Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

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1. General methods

All chemicals were used as supplied. Raman spectra were recorded in a glass tube with a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser excitation up to 1000 mW (at 1064 nm). Infrared spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths Dura/SamplIR II ATRdevice. All spectra were recorded at ambient (25 °C) temperature. NMR spectra were recorded with JEOL/Bruker instruments and chemical shifts were determined with respect to external Me_4Si (^1H, 399.8 MHz; ^{13}C, 100.5 MHz) and $MeNO_2$ (^{14}N, 28.9 MHz; ^{15}N, 40.6 MHz). Analyses of C/H/N were performed with an Elemental Vario EL Analyzer. Melting and decomposition points were measured using differential thermal analysis (DTA) at a heating rate of 5° C min^{-1} with an OZM Research DTA 552-Ex instrument. The sensitivity data were explored using a BAM drop hammer and a BAM friction tester. [1] The heats of formations were calculated by the atomization method based on CBS-4M electronic enthalpies. All calculations affecting the detonation parameters were carried out using the program package EXPLO5 6.03. [2, 3]

2. X-Ray diffraction

For the measurement, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo-*K*α radiation (λ = 0.71073 Å). By using the CRYSALISPRO software[4] the data collection and reduction was performed. The structure was solved by direct methods (SIR92, [5,6]) and refined by full-matrix least-squares on *F*2 (SHELXL [7,8]) and finally checked using the PLATON software [9] integrated in the WinGX software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a SCALE3 ABSPACK multiscan method. [10] All DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

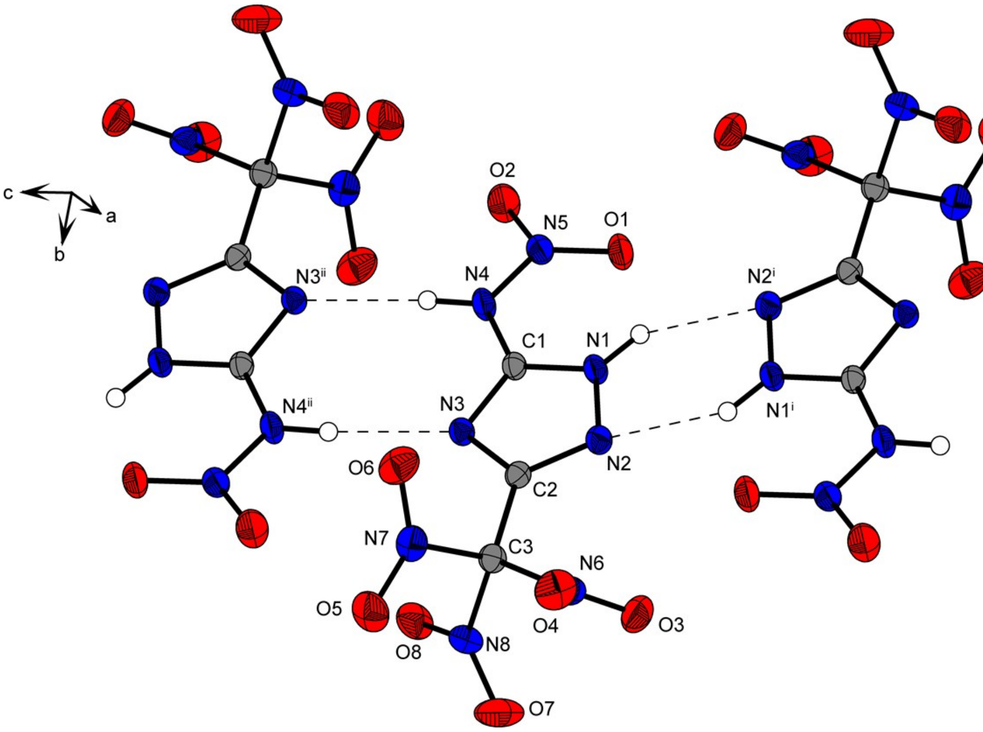

Figure S1: Crystal structure of **1** with intermolecular hydrogen bonds.

A suitable single crystal for X-ray diffraction experiments of compound **1** was obtained during the nitration work up. The crystal structure is shown in Figure 1 in the main manuscript and structure refinement data of the structure determinations are given in Table S1.

3-Nitramino-5-trinitromethyl-1*H*-1,2,4-triazole (**1**) crystallizes in the monoclinic space group $P2_1/n$ with 4 formula units per unit cell and a calculated density of 1.95 g cm^{-3} at 173 K. The bond length and angles are in the typical range of CHNO based compounds containing a trinitromethyl moiety. [11,12,13] Due to the typical shape of triazoles the heterocycle shows a large planar arrangement area. This area consists of a heterocycle with three nitrogen atoms arranged in 1,2,4 position and two carbon atoms. This planarity is displayed by the torsions angles of C1-N1-N2-C2 = 0.28°, C2-N3-C1-N1 = −0.69°, N2-N1-C1-N3 = 0.28° of almost 180° C. The C-N bonds in compound **1** are slightly different to typical C-N bonds. Compared to regular C=N bonds, all C=N bonds in the heterocycle are a slightly longer with lengths of around 1.36 Å. This can be explained by the adjacent trinitromethyl moiety. [14,15] Another very typical characteristic of trinitromethyl moiety is the propeller shaped arrangement of the three nitro groups. All C-C-N-O torsion angles are in the range of 20°−62° of the trinitromethyl moiety, which implements a real propeller-type orientation. The N-O bonds are 1.21 Å in average. The C2-N2 and C1-N3 bond lengths are around 1.31 Å and therefore in the double bond range. The bond lengths of C2-N3, C1-N1 and C1-N4 are in the range of single bonds. Figure S1 displays intermolecular hydrogen bonds via the CNC nitrogen of the triazole units to the nitramine nitrogen (N···H-N 2.01 Å). Figure S2 shows the view along the c-axis, where the rings are connected slightly shifted over the hydrogen bonds. Furthermore, the trinitromethyl moiety builds oxygen-oxygen contacts in the c-axis.

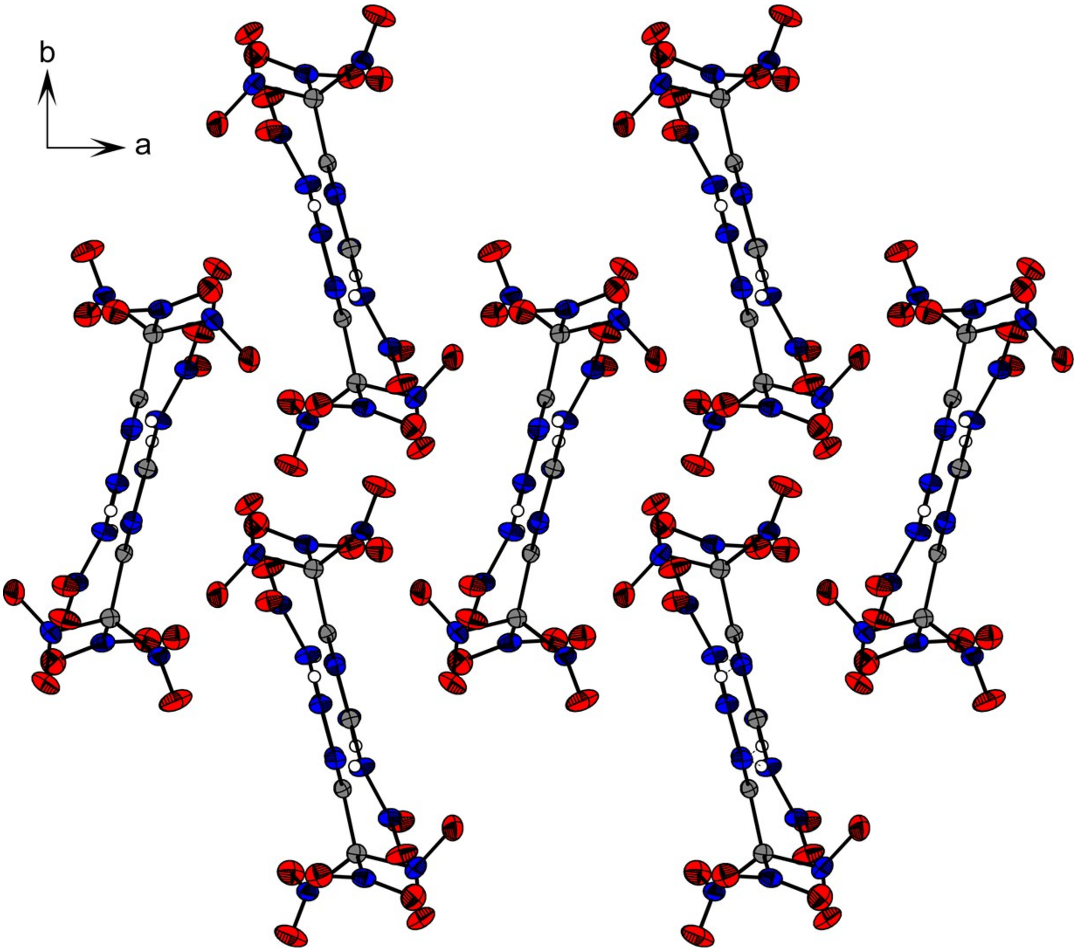

Figure S2: View on the crystal structure of **1** along the *c*-axis.

Table S1. Crystal and structure refinement data of **1**.

	1
Empirical formula	$C_3H_2N_8O_8$
Formula mass (g mol^{-1})	278.10
Temperature (K)	173
Crystal size (mm^3)	0.4x0.4x0.11
Crystal description	Colorless block
Crystal system	monoclinic
Space group	$P\,2_1/n$
a (Å)	9.1597(7)
b (Å)	10.5684(7)
c (Å)	9.9433(7)
β (°)	101.110(7)
V (Å^3)	944.51(12)
Z	4
ρ_{calc} (g cm^{-3})	1.95

μ (mm^{-1})	0.192
F (000)	560
Θ range (°)	4.39-26.50
Index range	$-11<h<10$
	$-13<k<13$
	$-11<l<12$
Reflection collected	7214
Reflection observed	1958
Reflection unique	1746
R1, wR2 (2σ data)	0.0327, 0.0795
R1, wR2 (all data)	0.0373, 0.0838
Data/restraints/parameters	1958/0/180
GOOF an F^2	1.066
Larg. diff. peak/hole (e Å^{-3})	0.344, −0.334
CCDC entry	1701785

The highest density is observed for the neutral compound **1** with Ω_{CO} = 23 % and ρ_{173K} = 1.95 g cm^{-3}. For the corresponding salts, density measurements were carried out using gas pycnometry. The densities for the salts are significantly lower than the neutral compound **1**.

3. Heat of formation calculations

All calculations were carried out using the Gaussian G09W (revision A.02) program package. 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) geometry 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. [16,17] The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq.1).

$$\Delta_f H^\circ_{(g,\ M,\ 298)} = H_{(\mathrm{Molecule},\ 298)} - \sum H^\circ_{(\mathrm{Atoms},\ 298)} + \sum \Delta_f H^\circ_{(\mathrm{Atoms},\ 298)} \quad (1)$$

Table S2. CBS-4M results and calculated gas-phase enthalpies

	M	$-H^{298}$ / a.u.	$\Delta_f H°(g,M)$ / kcal mol^{-1}
1	278.1	1153.552952	64.2
monoanion	277.1	1153.062215	5.6
dianion	231.1	948.178386	11.2
AG$^+$	75.1	260.701802	160.4
TAT$^+$	115.1	408.091922	206.9
$N_2H_5^+$	66.1	112.030523	184.9

Table S3. CBS-4M values and literature values for atomic $\Delta H°_f{}^{298}$ / kcal mol^{-1}

	$-H^{298}$ / a.u.	NIST [18]
H	0.500991	52.1
C	37.786156	171.3
N	54.522462	113.0
O	74.991202	59.6

In the case of the ionic compounds, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding X-ray molecular volumes according to the equations provided by Jenkins and Glasser. With the calculated lattice enthalpy (Table S5) the gas-phase enthalpy of formation (Table S4) was converted into the solid state (standard conditions) enthalpy of formation (Table S5). These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation 2.

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad \textbf{(2)}$$

(Δn being the change of moles of gaseous components)

Table S4. Calculated gas phase heat of formation, molecular volumes, lattice energies and lattice enthalpies of **1**-**4**.

	$\Delta_f H°(g,M)$ / kcal mol^{-1}	V_M / nm^3	U_L / kJ mol^{-1}	ΔH_L / kJ mol^{-1}
1	64.2			
2	166.0	0.317	447.9	451.3
3	212.5	0.354	435.6	439.0
4	11.2	0.258	1379.1	1386.6

The standard molar enthalpy of formation of solid **1** was calculated using $\Delta_f H(g)$ subtracting the enthalpy of sublimation estimated by applying Trouton´s rule. [19,20] ($\Delta H_{sub} = 188 \cdot T_m$). (**1**: T_m 125°C, ΔH_{sub} = 74.9 kJ mol^{-1}).

Table S5. Solid state energies of formation ($\Delta_f U°$)

	$\Delta_f H°(s)$ / kcal mol^{-1}	$\Delta_f H°(s)$ / kJ mol^{-1}	Δn	$\Delta_f U°(s)$ / kJ mol^{-1}	M / g mol^{-1}	$\Delta_f U°(s)$ / kJ kg^{-1}
1	46.3	193.8	9	216.1	278.1	777.1
2	58.2	243.9	14	278.6	352.2	790.8
3	107.7	450.8	15	488.0	392.3	1244.1
4	49.9	208.8	14	243.5	297.2	819.2

Notes: Δn being the change of moles of gaseous components when formed.

4. References

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