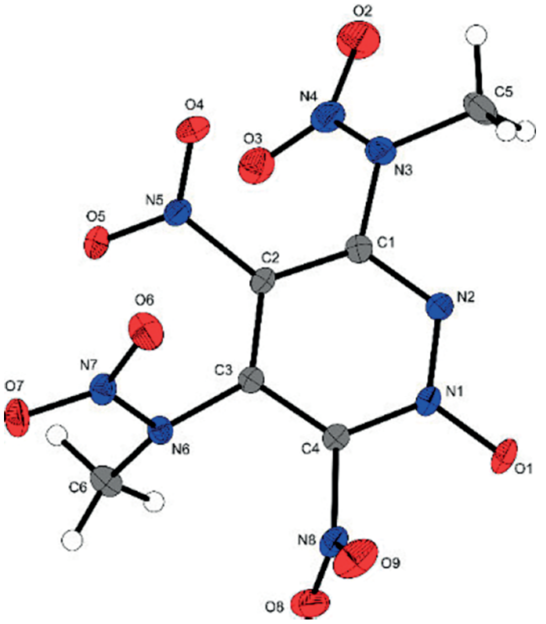


Figure 3. Molecular unit of compound **9** in the crystalline state. Ellipsoids correspond to 50 % probability levels. Hydrogen radii are arbitrary. Selected bond lengths reported in Å and angles reported in °: N1–N2 1.335(2), C4–N1 1.358(2), N2–C1 1.325(2), C1–C2 1.399(3), C2–C3 1.384(3), C4–C3 1.372(2), O1–N1 1.2561(17), N3–C1 1.403(2), N3–N4 1.408(3), N4–O2 1.215(2), N3–C5 1.462(3), N5–C2 1.465(2), O4–N5 1.221(2), N6–C3 1.417(2), N6–N7 1.385(2), C4–N8 1.459(2), O1–N1–N2 118.26(15), N2–C1–N3 112.77(16), N2–C1–C2 124.01(18), N4–N3–C5 116.68(18), N1–N2–C1–C2 –0.1(3), N2–C1–C2–C3 –2.7(3), C1–C2–C3–C4 3.4(2), C5–N3–C1–N2 –26.0(2), C5–N3–N4–O2 –17.0(3), N3–C1–C2–N5 –5.4(3), O4–N5–C2–C1 –40.3(2), N5–C2–C3–N6 9.4(3), N7–N6–C3–C2 –58.0(2), C3–N6–N7–O6 –17.2(2), N8–C4–N1–O1 1.9(2), C3–C4–N8–O8 81.8(2).

and c = 8.7037(4) Å with β = 96.137(4)°. The calculated density at 143(2) K is 1.58 g·cm^{-3}.

Compared to 3,5-diamino-4,6-dinitropyridazine-1-oxide (DADNP) with 1.89 g·cm^{-3} and related 3,5-bis(methylamino)-4,6-dinitropyridazine-1-oxide (**8**) with 1.67 g·cm^{-3} its crystal-structure is clearly less dense.[13] The N–N bond length in the pyridazine ring is 1.3289(17) Å (Figure 4). The ring-internal N–C bonds are 1.3645(18) Å and 1.3553(18) Å and the remaining C–C distances are 1.426 Å on average. These length values are all in the aromatic range and show no significant difference to the bonds inside the pyridazine ring of **8**.[13,14,15,16] Indeed, despite the existing aromaticity the expected flat pyridazine ring is drastically deformed. The C1–C2–C3–C4 and N2–C1–C2–C3 torsions angles aberrate from the ring plane with –19.07(19)° and even 28.2(2)°, respectively. Compared to the dihedral angles C1–C2–C3–C4 with 2.8(2)° and N2–C1–C2–C3 –6.6(2)°, the aberration of planarity found for related **8** is eminently smaller. Also, the ring-internal bond angles diverge from the regular angle of 120° for sp^2-hybridized bond centers. Among them is the C4–C3–C2 bond angle with the divergence of 6.5°. The bond length between the nitrogen and oxygen inside the N$^+$–O$^-$ function is 1.2577(15) Å (N1–O1).

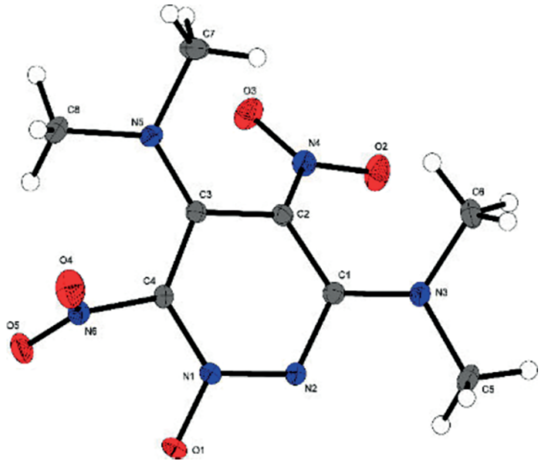


Figure 4. Molecular unit of compound **10** in the crystalline state. Ellipsoids correspond to 50 % probability levels. Hydrogen radii are arbitrary. Selected bond lengths reported in Å and angles reported in °: N1–N2 1.3289(17), N1–C4 1.3645(18), N2–C1 1.3553(18), C1–C2 1.4408(19), C2–C3 1.432(2), C3–C4 1.4057(19), O1–N1 1.2577(15), N3–C1 1.3238(19), N3–C5 1.4717(19), N4–C2 1.4234(18), O2–N4 1.2403(17), O4–N6 1.2215(17), N5–C7 1.4611(19), N1–N2–C1 116.76(12), C4–C3–C2 113.49(12), O1–N1–N2 117.12(11), C1–N3–C5 120.74(13), C6–N3–C5 115.07(13), C7–N5–C8 113.46(12), N1–N2–C1–C2 –14.7(2), N2–C1–C2–C3, C1–C2–C3–C4 –19.07(19), N2–C1–C2–C3 28.2(2), N1–N2–C1–N3 166.97(13), C5–N3–C1–N2 5.0(2), N3–C1–C2–N4 50.1(2), O2–N4–C2–C1 –17.9(2), C7–N5–C3–C2 –21.6(2), N5–C3–C4–N6 –2.5(2), O4–N6–C4–C3 –71.22(19).

In comparison, this N–O distance is markedly shorter than those found in precursor **7** [1.268(2) Å], 3,5-diamino-4,6-dinitropyridazine-1-oxide [1.2681(19) Å, DADNP] and even 3,5-bis(methylamino)-4,6-dinitropyridazine-1-oxide [**8**, 1.2635(17) Å].[13] Besides, the N–C bonds connecting the spatially demanding dimethylamino substituents to the molecular backbone of **10** have no significant difference. Against this, the amount of rotation noticeably differs. The dimethylamino substituent connected to the C1-carbon shows only a slight turn against the ring plane, whereas the other one in between of both nitro groups is significantly more rotated against the plane according to the C7–N5–C3–C2 torsions angle of –21.6(2)°. The medium length of the four bonds between the methyl groups and the tertiary substituted amino groups is 1.463 Å, which is in the typical range for N–C single bonds.[14] Despite the relatively high spatial demand of dimethylamino substituents, the nitro group in between is slightly rotated against the molecule plane [O2–N4–C2–C1 –17.9(2)°]. In contrast, the torsions angle of O4–N6–C4–C3 with –71.22(19)° displays the very high aberration of the other nitro group. In spite of the higher spatial need concerning the vicinal tertiary amino substituent, the amount of rotation for this substituent is even lower than that found in compound **8** [–74.69(18)°].

Single crystals of **11** were obtained by evaporating a solution of compound **11** in acetone. Compound **11** crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with four formula units per cell and has a cell volume of 1165.20(11) Å^3. The cell constants are a = 6.6388(4) Å, b = 22.0275(12) Å and c = 8.0977(4) Å with β = 100.271(5)°. The calculated density at 416(2) K is 1.73 g·cm^{-3}.

The N–N, N–C and C–C distances inside the pyridazine ring are all in the range for typical single and double bond lengths concerning these elements (Figure 5).[13,14,15,16] Among them, the N1–N2 distance is 1.328(2) Å and the N2–C4 distance is 1.358(2) Å. Also, the internal bond angles such as N2–N1–C1 of 122.74(14)°, C2–C3–C4 of 119.07(15)°, and N2–C4–C3 of 122.14(15)° are all near to the characteristic 120° for sp^2 hybridized bond centers. All of these bond lengths and angles indicate the existing aromaticity.[14] The N–O bond lengths in the $N^+–O^-$ moiety is 1.2603(17) Å, which is somewhat shorter than that found in precursor **7** [1.268(2) Å] and related compound **8** [1.2635(17) Å].[13] The interatomic distances between the nitrogen atoms of the (2-(hydroxyl)ethyl)amino substituents and the pyridazine backbone also show an aromatic participation. All torsions angles between the ring-internal atoms show only slight deformation [$|\Theta_{\text{out of plane}}| \leq 2.1(3)°$] and is lower than that in precursor **7** [$|\Theta_{\text{out of plane}}| \leq 6.6°$]) and even **10** [$|\Theta_{\text{out of plane}}| \leq 28.2(2)°$]. The nitro group next to the *N*-oxide shows the significant twist of 70.1(2)° (O2–N3–C1–N1). This amount of rotation is in the range of those found for the analogous substituents in **8** [–74.69(18)°] and **10** [–71.22(19)°].

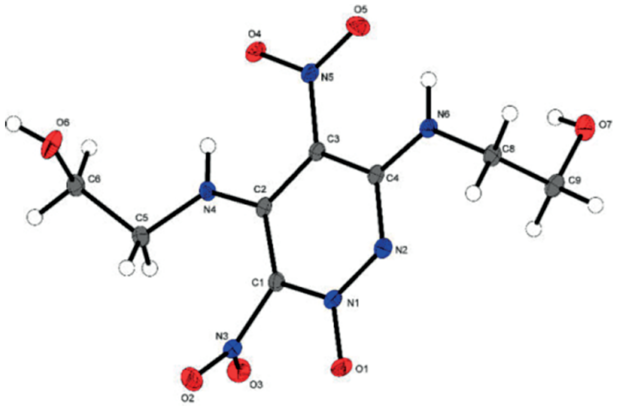


Figure 5. Molecular unit of compound **11** in the crystalline state. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary. Selected bond lengths reported in Å and angles reported in °: N1–N2 1.328(2), N1–C1 1.353(2), N2–C4 1.358(2), C1–C2 1.411(2), C2–C3 1.428(2), C3–C4 1.433(2), O1–N1 1.2603(17), N6–C4 1.329(2), N6–C8 1.462(2), C8–C9 1.513(3), C9–O7 1.422(2), N5–C3 1.420(2), O4–N5 1.2423(18), N2–N1–C1 122.74(14), C2–C3–C4 119.07(15), N2–C4–C3 122.14(15), C4–N6–C8 122.87(15), N6–C8–C9 111.10(15), O7–C9–C8 112.11(16), C2–N4–C5 129.24(15), O6–C6–C5 109.28(15), C1–N1–N2–C4 1.7(2), N1–N2–C4–C3 –0.6(2), C1–C2–C3–C4 –0.1(2), O1–N1–N2–C4 179.54(14), N2–N1–C1–N3 174.94(14), O2–N3–C1–N1 70.1(2), N1–C1–C2–N4 –179.50(16), C5–N4–C2–C1 14.6(3), C2–N4–C5–C6 150.46(18), N4–C2–C3–N5 3.6(3), O4–N5–C3–C2 2.5(2), N1–N2–C4–N6 179.21(15), C8–N6–C4–N2 6.5(2), C4–N6–C8–C9 82.1(2).

^{15}N NMR Spectroscopy

In addition, ^{15}N NMR spectra of compounds **8** and **11** were recorded (Figure 6). Compound **8** exhibits six resonances in the ^{15}N spectrum; both NO_2 groups are observed at –17.1 and 22.2 ppm, the pyridazine nitrogen atoms at –69.8 ($N^+–O^-$) and –113.2 ppm. Both methylamine nitrogen atoms show a low intensity and can be observed at –317.9 and –323.1 ppm as singlet.

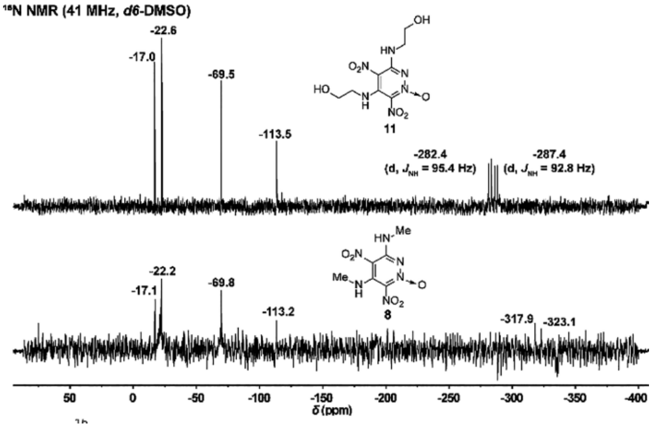


Figure 6. ^{15}N NMR spectra of compounds **8** and **11**.

Six resonances can be observed in the ^{15}N spectrum of compound **11**. The nitro groups appear at –17.0 and –22.6 ppm and the pyridazine nitrogen atoms exhibit similar shift as compound **8** –69.5 (*N*-oxide) and 113.5 ppm. Both duplets at –282.4 (J_{NH} = 95.4 Hz) and –287.4 (J_{NH} = 92.8 Hz) ppm can be assigned to both NH atoms.

Detonation Properties

Compounds **8**–**11** can be classified as energetic materials, therefore their energetic properties were investigated. All theoretically and experimentally determined values for all four compounds are reported in Table 1. In addition, the thermal behavior was investigated with an OZM Research DTA 552-Ex instrument with a heating rate of 5 K·min^{-1}. All compounds

Table 1. Physico-chemical properties of compounds **8**–**11**.

	8	**9**	**10**	**11**
IS [a] /J	10	5	30	18
FS [b] /N	360	120	360	360
ESD [c] /J	0.203	0.033	0.37	0.25
Ω [d] /%	–72	–29	–100	–79
T_{dec} [e] /°C	250	120	217	170
ρ [f] /g·cm^{-3}	1.63	1.68	1.54	1.69
$\Delta_f H°$ [g] /kJ·kg^{-1}	420.6	892.7	574.6	–824.4
$\Delta_f H°$ [h] /kJ·mol^{-1}	102.7	298.3	156.4	–250.8
EXPLO5 6.03				
$-\Delta_E U°$ [i] /kJ·kg^{-1}	4403	5844	4267	3828
$T_{\text{C–J}}$ [j] /K	3036	4164	2790	2632
$p_{\text{C–J}}$ [k] /kbar	204	291	176	202
$D_{\text{C–J}}$ [l] /m·s^{-1}	7365	8276	6994	7389
V [m] /L^3·kg^{-1}	756	753	767	757

a) Impact sensitivity (BAM drophammer, method 1 of 6). b) Friction sensitivity (BAM drophammer, method 1 of 6). c) Electrostatic discharge device (OZM research). d) Oxygen balance with respect to CO_2. e) Temperature of decomposition (DTA, β = 5 °C·min^{-1}). f) Density at 298 K. g) Standard weight enthalpy of formation. h) Standard molar enthalpy of formation. i) Detonation energy. j) Detonation temperature. k) Detonation pressure. l) Detonation velocity. m) Volume of detonation gases at standard temperature and pressure conditions.

show sharp decomposition in the DTA plots and decompose without melting prior. Compound **8** decomposes at 250 °C, whereas the nitrated derivative **9** shows sharp decomposition at 120 °C. The reason for the drastic change in the thermal behavior from compound **8** to **9** can be explained with the formation of the thermally sensitive –$NHNO_2$ moiety in 3,5-bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (**9**). DTA plots of compounds **8**, **9** and **11** are shown in Figure 7. Compounds **10** and **11** decompose at 217 and 170 °C, respectively.

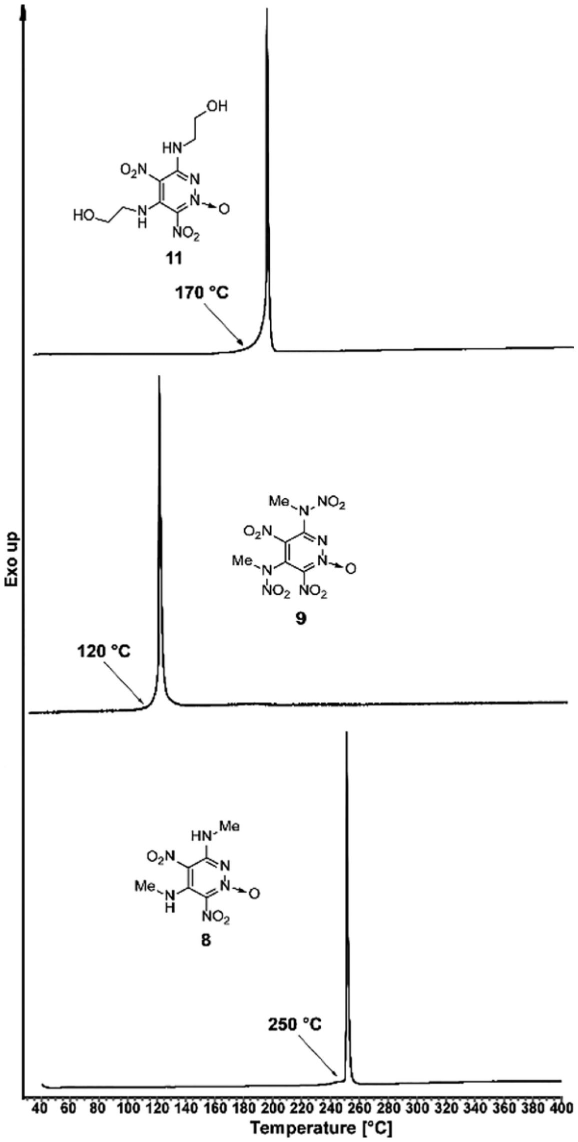


Figure 7. DTA plots of compounds **8**, **9** and **11**.

Further, the sensitivities of all compounds were determined toward external stimuli (friction and impact) by using the BAM standards and the theoretical detonation properties were calculated by using the EXPLO5_V6.03 computer code.[17] For all computer calculations with the EXPLO5 code the room temperature densities of all compounds were calculated by using the obtained X-ray structures as reported in the literature.[18]

The highest room temperature density was measured for compound **11** with 1.69 $g\cdot cm^{-3}$ and the lowest was determined for **10** with 1.54 $g\cdot cm^{-3}$. The sensitivity values of all four compounds toward impact, friction and electrostatic discharge were determined. Compounds **8**, **10**, and **11** exhibit impact sensitivity of 10, 30, and 18 J, respectively. The determined friction sensitivity for all three compounds is 360 N. Compound **9** is the most sensitive compound with values of IS = 5 J, FS = 120 N and ESD = 0.033 J. Compound **9** contains the nitramino moiety (–$NHNO_2$), which leads to lower thermal stability of the molecule and higher sensitivity toward external stimuli. This is supported with the obtained physico-chemical properties for the pyridazine derivative **9**. According to the EXPLO5 calculations compound **9** shows the best performance with detonation pressure and detonation velocity of 291 kbar and 8276 $m\cdot s^{-1}$, respectively. Compounds **8** and **11** have similar properties with p_{C-J} = 204 kbar and D_{C-J} = 7365 $m\cdot s^{-1}$ for **8** and p_{C-J} = 202 kbar and D_{C-J} = 7389 $m\cdot s^{-1}$ for **11**. The calculated detonation properties for **9** in comparison to its precursor **8** and compound **11** can be explained again with the introduced nitramino groups, which result in a good performance but decreases the stability of the molecule.

Conclusions

In conclusion, we report on the synthesis of four new *N*-oxidized pyridazine based energetic materials (**8–11**). For this purpose, 3,5-dimethoxy-4,6-dinitropyridazine-1-oxide (**7**) was reacted with methylamine, dimethylamine and 2-aminoethanol to result in the formation of 3,5-bis(methylamino)-4,6-dinitropyridazine-1-oxide (**8**), 3,5-bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (**10**), and 3,5-bis((2-hydroxyethyl)-amino)-4,6-dinitropyridazine-1-oxide (**11**). Further, the acidity of the protons in the –NHMe moiety of compound **8** was used and it was nitrated in 100 % nitric acid to give 3,5-bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (**9**) in excellent yields. The synthesized energetic pyridazine derivatives (**8–11**) were characterized extensively using multinuclear NMR spectroscopy, vibrational spectroscopy, DTA, elemental analysis and BAM sensitivity methods. In addition, the crystal structures of all four compounds were obtained and extensively discussed. The experimentally and theoretically determined energetic properties were well investigated. Compounds **8** (IS = 10 J; FS = 360 N), **10** (IS = 30 J; FS = 360 N) and **11** (IS = 18 J; FS = 360 N) exhibit similar properties toward impact and friction, whereas compound **9** with the nitramino moiety exhibits higher sensitivity toward external stimuli (IS = 5 J; FS = 120 N).

Experimental Section

CAUTION! All investigated compounds are potentially explosive materials, although no hazards were observed during preparation and handling these compounds. Nevertheless, safety precautions (such as wearing leather coat, face shield, Kevlar sleeves, Kevlar gloves, earthed equipment and ear plugs) should be drawn.

^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded with JEOL 270 and BRUKER AMX 400 instruments. The samples were measured at room temperature in standard NMR tubes (Ø 5 mm). Chemical shifts are reported as δ values in ppm relative to the residual solvent peaks of [D$_6$]DMSO (δ_H: 2.50, δ_C: 39.5). Solvent residual signals and chemical shifts for NMR solvents were referenced against tetramethylsilane (TMS, $\delta = 0$ ppm) and nitromethane. Unless stated otherwise, coupling constants were reported in Hertz (Hz) and for the characterization of the observed signal multiplicities the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet) and br (broad). Infrared spectra (IR) were recorded from 4500 cm^{-1} to 650 cm^{-1} on a PERKIN–ELMER Spectrum BX-59343 instrument with a SMITHS DETECTION DuraSamplIR II Diamond ATR sensor. The absorption bands are reported in wavenumbers (cm^{-1}). Elemental analysis was carried on a Elementar Vario *el* by pyrolysis of the sample and subsequent analysis of the formed gases. Decomposition temperatures were measured via differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument at a heating rate of 5 K·min^{-1} and in a range of room temperature to 400 °C. All sensitivities toward impact (IS) and friction (FS) were determined according to BAM (German: Bundesanstalt für Materialforschung und Prüfung) standards using a BAM drop hammer and a BAM friction apparatus.[19] All energetic compounds were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN from OZM.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1917212 (**8**), CCDC-1917211 (**9**), CCDC-1917213 (**10**), and CCDC-1917210 (**11**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

3,5-Bis(methylamino)-4,6-dinitropyridazine-1-oxide (8): 3,5-Dimethoxy-4,6-dinitropyridazine-1-oxide (**7**, 1.00 g, 4.06 mmol, 1.0 equiv.) was dissolved in acetonitrile (50 mL) and an aqueous methylamine solution (40 %, 2.5 mL, 29 mmol, 7.1 equiv.) was added dropwise. The reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo. The residue was suspended in a small amount of water, filtered and washed with ice-water. Drying on air yielded compound **8** as yellow solid (841 mg, 3.44 mmol, 85 %). DTA (5 K·min^{-1}): 250 °C (dec.); BAM: drop hammer: 10 J (100–500 µm); friction tester: 360 N (100–500 µm); ESD: 203 mJ (100–500 µm). **IR** (ATR): $\tilde{\nu}$ = 3351 (m), 3236 (m), 2955 (vw), 1573 (s), 1537 (s), 1403 (s), 1327 (s), 1244 (s), 1189 (s), 1135 (s), 1037 (s), 986 (m), 799 (m), 768 (s), 715 (s), 649 (s), 625 (s), 510 (m) cm^{-1}. **^{1}H NMR** ([D$_6$]DMSO, 400 MHz, [ppm]): δ = 9.71 (s, 1 H), 9.27 (d, ^{3}J = 4.8 Hz, 1 H), 2.95 (d, ^{3}J = 4.9 Hz, 3 H), 2.86 (s, 3 H). **^{13}C NMR** ([D$_6$]DMSO, 101 MHz, [ppm]): δ = 152.2, 142.5, 133.9, 112.1, 30.0, 29.1. **^{14}N NMR** ([D$_6$]DMSO, 29 MHz, [ppm]): δ = –24, –71. **^{15}N NMR** ([D$_6$]DMSO, 41 MHz, [ppm]): δ = –17.1, –22.2, –69.7, –113.0, –288.7, –291.1. Elem. Anal. ($C_6H_8N_6O_5$, 244.17 g·mol^{-1}): calcd. C 29.56, H 3.30, N 34.42 %; found: C 29.56, H 3.20, N 34.42 %.

3,5-Bis(methylnitramino)-4,6-dinitropyridazine-1-oxide (9): 3,5-Bis(methylamino)-4,6-dinitropyridazine-1-oxide (**8**, 500 mg, 2.05 mmol, 1.0 equiv.) was added in small portions to 100 % HNO_3 (3.33 mL) at 0 °C and stirred for 3.5 h. After pouring onto crushed ice and stirring until the ice had melted, the resulting suspension was filtered and washed with ice-water until the filtrate was acid free. Drying on air gave compound **9** as yellow solid (625 mg, 1.87 mmol, 91 %). DTA (5 K·min^{-1}): 120 °C (dec.); BAM: drop hammer: 5 J (100–500 µm); friction tester: 120 N (100–500 µm); ESD: 33 mJ (100–500 µm). **IR** (ATR): $\tilde{\nu}$ = 1573 (s), 1557 (s), 1453 (w), 1426 (w), 1386 (vw), 1336 (m), 1301 (m), 1260 (vs), 1150 (vw), 1094 (w), 1064 (w), 999 (m), 911 (w), 799 (m) cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz, [ppm]): δ = 3.94 (s, 3 H), 3.74 (s, 3 H). **^{13}C NMR** ($CDCl_3$, 101 MHz, [ppm]): δ = 162.6, 148.0, 132.9, 121.8, 41.7, 39.4. **^{14}N NMR** ($CDCl_3$, 29 MHz, [ppm]): δ = –30, –38, –40, –42, –71. Elem. Anal. ($C_6H_6N_8O_9$, 334.16 g·mol^{-1}): calcd. C 21.57, H 1.81, N 33.53 %; found: C 21.83, H 1.98, N 33.29 %.

3,5-Bis(dimethylamino)-4,6-dinitropyridazine-1-oxide (10): 3,5-Dimethoxy-4,6-dinitropyridazine-1-oxide (**7**, 500 mg, 2.03 mmol, 1.0 equiv.) was dissolved in acetonitrile (25 mL) and an aqueous dimethylamine solution (40 %, 0.600 mL, 4.74 mmol, 2.3 equiv.) was added dropwise. The reaction was stirred at room temperature overnight. The resulting suspension was filtered and the solvent was removed under reduced pressure. The residue was resuspended in water, filtered and washed with ice-water. After drying on air compound **10** was obtained as orange solid (503 mg, 1.85 mmol, 91 %). DTA (5 K·min^{-1}): 217 °C (dec.); BAM: drop hammer: 30 J (100–500 µm); friction tester: 360 N (100–500 µm); ESD: 370 mJ. **IR** (ATR): $\tilde{\nu}$ = 1573 (s), 1521 (m), 1484 (m), 1464 (w), 1431 (w), 1378 (m), 1334 (w), 1250 (vs), 1210 (s), 1184 (s), 1135 (m), 1072 (s), 933 (vw), 906 (vw), 841 (w), 823 (w), 798 (w), 760 (m) cm^{-1}. **^{1}H NMR** ([D$_6$]DMSO, 400 MHz, [ppm]): δ = 3.15 (s, 6 H), 3.07 (s, 6 H). **^{13}C NMR** ([D$_6$]DMSO, 101 MHz, [ppm]): δ = 155.1, 145.5, 137.7, 111.6, 43.8, 41.1. **^{14}N NMR** ([D$_6$]DMSO, 29 MHz, [ppm]): δ = –20, –69. Elem. Anal. ($C_8H_{12}N_6O_5$, 272.22 g·mol^{-1}): calcd. C 35.30, H 4.44, N 30.87 %; found: C 34.78, H 3.99, N 30.24 %. *m/z* (DEI$^+$): 272(100) [M]$^+$.

3,5-Bis((2-hydroxyethyl)amino)-4,6-dinitropyridazine-1-oxide (11): 3,5-Dimethoxy-4,6-dinitropyridazine-1-oxide (**7**, 632 mg, 2.57 mmol, 1.0 equiv.) was dissolved in acetonitrile (30 mL) and 2-aminoethanol (0.330 mL, 5.39 mmol, 2.1 equiv.) was added dropwise. The solution was stirred at room temperature overnight. The solvent was removed in vacuo. Subsequently, the residue was suspended in a small amount of water, filtered and thoroughly washed with ice-water. Drying on air yielded compound **11** as yellow solid (709 mg, 2.33 mmol, 76 %). DTA (5 K·min^{-1}): 170 °C (dec.); BAM: drop hammer: 15 J (100–500 µm); friction tester: 360 N (100–500 µm); ESD: 250 mJ (100–500 µm). **IR** (ATR): $\tilde{\nu}$ = 3411 (w), 3327 (m), 3209 (w), 2950 (vw), 2887 (vw), 1593 (m), 1525 (s), 1427 (m), 1411 (m), 1337 (s), 1281 (m), 1236 (s), 1180 (s), 1123 (m), 1047 (s), 943 (w), 866 (m), 767 (s), 715 (s), 632 (s), 517 (m) cm^{-1}. **^{1}H NMR** ([D$_6$]DMSO, 400 MHz, [ppm]): δ = 9.90 (t, ^{3}J = 4.8 Hz, 1 H), 9.35 (t, ^{3}J = 5.3 Hz, 1 H), 5.25 (t, ^{3}J = 5.0 Hz, 1 H), 4.96 (t, ^{3}J = 5.2 Hz, 1 H), 3.63–3.56 (m, 4 H), 3.53 (q, ^{3}J = 5.3 Hz, 2 H), 3.15 (q, ^{3}J = 5.0 Hz, 2 H). **^{13}C NMR** ([D$_6$]DMSO, 101 MHz, [ppm]): δ = 152.1, 142.2, 133.9, 112.2, 58.5, 58.4, 45.4, 44.1. **^{14}N NMR** ([D$_6$]DMSO, 29 MHz, [ppm]): δ = –23, –71. **^{15}N NMR** ([D$_6$]DMSO, 41 MHz, [ppm]): δ = –17.0, –22.6, –69.5, –113.5, –282.4, –287.4. Elem. Anal. ($C_8H_{12}N_6O_7$, 304.22 g·mol^{-1}): calcd. C 31.59, H 3.98, N 27.63 %; found: C 31.58, H 3.87, N 27.43 %. *m/z* (DEI$^+$): 305(100) [M + H]$^+$.

Supporting Information (see footnote on the first page of this article): The Supporting Information file containes the following details: 1. Synthesis and general considerations; 2. X-ray diffraction; 3. Computations; 4. Detonations parameters; 5. Literature.

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