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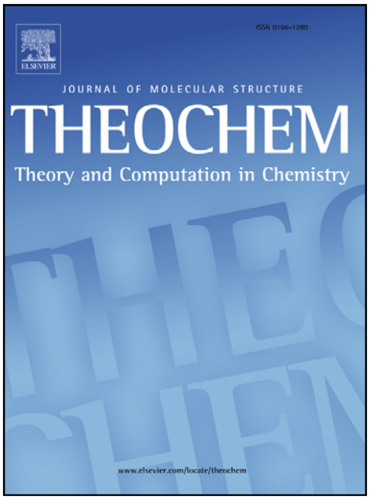

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Computational Study on 2,6-Diamino-3,5-dinitropyrazine and its 1-Oxide and 1,4-Dioxide Derivatives

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Abstract

The enthalpies of formation for 2,6-diamino-3,5-dinitropyrazine **(I)**, 2,6-diamino-3,5-dinitropyrazine 1-oxide **(II)** and 2,6-diamino-3,5-dinitropyrazine 1,4-dioxide **(III)** were calculated using the complete basis set (CBS-4M) method of Petersson and coworkers in order to obtain very accurate energies and compared with experimental values that were available for **I** and **II**. **I** was identified as the most stable compound, both thermodynamically (least endothermic) and with respect to its impact sensitivity. This is in good agreement with the experimental findings. The detonation parameters for all species were calculated using the EXPLO5 code. 2,6-Diamino-3,5-dinitropyrazine 1,4-dioxide (**III**) has been identified to be a

promising nitrogen-rich explosive which exceeds the explosive power of **II** and its performance is comparable or slightly superior to that of RDX.

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1. Introduction

Generally, there is a great demand for new high explosives (HEs) which are suitable for use in insensitive munitions (IMs). The necessity to know and understand the properties of such energetic materials is driven by the need to improve performance and enhance stability to various stimuli, such as thermal, friction and impact insult.

Pyrazine derivatives are six-membered heterocyclic compounds containing two nitrogen atoms in the ring system. As high-nitrogen heterocylic compounds, they have an ideal structure as energetic materials (EMs). Some of them have high formation enthalpy, fine thermal stability and good safety characteristics [1-11]. The basic structure of energetic pyrazine compounds is that of 3,5-dinitro-2,6-diaminopyrazine (**I** in Fig. 1). One of the most prominent members in this family, however, is the 1-oxide 3,5-dinitro-2,6-pyrazinediamine 1-oxide (**II**, also known as LLM-105 [1-3]). (*N.B.* The second N-oxide isomer of compound **II** has so far not been reported since experimentally oxidation of **I** always yields isomer **II**. For this reason we have not included the second isomer of **II** into our theoretical study).

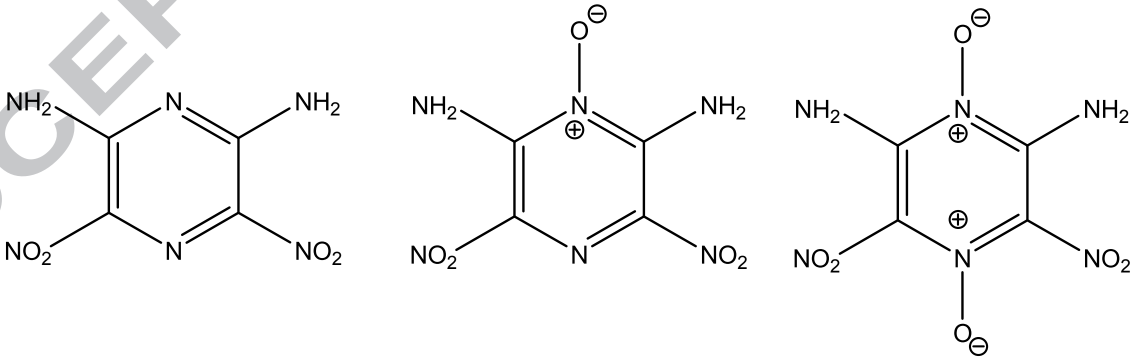
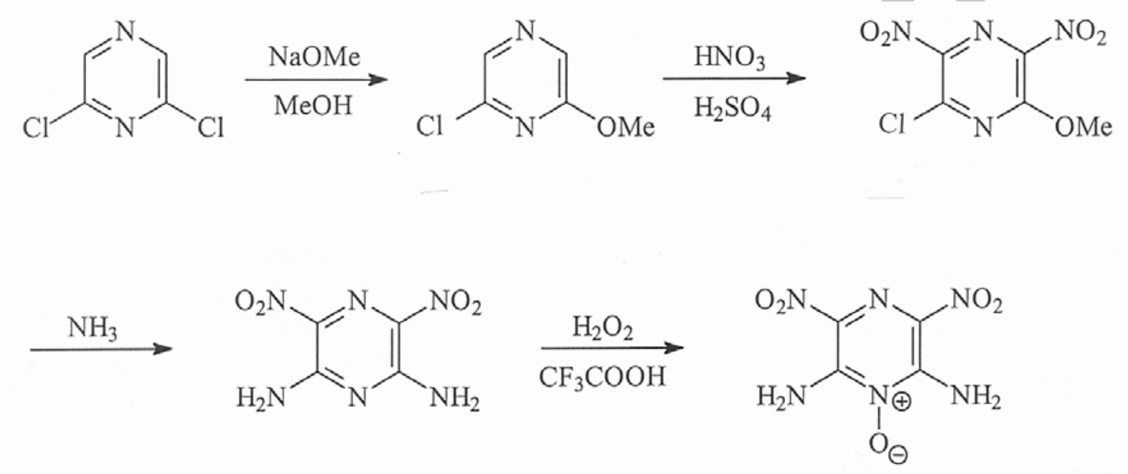


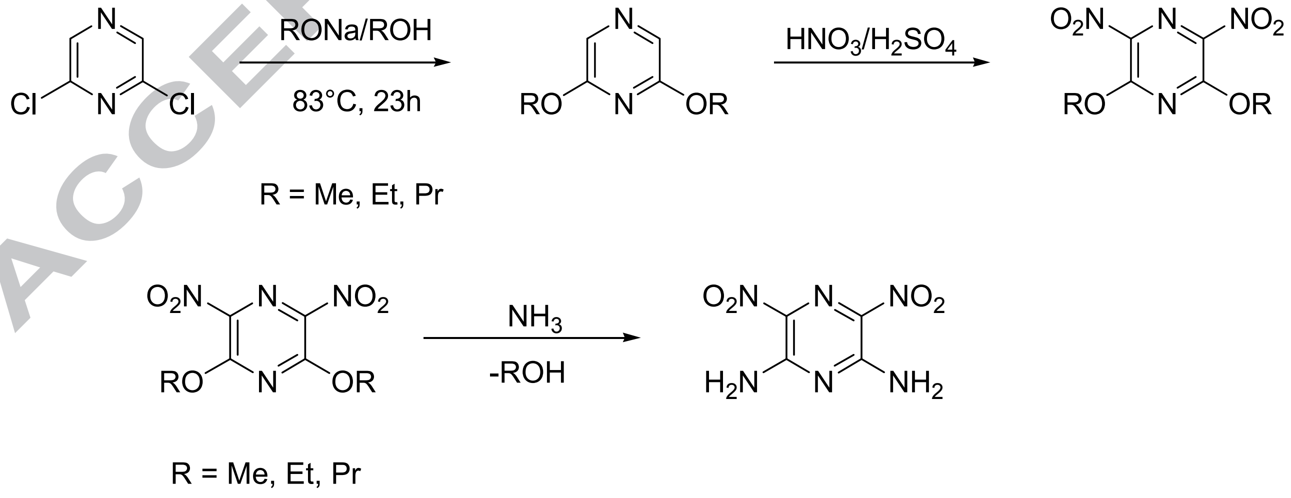
Fig. 1 Molecular structures of compounds **I**, **II** and **III**

LLM-105 has a high density of 1.92 g cm^{-3}, it also shows a detonation velocity of 8730 m s^{-1} and a detonation pressure of 359 kbar which are comparable to those of RDX (density = 1.80 g cm^{-3}, exptl. values: VoD = 8750 , $P_{C\text{-}J}$ = 347 kbar). LLM-105 is much less impact sensitive than RDX and is not sensitive towards electrostatics and friction [1-3, 8-11].

There are various methods to prepare compound **II**, most start from commercially available 2,6-dichloropyrazine (Scheme 1) and oxidize **I** in the final step to the 1- oxide **II** [1-3, 8-11].



I **II**



I

Scheme 1. Synthesis of **I** and **II** starting from 2,6-dichloropyrazine

The greatly enhanced detonation performance of **II** compared to **I** whilst remaining low in sensitivity prompted us to investigate theoretically their thermochemistry and to calculate the detonation parameters of the experimentally hitherto unknown dioxide **III**. A report of this study is given below.

2. Methods

All calculations (structures, energies, ESPs and NMR chemical shifts [12, 15-18]) were carried out using the Gaussian G03W (revision B.03) program package [12].

The enthalpies (*H*) and free energies (*G*) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) structure optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (**M** referring to the use of Minimal Population localization) which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections [13, 14].

3. Results and discussion

The molecular structures of compound **I**, **II** and **III** were fully optimized without symmetry constraints at HF/6-31G* level of theory to C_{2v}, C_{2v} and C_s symmetry, respectively (Fig. 2).

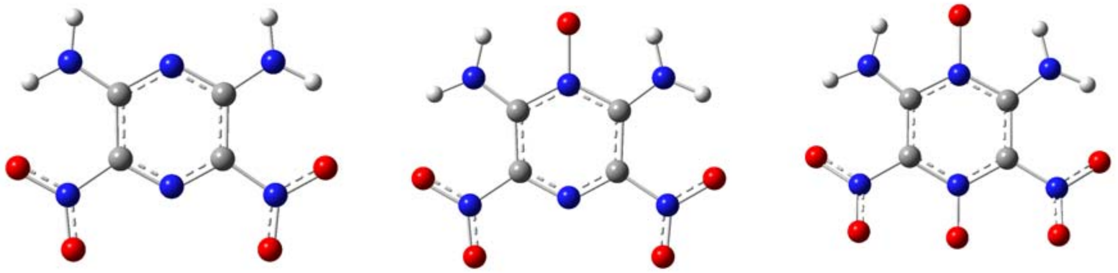


Fig. 2 Optimized molecular structures of compounds **I** (left), **II** (center) and **III** (right).

The enthalpies of formation of the gas-phase species M were computed according to the atomization energy method (eq. 1) (Tab. 1-3) [19-21]. In eq. (1) $\Delta_f H^\circ_{(g,M)}$ stands for the gas-phase enthalpy of formation of the molecule M under investigation, $H_{(M)}$ represents the CBS-4M calculated enthalpy of the molecule M (H^{298} in Tab. 1), ${}_{atoms}H^\circ$ denotes the CBS-4M calculated enthalpies for the individual atoms (see bottom of Tab. 1) and $\Delta_{atoms,f}H^\circ$ stands for the experimentally reported literature values for the enthalpies of formation for the corresponding atoms ($\Delta H^\circ{}_f^{298}$ in Tab. 2.). The excellent agreement between the reported experimental enthalpies of formation for compounds **I** and **II** with the CBS-4M calculated values (Tab. 5) gives credence that also the computed values for compounds **III** are quite accurate.

$$\Delta_f H^0_{(g,\,M)} = H_{(M)} - \sum_{atoms} H^0 + \sum_{atoms} \Delta_f H^0 \qquad (1)$$

Tab. 1 CBS-4M results

compound	p.g [a].	el.state [b]	$-H^{298}$/a.u. [c]	$-G^{298}$/a.u. [d]	*NIMAG* [e]	ν_1/cm^{-1}
I	C_{2v}	^{1}A	783.095183	783.144886	0	58
II	C_{2v}	^{1}A	858.170507	858.221962	0	65
III	C_s	^{1}A	933.217451	933.271921	0	38

[a] point group, [b] electronic state, [c] CBS-4M calculated enthalpy, [d] CBS-4M calculated free energy, [e] *NIMAG* number of imaginary frequencies.

Tab. 2 Literature values for atomic enthalpies of formation $\Delta H^\circ{}_f^{298}$ / kcal mol^{-1}

	Ref [19]	NIST [22]
H	52.6	52.1
C	170.2	171.3
N	113.5	113.0
O	60.0	59.6

Tab. 3 Enthalpies of formation of the gas-phase compounds M

compound	$\Delta_f H°(g,M)$ / kcal mol^{-1}
I	23.5
II	30.3
III	54.9

The enthalpies of sublimation for compounds **I**, **II** and **III** were estimated according to Trouton's rule (eq.2, Tab.4) [23] with melting points of 363°C[24], 302°C[24] for compounds **I** and **II**, respectively and estimated melting point of 250°C for compound **III** (based on the fact that the m.p. of **II** is 60°C lower than the m.p. of **I** and the assumption that **III** will have again a 60°C lower m.p. than **II**). The validity of Trouton's rule reflects the fact that the entropy of vaporization is approximately constant for many compounds and that $\Delta H_{sub.} \approx \Delta H_{vap.} + \Delta H_{fusion}$, with $\Delta H_{vap} \gg \Delta H_{fusion}$ so that $\Delta H_{sub.} \approx \Delta H_{vap.}$.

$$\Delta H_{sub.} = 188\ T_m\ \text{J mol}^{-1} \qquad (2)$$

Tab. 4 Enthalpies of sublimation ($\Delta H_{sub.}$) [23]

compound	T_m/K	ΔH_{sub} / kcal mol^{-1}
I	636	28.6
II	575	25.9
III	515	23.1

The calculated molar enthalpies of formation for the compounds **I**, **II** and **III** are summarized in Tab. 5. From Table 5 we further see that compound **III** is considerably more endothermic than either of compounds **I** or **II**, therefore, **III** is expected to be the best explosive in this series.

Tab. 5 Enthalpies of formation ($\Delta_f H°$) of the compounds

compound	$\Delta_f H°$(s,M) / kcal mol^{-1}	$\Delta_f H°$(s,M) / kcal mol^{-1}, lit. value
I	-5.1	-5.4 [24]
II	4.4	-3.10 [24]
III	31.8	--

Table 6 presents the calculated energies of formation for the compounds. The $\Delta_f H°$(s) values (Tab. 5) were converted into the $\Delta_f U°$(s) values using the correlation shown in eq. 3 [25].

$$H_m = U_m + \Delta n\,RT \qquad (3)$$

Tab. 6 Solid state energies of formation (${}_f U°$) [25]

compound	$\Delta_f H°$(s) / kcal mol^{-1}	Δn^a	$\Delta_f U°$(s) / kcal mol^{-1}	M / g mol^{-1}	$\Delta_f U°$(s) / kJ kg^{-1}
I	-5.1	-7.0	-2.13	200	-44.5
II	4.4	-7.5	6.2	216	120.0
III	31.8	-8.0	36.5	232	658.3

[a] change of molar number of gaseous species in the formation process of M from the elements (in their standard states).

The detonation parameters were calculated using the EXPLO5 (version 5.03) computer program [26]. The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon [27-29]. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation (4) in the following form was used with the BKWN set of parameters (α, β, κ, θ) as stated below the equations and X_i being the mol fraction of i-th gaseous product, k_i is the molar co-volume of the i-th gaseous product [27-29].

$$pV / \mathrm{R}T = 1 + x\mathrm{e}^{\beta x} \qquad (4)$$

$$x = (\kappa \Sigma X_i k_i) / [V(T + \theta)]^{\alpha}$$

$$\alpha = 0.5, \ \beta = 0.176, \ \kappa = 14.71, \ \theta = 6620$$

The detonation parameters calculated with the EXPLO5 program using the densities of 1.84 [24], 1.91 [24] and estimated density of 2.0 (based on the PM3 estimate of 2.06 g cm^{-3} [30]) for compounds **I**, **II** and **III**, respectively are summarized in Tab. 7.

Tab. 7 Detonation parameters for compound **I**, **II** and **III**[a]

	I	**II**	**III**
ρ / g cm^{-3}	1.8	1.9	2.0
Ω / %	-48.0	-37.0	-27.6
Q_v / kJ kg^{-1}	-4226	-4963	6005
T_{ex} / K	3365	3839	4449
P / kbar	260	320	401
D / m s^{-1}	7892	8516	9241
V_0 / L kg^{-1}	685	689	691

[a] ρ = density, Ω = oxygen balance, $Q_{v} =$ heat of detonation, T_{ex} = detonation temperature, P = detonation pressure, D = detonation velocity, V_0 = Volume of detonation gases.

The main reason for requiring a replacement for RDX is that it is rather vulnerable explosive material with relatively high sensitivity to both impact and friction. Besides being less sensitive than RDX, a replacement explosive must also be capable of performance comparable to that of RDX. In this regard, compound **III** would be a good candidate with calculated detonation velocity and detonation pressure even slightly higher than those of RDX (Fig.3).

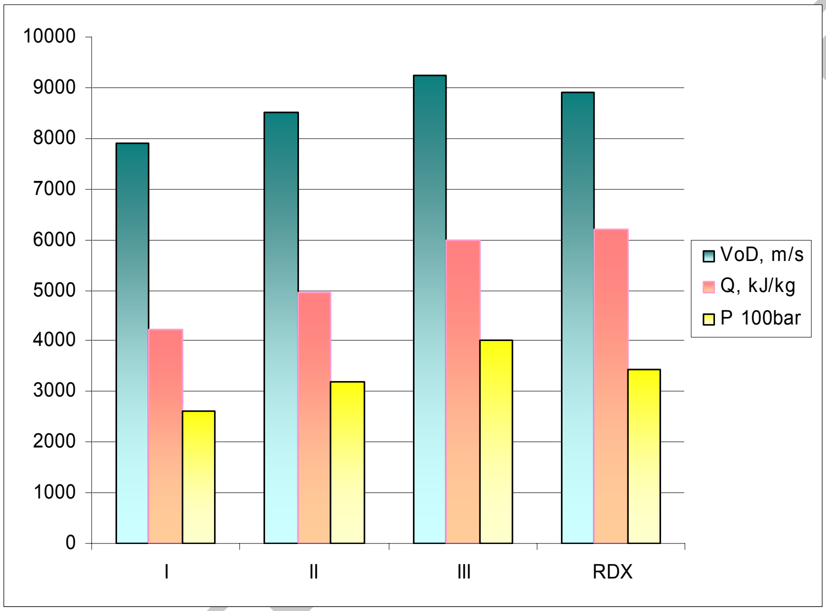


Fig. 3 Computed detonation velocities (VoD/ms^{-1}), heat of detonations (Q/kJkg^{-1}) and detonation pressures (P/100bar) for compounds **I**, **II**, **III** and RDX.

The electrostatic potentials (ESP) of compounds **I**, **II** and **III** were computed at the optimized structures at the B3LYP/6-31G(d) level of theory. Figure 4 shows the electrostatic potentials for the 0.001 electron/bohr^3 isosurfaces of electron density evaluated at the B3LYP level of theory. The colors range from –0.06 to +0.06 hartrees with dark blue denoting extremely electron-deficient regions ($V(r) > 0.06$ hartree) and red denoting electron-rich regions ($V(r) < -0.06$ hartrees). It has recently been found by Politzer, Murray et al. [31] and extensively used by Rice et al. [32] that the patterns of the computed electrostatic potential on the surface of molecules in general can be related to the sensitivity of the bulk material. The electrostatic potential at any point r is given by eq. (5) in which Z_A is the charge on nucleus A, located at R_A. Politzer et al. were able to show [31] that impact sensitivity can be expressed as a function of the extend of this anomalous reversal of the strengths of the positive and negative surface potentials.

$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr' \qquad (5)$$

It is known that the delocalization of π electrons over an aromatic ring is effected by both electron-withdrawing and –donating substituents attached to the ring. In their study Murray et al. [31] found that for the nitroaromatics, the ESP on the surface above the aromatic ring was positive reflecting the electron-withdrawing effect of the nitro groups. In addition to that, the same authors also found that electron-donating groups such as NH_2 or OCH_3 partially counteract the electron withdrawing effects of the nitro groups. The calculated electrostatic potential of compound **I** (see Fig. 4) reproduces these findings. The electron-withdrawing potential of the two nitro groups seems to be perfectly balanced by the electron-donating ability of the two amino groups. A similar behavior has already been observed for TATB (1,3,5-triamino-2,4,6-trinitrobenzene) [33]. The compounds under investigation in this study (**II** and **III**) differ from compound **I** only in one or two electron-withdrawing N-oxide substituents attached to the aromatic ring system. As it appears in Fig. 4, attaching one or two N-oxide oxygen atoms to the aromatic ring (compounds **II** and **III**) makes the regions of positive potential over the ring considerable stronger than the negative ones. This atypical imbalance between stronger positive regions and weaker negative ones can be related to the impact sensitivities. From this finding, the better performing (see above) compound **III** would be expected to also show somewhat higher sensitivity towards impact stimulus than compound **II** (LLM-105). Only experimental studies will be able to quantitatively establish the exact sensitivities of **III**. Such studies are underway in our laboratories.

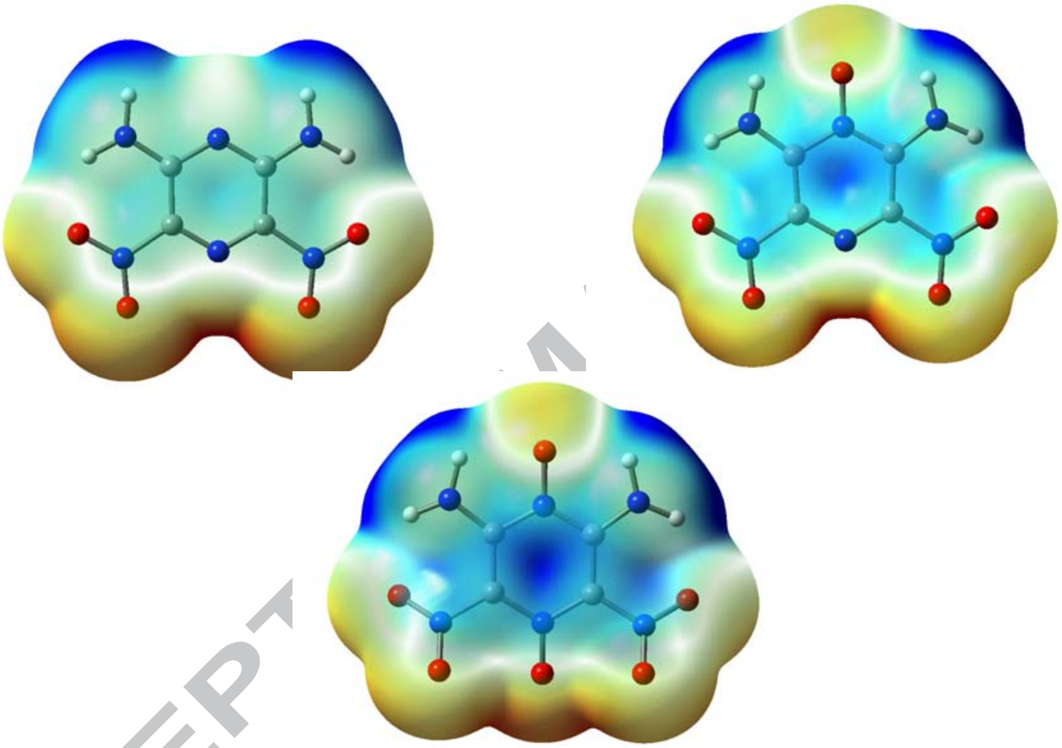


Fig. 4 Electrostatic potentials of compounds **I** (left), **II** (right) and **III** (bottom) (B3LYP/6-31G(d), 0.001e bohr $^{-3}$ isosurface, energy values -0.06 H to +0.06 H); color coding: red (very negative), orange (negative), yellow (slightly negative), green (neutral), turquoise (slightly positive), light blue (positive), dark blue (very positive)

In order to calculate the NMR chemical shifts for ^{15}N, the isotropic magnetic shieldings were computed using the GIAO (Gauge-Independent Atomic Orbital) method implemented in G03 [12,15-18]. The NMR shielding tensors were calculated at the MPW1PW91/aug-cc-pVDZ level of theory. Table 8 summarizes the computed isotropic magnetic shieldings and relative ^{15}N NMR chemical shifts (ppm) referenced to H_3CNO_2. The excellent agreement between the computed and experimentally observed chemical shifts for II (Tab.9) provides further credence that also the computed chemical shifts of compounds **I** and particularly **III** are reliable. This should help to guide the identification and characterization of compound **III** during efforts to synthesize this highly promising (see above) but experimentally still unknown species.

Tab. 8 Computed isotropic magnetic shieldings (GIAO method [15-18], MPW1PW91/aug-cc-pVDZ) and relative ^{15}N NMR chemical shifts δ (ppm) referenced to H_3CNO_2

	compound **I**		compound **II**		compound **III**	
	abs.isotropic shielding	rel. shift, δ	abs.isotropic shielding	rel. shift, δ	abs.isotropic shielding	rel. shift, δ
H_3CNO_2	-116.8	0.0	-116.8	0.0	-116.8	0.0
N (amino)	+168.3	-285.1	+177.4	-294.2	+180.3	-297.1
N-oxide	+19.4	-136,2	+17.0	-133.8	+48.6	-165.4
N (second ring)	-62.1	-54.7	-25.5	-91.3	-33.0	-83.8
N (nitro)	-102.9	-13.9	-102.4	-14.4	-90.6	-26,2

Tab. 9 Computed and experimentally observed relative ^{15}N NMR chemical shifts δ (ppm) of compound **II** (LLM-105)

	abs. isostropic shielding	rel. shift, δ	exptl. δ [34]
H_3CNO_2	-116.8	0.0	0.0
N (amino)	+177.4	-294.2	-292.1
N-oxide	+17.0	-133.8	-139.8
N (second ring)	-25.5	-91.3	-106.6
N (nitro)	-102.4	-14.4	-16.1

4. Conclusions

From this computational study the following conclusions can be drawn:

(i) The enthalpies of formation for 2,6-diamino-3,5-dinitropyrazine **(I)**, 2,6-diamino-3,5-dinitropyrazine 1-oxide **(II)** and 2,6-diamino-3,5-dinitropyrazine 1,4-dioxide **(III)** were calculated using the complete basis set (CBS-4M) method in order to obtain very accurate energies and compared with experimental values that were available for **I** and **II**.

(ii) The detonation parameters of **I**, **II** and **III** were calculated and shown to increase from **I** via **II** to **III**.

(iii) The dioxide **III** is expected to be a good candidate with calculated detonation velocity and detonation pressure even slightly higher than those of RDX.

(iv) The computed electrostatic potentials of compounds **I**, **II** and **III** revealed that attaching N-oxide substituents to the aromatic ring (compound **II** and **III**) gives rise to a considerable imbalance between stronger positive regions and weaker negative ones which can be related to the impact sensitivities. Although compound **III** would be expected to show higher sensitivity than compound **II** (LLM-105), since it exceeds the explosive power of **II** and its performance is comparable or even slightly higher than that of RDX, it is still very interesting and might be a suitable replacement explosive for RDX.

(v) The computed ^{15}N NMR chemical shifts are in good agreement with the experimentally observed values for compound **II** (Tab. 9) which gives credence to the reliability of the computed chemical shifts for compounds **I** and **III**.

The results obtained in this study should encourage synthetic work in order to prepare 2,6-diamino-3,5-dinitropyrazine 1,4-dioxide (**III**) on a laboratory scale and to experimentally evaluate its properties, first and foremost its thermal stability.

5. Acknowledgments

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