Supporting Information

5-(Dinitromethyl)-3-(trinitromethyl)-1,2,4-triazole and Its Derivatives: A New Application of Oxidative Nitration Towards *Gem*-trinitro-based Energetic Materials

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In Figures S1 and S2, ^{15}N NMR spectra of **6** and **8** are given. The assignments are based on the literature values of resonance peaks in similar compounds[1,2] and compared with calculated spectra [B3LYP/6-311+g(2d,p) with IEF-PCM continuum solvation models of the Gaussian 03 program].[3,4]

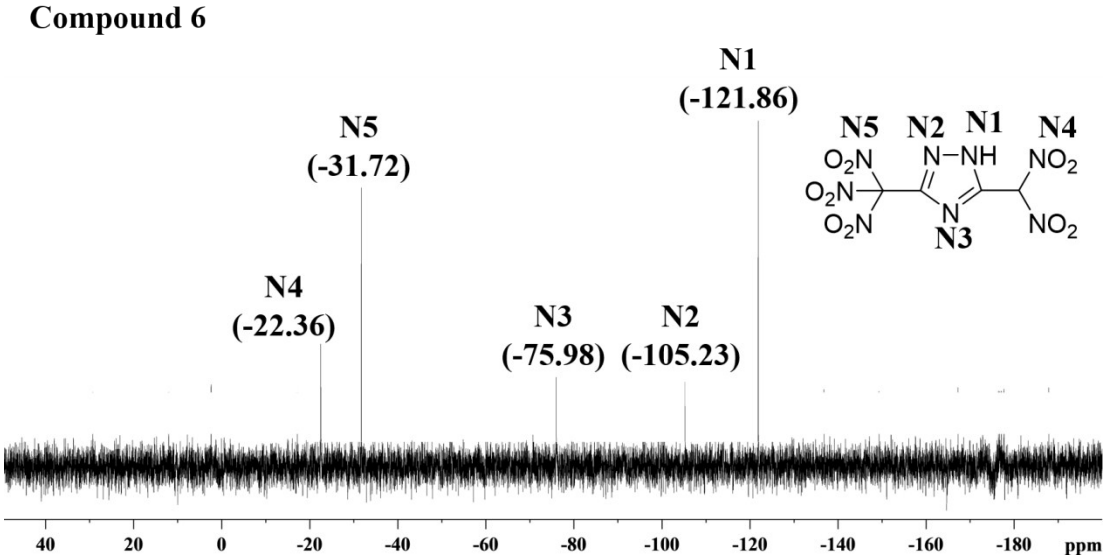


Figure S1. ^{15}N spectrum of **6** in DMSO-d_6.

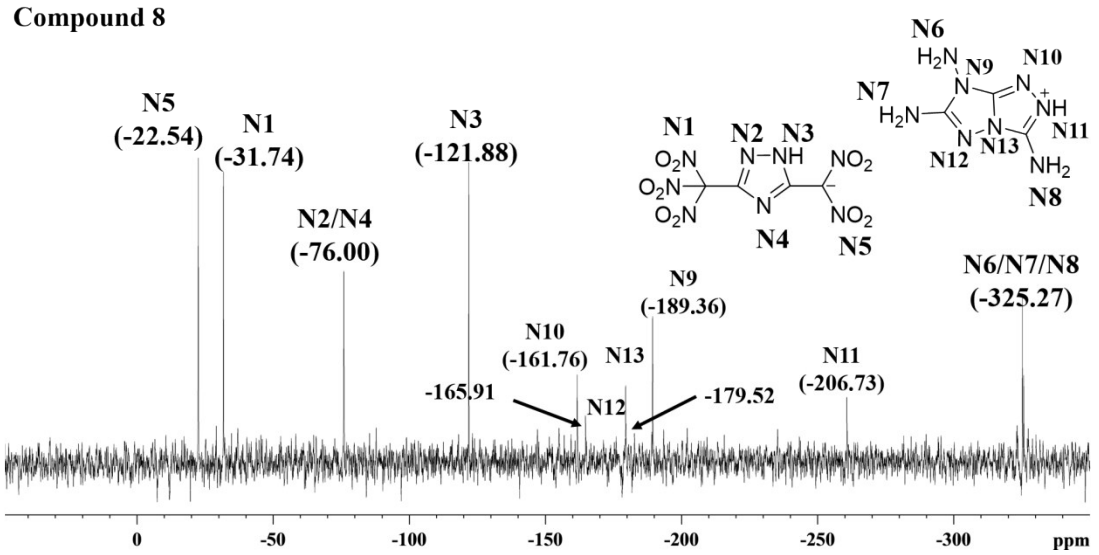


Figure S2. ^{15}N spectrum of **8** in DMSO-d_6.

X-ray Crystallography of 8

An orange crystal of dimensions 0.431 x 0.190 x 0.040 mm^3 was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation ($\lambda = 0.71073$). An Oxford Cobra low temperature device was used to maintain the crystals at a constant 150(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2014.3-0].[5] Data reduction was performed using *SAINT* [v7.68A][6] and *XPREP* [v2014/2].[7] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[8] The structure was solved and refined with the aid of the programs SHELXL-2014/7 within WingX.[9] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model (Table S1).

Table S1. Selected crystal parameters of **8**

Empirical formula	$C_7H_8N_{16}O_{10}$
	(8)
Formula weight	476.29
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.337(2)
b/Å	11.4124(19)
c/Å	11.8204(19)
α/°	90
β/°	100.961(6)
γ/°	90

Volume/Å^3	1633.8(5)
Z	4
ρ_{calc}/g cm^{-3}	1.936
μ/mm^{-1}	0.177
F(000)	968
CCDC number	1510982

Figures S3 to S6

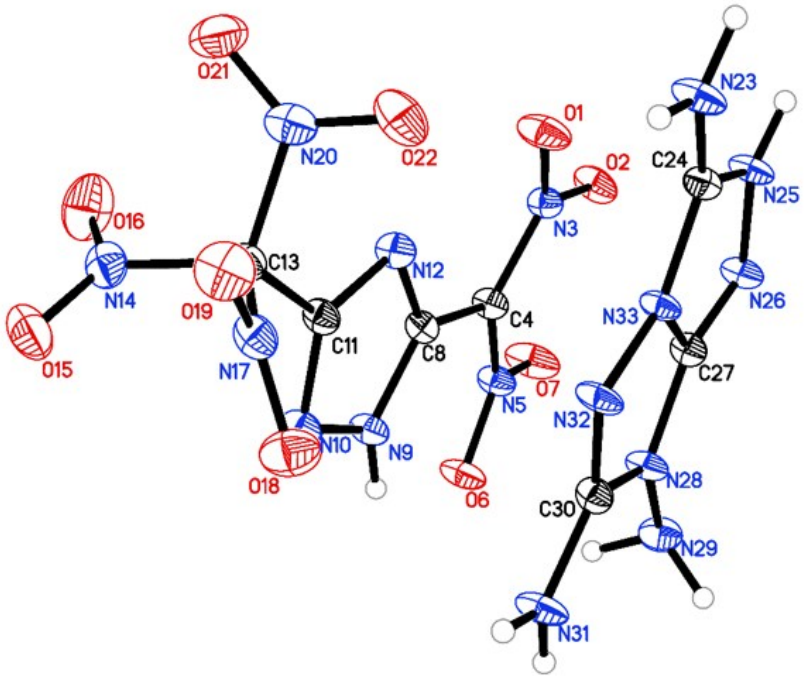


Figure S3. Single-crystal X-ray structures of **8** with numbering.

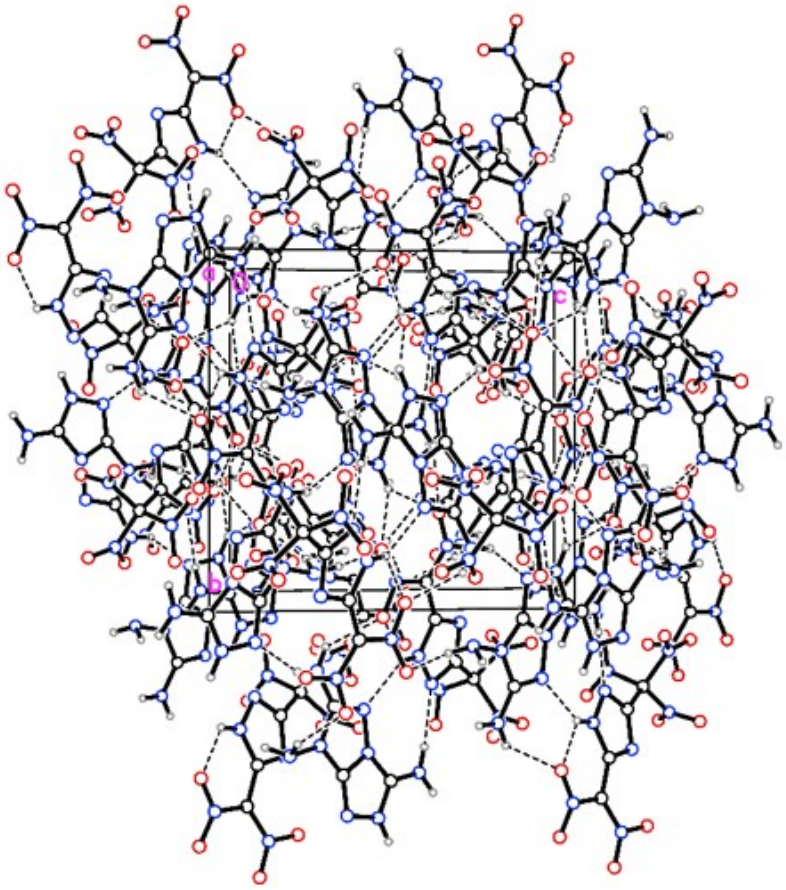


Figure S4. Unit cell view for **8** along *a* axis, hydrogen bonds are marked as dotted lines.

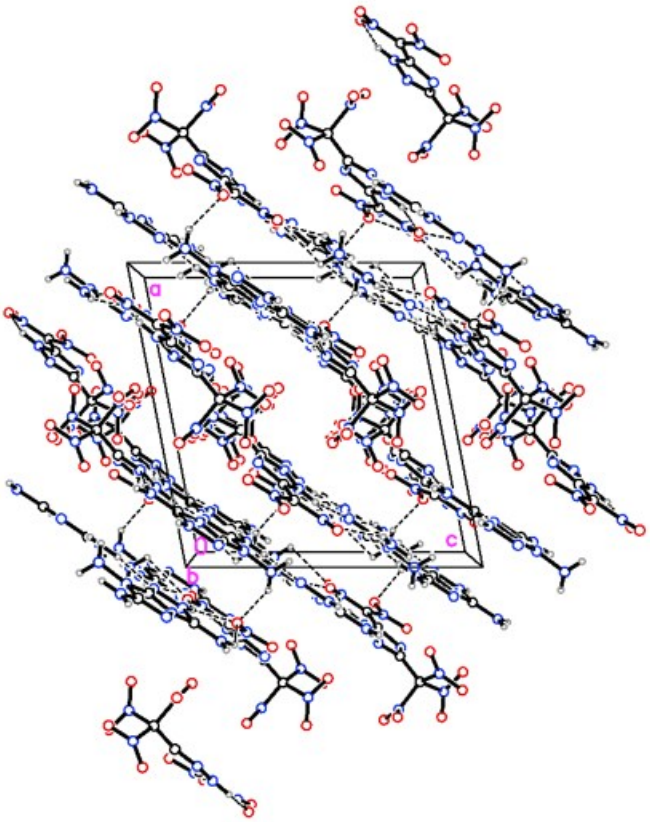


Figure S5. Unit cell view for **8** along *b* axis, hydrogen bonds are marked as dotted lines.

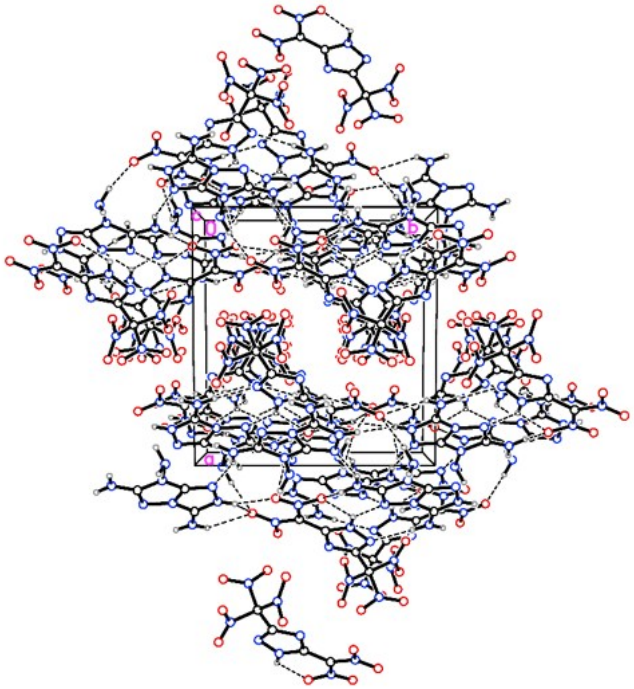


Figure S6. Unit cell view for **8** along *c* axis, hydrogen bonds are marked as dotted lines.

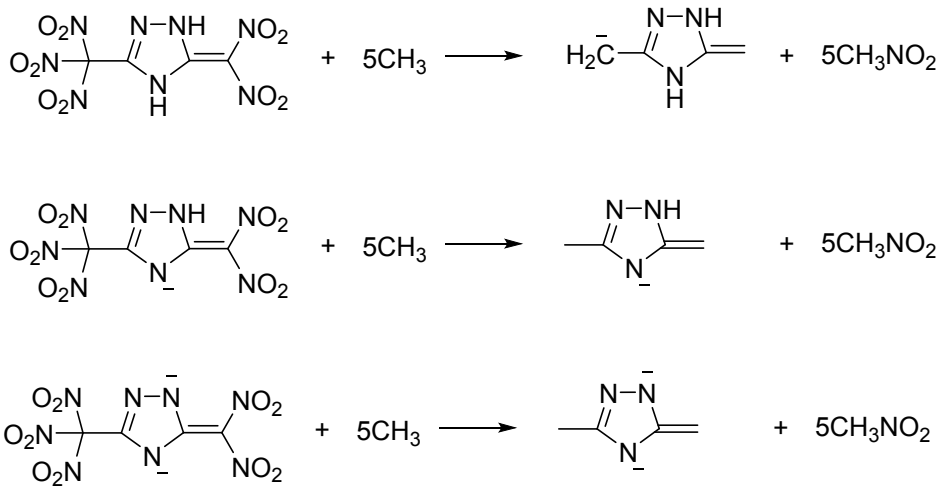
Table S2. Hydrogen bonds for **8** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(31)-H(31A)...O(6)#2	0.88	2.20	2.922(2)	139.6
N(31)-H(31B)...N(26)#1	0.88	2.22	3.032(2)	153.4
N(29)-H(29B)...O(2)#1	0.88(2)	2.19(2)	2.996(2)	151.3(18)
N(9)-H(9)...N(32)#3	0.88	2.16	2.909(2)	143.4
N(9)-H(9)...O(6)	0.88	1.95	2.515(2)	120.2
N(23)-H(23B)...O(21)#4	0.88	2.55	3.278(2)	140.7
N(23)-H(23B)...O(2)#5	0.88	2.30	2.981(2)	133.7
N(23)-H(23A)...N(10)#2	0.88	2.14	3.015(2)	174.3
N(25)-H(25)...O(7)#5	0.88	2.01	2.764(2)	143.3
N(25)-H(25)...O(2)#5	0.88	2.05	2.773(2)	138.7

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y-1/2,-z+1/2 #2 x,-y+1/2,z+1/2 #3 x,-y+1/2,z-1/2
#4 -x+1,-y+1,-z+1 #5 x,-y+3/2,z+1/2

Theoretical calculations

As mentioned in the manuscript, the heats of formation for 5-(dinitromethyl)-3-(trinitromethyl)-*1H*-1,2,4-triazole as well as its monoanion and dianion were determined using isodesmic reactions (Scheme S1). The calculations were carried out using Gaussian 03 (Revision D.01) suite of programs.[3] The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level,[10] and single energy points were calculated at the MP2/6-311++G** level.[11] The heats of formation for the ammonium, the hydrazinium, guanidinium, and triaminoguanidinium ions were obtained by an atomization approach using G2 ab initio method[12] (Table S3). The heat of formation for the 3,6,7-triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium ion was obtained from the literature.[2] The heats of formation of other compounds in Scheme S2 were obtained from the NIST WebBook.[13]



Scheme S1. Isodesmic reactions for calculating heats of formation for 5-(dinitromethyl)-3-(trinitromethyl)-*1H*-1,2,4-triazole as well as its monoanion and dianion.

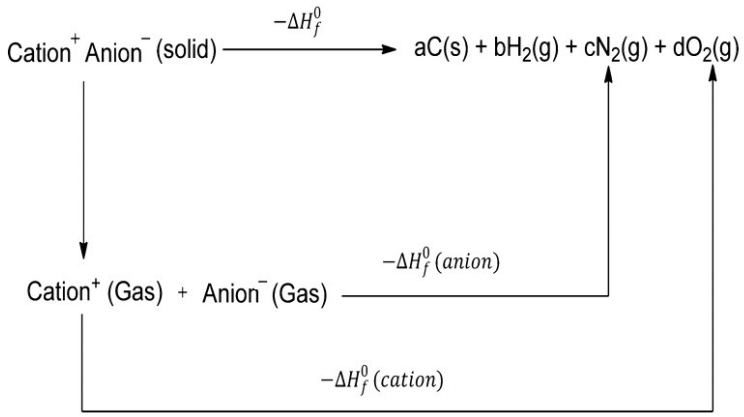
Table S3. Enthalpies of the gas-phase species.

M	ΔH_f° (kJ mol^{-1})
5-(dinitromethyl)-3-(trinitromethyl)-*1H*-1,2,4-triazole	122.1
5-(dinitromethylene)-3-(trinitromethyl)-1,5-dihydro-1,2,4-triazol-4-ide	-146.4
5-(dinitromethylene)-3-(trinitromethyl)-1,2,4-triazole-1,4-diide	-29.2
ammonium ion	626.4
hydrazinium ion	770.0
3,6,7-triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium	1090.6
guanidinium	575.9
triaminoguanidinium	883.6

The solid-state enthalpy of formation for a neutral compound can be estimated by subtracting the heat of sublimation from the gas-phase heat of formation. Based on the literature,[14] the heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$\Delta H_{sun}^{\circ} = 188/\text{J mol}^{-1}\text{K}^{-1} * T_{m(d)}$ (1)

For energetic salts, the solid-phase heat of formation is calculated on the basis of a Born-Haber energy cycle (Scheme S3).[15] The number is simplified by equation 2:



Scheme S3. Born−Haber Cycle for the formation of energetic salts.

ΔH_f° (salt, 298 K) = ΔH_f° (cation, 298K) + ΔH_f° (anion, 298K) – ΔH_L (2)

in which ΔH_L can be predicted by using the formula suggested by Jenkins, et al.[15](equation 3):

$\Delta H_L = U_{pot} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (3)

In this equation, n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively. The equation for lattice potential energy U_{pot}(equation 4) has the form:[15]

U_{POT} [kJ mol^{-1}] = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (4)

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for g and the coefficients γ (kJmol^{-1}cm) and δ (kJmol^{-1}) are assigned literature values.[15] By using the measured room temperature densities, all the new compounds are listed in Table S4.

Table S4. Densities, calculated lattice energies, and calculated heats of formation of **6** **12**.

	d[a] [g cm^{-3}]	$\Delta_f H_{Lat}$[b] [kJ mol^{-1}]	$\Delta_f H$[c] [kJ mol^{-1} /kJ g^{-1}]
6	1.97	-	56.3/0.17
7	1.87	458.8	21.3/0.06
8	1.90	424.1	520.2/1.09
9	1.79	1224.1	286.7/0.70
10	1.65	1225.7	-2.1/-0.005
11	1.71	1146.0	-23.4/-0.05
12	1.73	1069.8	668.2/1.25

[a] Density - gas pycnometer at room temperature. [b] Calculated lattice energy. [c] Calculated heat of formation.

It has recently been found that an electrostatic potential (ESP) that is dominated by a positive region usually relates to a higher sensitivity towards mechanical stimulus.[4] The positive regions of **6** was calculated at B3LYP/6-311+G(2d,p) optimized structure, and the 0.001 electron Bohr^{-3} isosurface of electron density is shown in Figure S7. The positive regions were found to concentrate at the dinitro-methyl group and extend into the triazole ring, while the negative regions were mainly in the trinitromethyl group. Therefore, the atypical imbalance between positive regions and negative ones of **6** can result in higher sensitivity, which agrees with its experimental data.

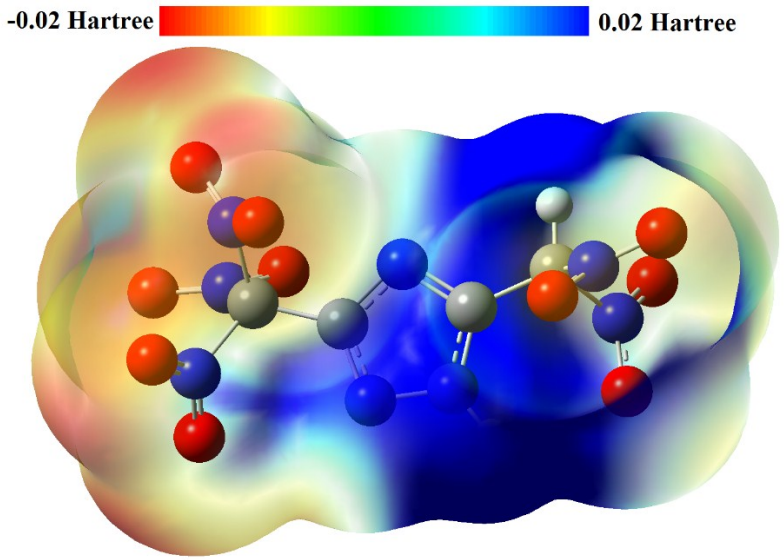


Figure S7. Electrostatic potential of **6** [B3LYP/6-311+G(2d,p), 0.001 electron/b^3 isosurface, energy values -0.02 to +0.02 Hartree].

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