Full Paper

Heat of Formation of Triazole-Based Salts: Prediction and Experimental Validation

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Abstract: This work contributes to the growing interest in predictions linked with energetic salts. A reliable method to accurately compute the heat of formation of triazole-based salts was investigated. Calculations were based on Born-Haber energy cycles: gas-phase enthalpy of ions and lattice enthalpy were calculated separately. Ten triazole-based salts were synthesized and fully characterized. Their heat of combustion was measured by bomb calorimeter. Gas-phase heat of formation of cations and anions were computed at four different levels of theory: B3LYP 6-31G(d,p), CBS-4M, CBS-QB3, and G4. Ionic volumes were calculated at the B3LYP 6-31G(d,p) level with and without corrections. Lattice enthalpy estimations, based on calculated ionic volumes, were performed with the help of Jenkins and Gutowski methods. Combinations of the obtained results (gas-phase enthalpy of ions and lattice enthalpy) were used in the Born-Haber approach to predict solid phase enthalpy of formation of studied energetic salts. Direct comparison with experimental measurements enabled the identification of the most reliable path for energetic salt standard enthalpy of formation prediction.

Keywords: Energetic salts · Heat of formation · Computational chemistry · Bomb calorimetry

1 Introduction

New generation of energetic materials comes with an extended list of standards that have to be met. Although high performances are undoubtedly required, it is nowadays demanded to ensure safe handling and to avoid environmental pollution and health risks. Azole-based salts (or ionic liquids) are one advanced family of energetic compounds that agree with the mentioned requirements [1]. The high nitrogen content provides to the material positive aspects: enhanced density, good oxygen balance (less carbon and hydrogen content), high thermal stability, and environmentally friendly (N_2 as a main combustion product). Some of them are greatly insensitive towards outer stimuli, their impact sensitivity (IS) can reach 100 J (e.g. IS = 4.4 J for HMX and 5.4 J for RDX, measured values based on 1 reaction in 6 trials according with the BAM procedure). For the gun propellant purpose, azole-based salts combustion delivers a low flame temperature, which could prevent erosion in the gun tube, and maintains a valuable force (around 1000 J g^{-1}). In addition, they are known for their high heat of formation, which is strongly coupled with their high nitrogen content. The heat of formation is a key property, such as density, because it enables to estimate other properties of interest like a specific impulse, detonation velocity, and pressure [2,3], and sensitivity [4].

A triazole consists of a five membered heterocycle that contains 3 nitrogen atoms with two possible isomeric configurations: 1,2,3-triazole and 1,2,4-triazole. Although they have a potentially lower energy content (linked with the number of nitrogen content) than tetrazoles, triazoles can

be more derivatized thanks to their two carbon atoms in the ring [5]. It was shown by Schmidt et al. that substitution does not hinder the ability of the triazolium cation to form ionic liquids [6]. Many synthesis works concerning triazole-based energetic salts were reported by Shreeve [1,7,8].

Darwich et al. synthesized and fully characterized (purity, molecular structure, sensitivity, and thermal stability) 1,2,4-triazolium-cation-based (methylguanazinium) energetic salts [5]. The authors calculated solid-phase heats of formation through the Born-Haber cycle using ions electronic energies and approximated lattice enthalpies. Ions electronic energies were computed using Møller-Plesset perturbation theory truncated at the second order (MP2). Predicted salt solid enthalpies of formation were post-processed by EXPLO5 [9] to obtain detonation pressure and velocity. This approach is often applied in the literature concerning energetic salts. Different levels of theory can be used to calculate ions gas-phase heats of formation: CBS-4M [2,10,11], DFT-B3LYP [12,13], MP2 [14,15,16,17], G2 [18] and G3 [19]. A few studies report back-calculated solid salt heat of formation from bomb calorimeter measurements [20,21]. In most of the references, calculated or back-calculated, the heat of formations are used in thermochem-

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ical programs that predict performances such as EXPLO 5 [9] or CHEETAH 4.0 [22].

Energetic salts synthesis and testing are costly in terms of time and money. Since heat of formation is a key property, relevant predictions seem essential to obtain consistent performance properties. The accuracy of calculated enthalpies of formation is not necessarily discussed in all the reported studies. Byrd and Rice investigated a variety of methods able to predict accurately the solid phase heat of formation of energetic salts $\Delta_f H^0_{(salt,\ 298.15\ K)}$ [23]. They compared computed data with experimental values and they obtained their best predictions using G3MP2B3 level of theory combined with lattice enthalpy calculations using the Jenkins [24,25,26] and Gutowski model [27]. These models are extensively used in the community and will be described in the computational approach section. The authors also pointed out the lack of experimental data, which might mitigate conclusions on the accuracy of their methodology. More recently, Forquet et al. evaluated calculation methods to determine solid phase heats of formation for 2,2-dimethyltriazanium-cation-based energetic salts [28]. Their comparison between computed and experimental data led to a reliable methodology combining a CBS-QB3 level for the gas phase enthalpy calculation of ions of interest, a non-corrected B3LYP/6-31G(d,p) calculation for the molecular volume, and the Gutowski model to obtain the lattice enthalpy.

In this paper, both experimental measurement and calculations of the heat of formation are considered. Ten triazole-based-salts were synthesized and characterized. Their heats of combustion (Q_{comb}) were experimentally measured by bomb calorimetry. Electronic energies were computed at four different level of theories to calculate ions gas-phase enthalpy of formation. Molecular volumes were also computed and Jenkins and Gutowski models were applied to obtain the lattice enthalpy. Calculated $\Delta_f H^0_{(salt,\ 298.15\ K)}$ are post-processed to determine Q_{comb}. Combinations between various quantum chemical methods and lattice energy models were confronted with experimental data and the methodology that provided the best agreement is reported.

2 Theoretical Approach

An equation obtained from the Born-Haber cycle approach (Equation (1)) is used to estimate the solid phase standard heat of formation $\Delta_f H^0_{(salt,\ 298.15\ K)}$ of the energetic salt [1]. It requires 3 main physicochemical properties that can be predicted thanks to ab initio calculations: Gas-phase standard heat of formation of the anion and the cation $\Delta_f H^0_{(g,\ cation,298.15\ K)}$ and $\Delta_f H^0_{(g,\ anion,298.15\ K)}$ and the lattice enthalpy (ΔH_L).

$$\Delta_f H^0_{(salt,\ 298.15\ K)} = \Delta_f H^0_{(g,\ cation,298.15\ K)} + \Delta_f H^0_{(g,\ anion,298.15\ K)} - \Delta H_L \tag{1}$$

Calculations were performed with the Gaussian 16® software [29].

2.1 Ions Enthalpy of Formation

Anions and cations electronic energies were computed at four different levels of theory. For each ions, 5 to 10 distinct conformers (depending on the complexity of the molecular structure) were investigated and the chemical structure that ensured the lowest energy was selected.

First, ions gas-phase standard enthalpy of formation $\Delta_f H^0_{298.15K(g)}$ was computed by following the procedure proposed by Osmont et al. [30]. This method has been developed for the prediction of thermochemical data of energetic materials. It is based on a geometry optimization and frequency calculation at the DFT B3LYP/6-31G(d,p) level. The gas-phase enthalpy of formation is then determined with the Equation (2).

$$\Delta_f H^0_{298.15K(g)} = 2625.5 \times \left(E + \Delta H_{corr} + \sum_i \alpha_i c_i \right) \tag{2}$$

Gaussian 16® software [29] outputs energies in Hartree. molecule-1. In Equation (2), 2625.5 is the conversion factor from Hartree.molecule^{-1} to kJ.mol^{-1}. E and ΔH_{corr} are, respectively, the electronic energy and the thermal correction. α_i is the number of atom i and c_i is the atomic correction for atom i, more details are reported in Osmont et al. [30].

Compound methods were also performed to obtain ions gas-phase standard enthalpies of formation. Enthalpies of formation were obtained by using an atomization energy scheme (Equation (3)).

$$\Delta_f H^0_{(g,\ ion,298.15\ K)} = H^\circ_{(ion,298.15\ K)} + \sum H^\circ_{(atom,298.15\ K)} + \sum \Delta_f H^0_{(atom,298.15\ K)} \tag{3}$$

Enthalpies of the ions ($H^\circ_{(ion,298.15\ K)}$) were computed with three different compound methods: CBS-4M, CBS-QB3, and G4. While CBS-4M is routinely used by Klapötke et al. [2,10,31,32] and Hermann et al. [33], Forquet et al. [28] demonstrated the effectiveness of using the CBS-QB3 method. The last compound method used in this study is the G4 method [34]. The G4 was designed to be a highly accurate method. However, it has a considerable calculation cost compared to the previously mentioned methods. One of the goal here is to evaluate the gain in accuracy when increasing the calculation cost. Values for calculated atom en-

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thalpy ($H^°_{(atom,298.15\ K)}$) and experimental ($\Delta_f H^0_{(atom,298.15\ K)}$) standard enthalpy were collected from, respectively, the Computational Chemistry Comparison and Benchmark DataBase (CCCBDB) [35] and the NIST chemistry WebBook [36].

2.2 Lattice Enthalpy Calculation

Lattice enthalpy was estimated thanks to volume based calculations introduced by Mallouk et al. [37] and Jenkins et al. [24,25]. The first step is to separately optimize the structures of the cation M^{q+} and the anion X^{p-}. The volume of ions was obtained from an isodensity surface polarized continuum model (IPCM) calculation at the DFT B3LYP/6-31G(d, p) level, similar method as Forquet et al. [28]. Corrections proposed by Rice et al. [38] were evaluated. Results from ion volume calculations were used in Equation (4).

$$V\left(M_p X_q\right) \approx pV(M^{q+}) + qV(X^{p-})\qquad(4)$$

Volumes calculated from equation 4 were validated thanks to density measurements, after comparison with experimental data it was decided to use, or not, Rice et al. [38] corrections. Volumes were then used in Equation (5) to obtain lattice energies.

$$\Delta U_L\left(M_p X_q, s\right) = (pq^2 + qp^2)\left(\frac{\alpha}{\sqrt[3]{V}} + \beta\right)\qquad(5)$$
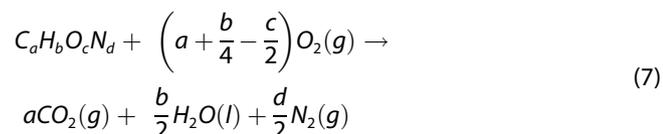
α and β are coefficients taken from Jenkins et al. [25] and Gutowski et al. [39]. Lattice energy estimations are used in Equation (6) to obtain lattice enthalpies.

$$\Delta H_L\left(M_p X_q, s\right) = \Delta U_L + \left(p\left(\frac{n_M}{2} - 2\right) + q\left(\frac{n_X}{2} - 2\right)\right)RT\qquad(6)$$

n_M and n_X values are, for the cation and the anion, 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

2.3 Heat of Combustion Calculation

Calculated heats of combustion were obtained with calculated solid-phase standard enthalpy of formation that are based on Jenkins and Gutowski methods. During Q_{comb} bomb calorimeter measurements, the studied energetic salt burns in excess of oxygen. In this case, CHNO species combustion products are liquid H_2O, gaseous CO_2, and N_2:

$$C_a H_b O_c N_d + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) \rightarrow$$
$$aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g)\qquad(7)$$

Enthalpy of combustion (ΔH_{comb}) is then calculated by the difference between the standard enthalpy of combustion of the products and reactants according to reaction (7). Since $N_2(g)$ and $O_2(g)$ correspond to the most stable forms of nitrogen and oxygen in their standard state, at the reference temperature of 298.15 K, their standard enthalpies of formation are equal to zero.

$$\Delta H_{comb} = a\Delta_f H^0_{CO2(g)} + \frac{b}{2}\Delta_f H^0_{H2O(l)} - \Delta_f H^0_{(salt,\ 298.15\ K)}\qquad(8)$$

ΔH_{comb} is the enthalpy of reaction according to reaction (7), the heat of combustion is obtained by $Q_{comb} =- \Delta H_{comb}$. $\Delta_f H^0_{CO2(g)}$ and $\Delta_f H^0_{H2O(l)}$ are taken from the NIST database [35], respectively, −393.52 and −285.83 kJ.mol^{-1}.

3 Results and Discussion

3.1 Volume Calculations

Since lattice energy predictions are based on computed volumes, energetic salts volumes should be accurately predicted. To validate computed volumes, density measurements for each salt were conducted with a gas pycnometer. Experimental salts molecular volumes could be obtained thanks to $V = M/\rho$.

Volume calculations were performed for each ion presented in Figure 1. The calculation protocol is explained in section 2 and computed ion volumes are listed in Table 1.

Calculated salts volumes are plotted against experimental ones (Figure 2). Corrected and non-corrected volumes are in good agreement with experimental measurements. Mean errors for non-corrected and corrected are, respectively, 4.0 % and 2.8 %.

Better accuracy was obtained by using Rice et al. corrections, they were then applied for lattice enthalpy estimations. Lattice enthalpy was estimated twice for each salt:
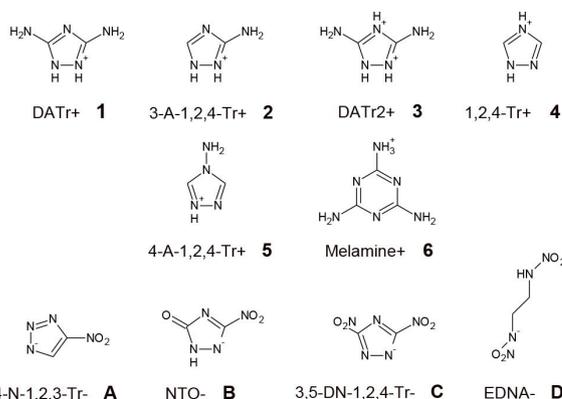

Figure 1. Cations (from 1 to 6) and anions (from A to D).

Table 1. Calculated ion volumes with and without Rice et al. corrections.

Ions	Calculated volume (Å^3)	Calculated volume with Rice et al. corrections (Å^3)
1	111.1	104.7
2	96.6	91.2
3	108.6	101.4
4	79.3	74.8
5	98.2	92.8
6	140.2	132.9
A	117.0	115.4
B	121.8	120.2
C	139.0	138.4
D	156.8	151.4

Table 2. Calculated ion enthalpy of formation at different levels of theory. The results are in kJ.mol^{-1}.

Ions	B3LYP/ 6-31G (d,p)	CBS-4M	CBS-QB3	G4
1	698.4	818.4	819.5	726.5
2	842.1	847.5	851.9	767.9
3	1907.4	1914.4	1916.6	1826.7
4	806.6	834.4	832.3	755.9
5	1103.1	1121.9	1116.7	1032.9
6	818.6	711.4	712.9	617.4
A	90.4	56.5	53.1	−27.2
B	−146.7	−204.4	−214.0	−299
C	−17.9	−52.3	−61.5	−150.5
D	−84.3	−124.0	−152.9	−249.4
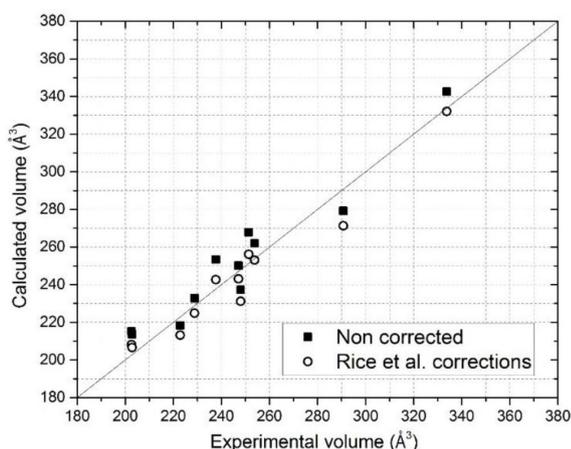
Figure 2. Non corrected vs corrected calculated salt volume plotted against experimental salt volume.

one with Gutowski method and the other with Jenkins method.

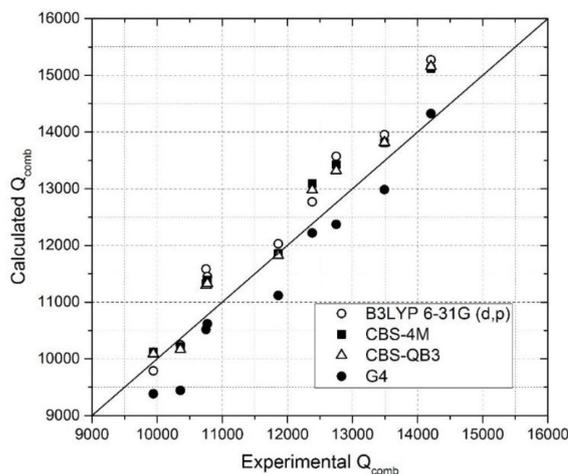### 3.2 Calculated Heat of Combustion

As it is explained in Section 2, 4 types of calculations were performed for ion standard enthalpy of formation. Results are presented in Table 2. For each ion, calculated values at different levels of theory are in the same range. However, differences from few decades kJ mol^{-1} to few hundreds can be observed from a levels of theory to another. Results from CBS methods are quite similar. Predictions obtained with CBS methods are 100 kJ mol^{-1} higher than G4 ones. Results calculated with DFT B3LYP/6-31G(d,p) are in the same range or higher than CBS methods calculated ones. These differences will certainly impact the accuracy of the final result. The level of theory used for calculations of ions enthalpy of formation seems crucial.

Lattice enthalpy estimations and results from Table 2 made possible the calculation of enthalpy of formation of

each salt with Jenkins and Gutowski model and at four different levels of theory (Equation (1)). Based on these computed enthalpies of formation, heats of combustion were calculated and used for direct comparison with experimental heat of combustion (Figures 3 and 4). Since Gutowski coefficients only applies to 1:1 salts, the heat of combustion for the 3.A.A. salt (Diamino-1,2,4-triazolium-bis-(4-nitro-1,2,3-triazolate)) does not appear in Figure 3.

For each energetic salt investigated, bomb calorimeter measurements were conducted 3 times. Since the mean experimental deviation was found to be 0.2% at the most. Disparities observed, between calculated and experimental heat of combustion, are essentially caused by calculation errors.

Figure 3 reports calculated energetic salts heat of combustion based on a lattice enthalpy estimated with Gutowski method and at four different levels of theory for ions enthalpy of formation. A good overall agreement can be noted.

Figure 3. Calculated heat of combustion with lattice enthalpy estimated Gutowski et al. method vs experimental heat of combustion (kJ.mol^{-1}).
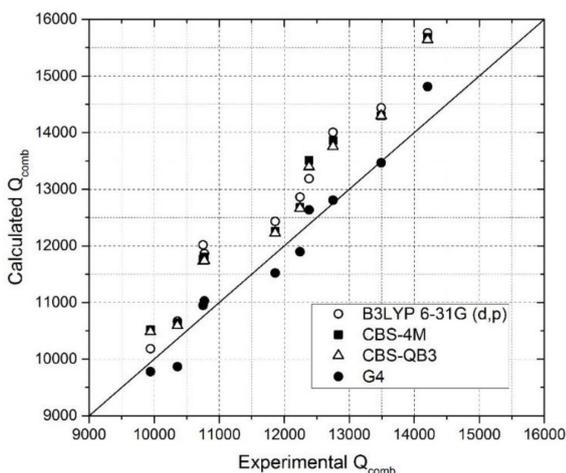
Figure 4. Calculated heat of combustion with lattice enthalpy estimated Jenkins et al. method vs experimental heat of combustion (kJ.mol^{-1}).

Figure 4 presents results obtained by applying Jenkins coefficients. It can be observed that applying G4 method leads to more accurate results. This trend is discernible in Figure 4 and confirmed by the calculated mean error of 2.3% (Table 3). This result was expected since the accuracy of the G4 level of theory, for nitrogen-rich cations, have been reported by Nirwan and Ghule [40]. The other tested levels of theory (B3LYP/6-31G(d,p), CBS-4 M, and CBS-QB3), combined with Jenkins coefficients, overestimated the heat of combustion.

For both methods, Gutowski and Jenkins, the worst agreement was obtained using B3LYP/6-31G(d,p), 7.2%, and 4.3%, respectively. According to Table 3, similar mean errors (3.6% with CBS-QB3, 3.7% with G4 to 3.8% with CBS-4 M) are reported when using compound methods and Gutowski coefficient. Forquet et al. [28] and Klapötke et al. [2] obtained their most accurate results using a CBS level combined with Gutowski method. The large differences of calculated ions gas-phase enthalpy observed in Table 2 revealed the importance of the level of theory applied. Since calculations involving a G4 level combined with Jenkins method were found to be most accurate, it can be expected that Gutowski lattice model absorbs a part of the

deficiencies coming from the ion gas-phase enthalpy calculated with CBS methods.

It is important to mention that performing calculations at the G4 level is more expensive in terms of calculation time than the other tested compound methods. However, the calculation time for each studied ion did not exceed 30 hours at the G4 level (4 cores involved), which can be considered reasonable. CBS methods calculations and B3LYP 6–31/G(d,p) did not exceed, respectively, 15 hours and 45 minutes.

4 Conclusion

The synthesis of 10 triazole-based salts have been successfully conducted. In addition to a full characterization, their heat of combustion has been measured for each energetic salt by a bomb calorimeter.

Relevant predictions of heat of formation were obtained thanks to quantum chemical calculations. The most accurate calculation path involves a G4 level coupled with atomization reactions for ions standard enthalpy of formation prediction. Lattice enthalpy were based on ionic volume calculation at B3LYP/6-31G(d,p) with Rice et al. corrections for ionic volumes and Jenkins coefficients. Computed enthalpies of formation were converted to the heat of combustion for direct comparisons with experimental measurements. A 2.3% mean error was estimated following this calculation path and calculation time is reasonable.

This work aims at improving predictions concerning azole-based salt materials. It will support future activities involving triazole-based salts. In future works, it is planned to check the reliability of the method for other types of energetic salts such as tetrazole and/or ammonium-based salts.

5 Experimental Section

5.1 General Methods

The isoperibolic Q_{comb} measurements were conducted using an IKA 2000 basic bomb calorimeter. A decomposition vessel is equipped with an oxygen valve, outlet valve for the combustion gases and a holding and electrical ignition device. For the Q_{comb} measurement, the EM sample was pressed into a pellet of 1 g, placed in the decomposition vessel which was filled with 3 MPa of pure oxygen to ensure complete combustion. The decomposition vessel is immersed in a measuring cell filled with water at a temperature of 25 °C. The measuring cell consists of an inner vessel surrounded by an insulating water jacket with a fixed temperature to ensure constant parameters. The temperature curve of the inner water vessel is registered during the combustion process and the temperature increase permits the calculation of heat of combustion. Results of Q_{comb} with Wash-

Table 3. Heat of combustion calculated mean errors (%) and root mean squarred errors (kJ.mol^{-1}).

Method	Mean errors (%)		RMSE (kJ.mol^{-1})	
	Jenkins	Gutowski	Jenkins	Gutowski
B3LYP 6-31G(d,p)	7.2	4.3	978.4	609.6
CBS-4 M	6.9	3.8	922.9	571.1
CBS-QB3	6.5	3.6	873.4	522.8
G4	2.3	3.7	323.4	460.5

burn corrections applied can be found in the supplementary materials.

IR spectra were recorded by using ATR for solids on a Bruker Tensor 27 spectrometer.

The density was measured by a pycnometer Pycnomatic from Porotec at standard conditions (293.15 K, 10^5 Pa) with helium.

^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded with Varian MR 400 nuclear magnetic resonance spectrometer operating at 400, 100, and 41 MHz, respectively at 25 °C. Chemical shifts are reported relative to TMS for 1H and ^{13}C NMR spectra and to CH_3NO_2 for ^{15}N spectra. The solvent was dimethyl sulfoxide-d_6. NMR spectra are given in the supplementary material.

The differential thermal analysis was measured using SII TG/DTA7200 and the differential scanning calorimetry by using SII X–DSC7000 (SII NanoTechnology Inc.) with a heating rate of 5 K min^{-1}. The chemicals as well as their purities and suppliers are listed in Table 4.

5.2 Physicochemical Properties

The thermal stabilities of the triazole-based salts were determined by differential thermal analysis (DTA) measurements (Table 4). Given that the salts have good thermal stability with decomposition temperatures ranging from 187 (2.D.) to 303 °C (6.B.). The density was measured at standard conditions (293.15 K, 10^5 Pa) with a helium pycnometer and the values are in the range of 1.621 (2.A.) to 1.722 g cm^{-3} (5. C.). Melting temperatures are reported except for 1.B. and 6. B. No melting points were observed for both ionic salts 1.B. and 6.B. They have NTO anions in common, which, in its molecular form, is known for its high melting temperature (more than 270 °C).

Impact and friction sensitivities were measured according to the standard BAM methods [41]. Most of the salts can be considered as highly insensitive to impact. The lowest measured impact sensitivity is 10.4 J (4.C.) which is still higher than classical insensitive energetic materials (For RDX and HMX, IS ≈7.4 J). Studied ionic salts are highly insensitive to friction since the lowest value is 288 N (1.D.). Back-calculated standard heat of formation from experimentally measured heat of combustion are presented. Reported calculated standard enthalpies are the ones computed with the most accurate path (G4 calculation and Jenkins method) previously presented. Oxygen balance and Nitrogen content are also reported in Table 5.

5.3 Synthesis

The studied ions are presented in Figure 1 and the syntheses, based on the Xue et al. work were slightly modified [42].

Table 4. Specification of Chemical Samples.

Chemical name	Source	Initial mole fraction purity	CAS no.	Purification method	Final mole fraction purity	Analysis method
3-nitro-1,2,4-triazol-5-one	EURENCO France	>0.98	932-64-9	recrystallization	>0.99	^{1}H ^{13}C NMR[a], IR[b], DTA[c]
3,5-diamino-1,2,4-triazole	Alfa Aesar France	0.95	1455-77-2	none		
3-amino-1,2,4-triazole	Sigma-Aldrich France	0.98	61-82-5	none		
4-amino-1,2,4-triazole	Sigma-Aldrich France	0.99	584-13-4	none		
1,2,4-triazole	Alfa Aesar France	0.99	288-88-0	none		
1,3,5-triazine-2,4,6-triamine (melamine)	Sigma-Aldrich France		108-78-1	none		
4-nitro-1,2,3-triazole	synthesis		84406-63-3	recrystallization	>0.99	^{1}H ^{13}C ^{15}N NMR[a], IR[b], DTA[c], DSC[d]
sodium-3,5-dinitro-1,2,4-triazolate	synthesis			recrystallization	>0.99	^{1}H ^{13}C ^{15}N NMR,IR[b], DTA[c], DSC[d]
ethylendinitramine	synthesis		505-71-5	recrystallization	>0.99	^{1}H ^{13}C ^{15}N NMR,IR[b], DTA[c], DSC[d]
acetone	Zundel Kohler France		67-64-1	none		
ethanol	VWR France		64-17-5	none		
Energetic salts	synthesis			recrystallization	>0.95	^{1}H ^{13}C ^{15}N NMR[a], DTA[c], DSC[d]

[a] Nuclear magnetic resonance, [b] Infrared spectroscopy, [c] Differential thermal analysis, [d] Differential scanning calorimetry

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Table 5. Physicochemical properties.

Salt	ρ^a	OB^b	T_m^c	T_d^d	N^e	$\Delta_f H\ exp^f$	$\Delta_f H\ calc^g$	IS^h	FS^i
1.B	1.658 ± 0.005	−59.3	–	238	55.0	-112.5 ± 0.2	−67.0	>30	360
1.C	1.734 ± 0.027	−43.4	204	236	54.3	133.2 ± 0.3	91.3	>24.5	360
1.D	1.635 ± 0.002	−61.0	134	187	50.6	-20.0 ± 0.1	−6.5	12.3	288
2.A	1.621 ± 0.001	−72.7	121	226	56.6	239.6 ± 0.3	235.1	>24.5	324
2.D	1.645 ± 0.0003	−75.4	110	187	52.8	-63.0 ± 0.1	0.2	19.6	324
3.A.A	1.627 ± 0.0002	−61.1	114	214	55.6	355.8 ± 0.3	242.7	12.3	>360
4.C	1.699 ± 0.014	−42.1	186	222	49.1	215.7 ± 0.2	104.0	10.4	360
5.A	1.623 ± 0.001	−72.7	97	214	56.6	381.0 ± 0.3	501.1	>24.5	360
5.C	1.722 ± 0.002	−42.8	120	215	51.9	328.7 ± 0.1	391.4	22.1	360
6.B	1.675 ± 0.026	−68.7	–	303	54.7	-85.8 ± 0.1	−161.2	>30	>360

[a] Measured density (g cm^{-3}, $p_0 = 10^5$ Pa, T = 293.15 K). [b] Oxygen Balance (%). [c] Melting Point under nitrogen (°C, $p_0 = 10^5$ Pa). [d] Decomposition temperature (°C). [e] Nitrogen Content (%). [f] Back-calculated standard heat of formation (kJ mol^{-1}), the uncertainties of the mean were calculated from the uncertainty of the measurements of the heat of combustion, with benzoic acid as standard. [g] Calculated standard heat of formation (kJ mol^{-1}). [h] BAM test Impact sensitivity (J). [i] Friction sensitivity (N). Uncertainties given in the table are expanded uncertainties at 0.95 level of confidence.

1.B. 3,5-Diamino-1,2,4-triazolium-3-nitro-1,2,4-triazol-5-onate

3-Nitro-1,2,4-triazol-5-one (1.31 g, 10 mmol) was dissolved in 50 ml warm ethanol and afterwards 3,5-diamino-1,2,4-triazole (1 g, 10 mmol) was added. The orange colored product precipitated while stirring. It was filtered off, washed with ethanol and dried under reduced pressure, yield 93.0% (2.15 g). IR (ATR): 3461, 3417, 3344, 2726, 1707, 1637, 1604, 1525, 1494, 1360, 1305, 1103, 1054, 1019, 988, 889, 846, 778, 761, 741, 678, 656, 616 cm^{-1}; ^{1}H-NMR δ: 9.06 ppm; ^{13}C-NMR δ: 154.0, 156.6, 162.6 ppm; ^{15}N-NMR δ: −22.4, −111.7, −175.9, −194.8, −199.1, −200.1, −225.8, −328.7 ppm.

1.C. 3,5-Diamino-1,2,4-triazolium-3,5-dinitro-1,2,4-triazolate

Sodium-3,5-dinitro-1,2,4-triazolate (5 g, 25 mmol) was suspended in diethyl ether and 10% aqueous HCl was dropped until the solution becomes clear. The organic phase was dried and concentrated under an air stream. The concentrated solution was added to a suspension of 3,5-diamino-1,2,4-triazole (1 g, 10 mmol) in ethanol. The solution was heated to boiling and the product precipitated while cooling. It was filtered off, washed with ethanol, and dried under reduced pressure. Yellow solid product at 45% yield (1.04 g). IR (ATR): 3467, 3423, 3361, 3288, 3189, 2609, 1670, 1610, 1545, 1492, 1397, 1353, 1300, 1129, 1059, 998, 872, 845, 832, 796, 766, 694, 647 cm^{-1}; ^{1}H-NMR δ: 6.95, 11.23 ppm; ^{13}C-NMR δ: 151.4, 162.9 ppm; ^{15}N-NMR δ: −20.2, −50.5, −146.3, −326.5 ppm.

1.D. 3,5-Diamino-1,2,4-triazolium-ethylendinitraminate

To a suspension of 3,5-diamino-1,2,4-triazole (0.99 g, 10 mmol) in 50 ml acetone a solution of ethylendinitramine (1.5 g, 10 mmol) in 40 ml acetone was added. The solvent was evacuated under reduced pressure. The precipitate was recrystallized in ethanol to produce white crystals. Yield at 76% (1.9 g).

IR (ATR): 3222, 3108, 1622, 1591, 1560, 1486, 1447, 1403, 1346, 1308, 1243, 1118, 1058, 788, 772, 596 cm^{-1}; ^{1}H-NMR δ: 3.60 ppm; ^{13}C-NMR δ: 42.4, 158.4 ppm.

2.A. 3-Amino-1,2,4-triazolium-4-nitro-1,2,3-triazolate

To a warm 100 ml acetone solution of 3-amino-1,2,4-triazole (0.84 g, 0.1 mol) was added 4-nitro-1,2,3-triazole (1.14 g, 0.1 mol) in 40 ml acetone. The clear solution was stirred, the solvent was evacuated to produce pale yellow crystals. The precipitate was recrystallized in ethanol. Yield at 100% (1.98 g).

IR (ATR): 3424, 3341, 3149, 2979, 2322, 1979, 1638, 1529, 1494, 1384, 1231, 1035, 966, 863, 827, 747, 612 cm^{-1}; ^{1}H-NMR δ: 7.69, 8.96 ppm; ^{13}C-NMR δ: 126.6, 146.5, 154.0, 157.0 ppm; ^{15}N-NMR δ: −21.7, −37.8, −41.2, −91.9, −119.6, −178.4, −193.0, −330.3 ppm.

2.D. 3-Amino-1,2,4-triazolium-ethylendinitraminate

Ethylendinitramine (0.75 g, 5 mmol) was dissolved at room temperature in 50 ml acetone and this solution was added to a boiling solution of 4-amino-1,2,4-triazole (0.84 g, 10 mmol) in 50 ml acetone. The clear solution was stirred, the solvent was evacuated to produce white crystals at 100% (1.59 g) yield.

IR (ATR): 3404, 3213, 2926, 2724, 1632, 1592, 1536, 1446, 1404, 1348, 1268, 1245, 1211, 1118, 1044, 967, 876, 825, 789, 727, 596 cm^{-1}; ^{1}H-NMR δ: 3.60, 5.75, 7.44, 12.09 ppm; ^{13}C-NMR δ: 42.3, 147.6, 157.8 ppm.

3.A.A. 3,5-Diamino-1,2,4-triazolium-bis-(4-nitro-1,2,3-triazolate)

To a suspension of 4-nitro-1,2,4-triazole (1.14 g, 10 mmol) in 50 ml acetone a solution of 3,5-diamino-1,2,4-triazole (0.5 g, 5 mmol) in 40 ml acetone was added. The solvent was evacuated under reduced pressure. The precipitate was recrystallized in ethanol to produce yellow crystals. Yield at 98 % (1.6 g).

IR (ATR): 3465, 3420, 3157, 2589, 1685, 1650, 1511, 1456, 1411, 1373, 1286, 1206, 1136, 1063, 1028, 1001, 853, 830, 784, 757, 730, 708, 661 cm^{-1}; ^{1}H-NMR δ: 8.79, 9.61 ppm; ^{13}C-NMR δ: 127.0, 153.7, 153.8 ppm; 15 N-NMR δ: −20.6, −28.5, −40.0, −78.7, −196.4, −225.3, −328.3 ppm.

4.C. 1,2,4-Triazolium-3,5-dinitro-1,2,4-triazolate

Sodium-3,5-dinitro-1,2,4-triazolate (2.8 g, 16 mmol) was suspended in diethyl ether and 10 % aqueous HCl was dropped until the solution becomes clear. The organic phase was dried and concentrated under an air stream. The concentrated solution was added to a solution of 1,2,4-triazole (1 g, 14 mmol) in ethanol. The yellow product precipitated while stirring. It was filtered off, washed with ethanol, and dried under reduce pressure. The precipitate was recrystallized in ethanol. Yellow solid product at 70 % yield (2.24 g).

IR (ATR): 3165, 3128, 3063, 2902, 2788, 2576, 2516, 2476, 1955, 1669, 1580, 1542, 1500, 1457, 1414, 1394, 1359, 1314, 1305, 1281, 1256, 1182, 1128, 1111, 1062, 1030, 1001, 956, 942, 931, 881, 840, 826, 772, 664, 649, 627, 606, 533 cm^{-1}; ^{1}H-NMR δ: 9.34, 15.2 ppm; ^{13}C-NMR δ: 143.2, 162.8 ppm.

5.A. 4-Amino-1,2,4-triazolium-4-nitro-1,2,3-triazolate

4-Amino-1,2,4-triazole (0.84 g, 10 mmol) and 4-nitro-1,2,3-triazole (1.14 g, 10 mmol) was dissolved in 30 ml acetone respectively and were put together to form a clear solution. The solvent was evacuated under reduce pressure. The precipitate was recrystallized in ethanol, pale yellow crystals at 95 % (1.9 g) yield.

IR (ATR): 3364, 3294, 3132, 3112, 2436, 1952, 1601, 1563, 1521, 1484, 1455, 1391, 1375, 1227, 1186, 1065, 1038, 1018, 981, 949, 916, 880, 824, 759, 698, 682, 622, 537 cm^{-1}; ^{1}H-NMR δ: 8.41, 9.10 ppm; ^{13}C-NMR δ: 126.0, 144.6, 153.9 ppm.

5.C. 4-Amino-1,2,4-triazolium-3,5-dinitro-1,2,4-triazolate

Freshly prepared 3,5-dinitro-1,2,4-triazole (~3 g, 19 mmol) was dissolved in 25 ml ethanol and 4-amino-1,2,4-triazole (1 g, 12 mmol) was added. The solution was heated to boiling and the product precipitated while cooling. The precipitate was recrystallized in ethanol. Yellow solid, yield up to 54 % (1.56 g)

IR (ATR): 3325, 3241, 3155, 2469, 1638, 1549, 1493, 1421, 1384, 1353, 1301, 1209, 1113, 1079, 1029, 992, 928, 871, 843, 827, 648, 614 cm^{-1}; ^{1}H-NMR δ: 9.04, 9.55 ppm; ^{13}C-NMR δ: 144.4, 163.1 ppm.

6.B. 2,4,6-Triamino-1,3,5-triazinium-3-nitro-1,2,4-triazol-5-onate

3-Nitro-1,2,4-triazol-5-one (2 g, 15 mmol) was dissolved in 40 ml warm ethanol and afterwards, melamine (1.94 g, 15 mmol) was added. The solution was heated to boiling and the product precipitated while cooling. Yield up to 85 % (3.35 g).

IR (ATR): 3195, 1690, 1542, 1474, 1338, 1187, 1006, 829, 785, 753, 723, 680, 602 cm^{-1}; ^{1}H-NMR δ: 6.99 ppm; ^{13}C-NMR δ: 157.7, 163.8, 163.7 ppm ; ^{15}N-NMR δ: −20.6, −111.8, −198.6, −206.4, −216.4, −294.2 ppm.

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Data Availability Statement

No data available.

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