Electronic Supplementary Information

Octanitropyrazolopyrazole: A Gem-trinitromethyl Based Green High-Density Energetic Oxidizer

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1. General Experimental

All the reactions were performed in an oven-dried round bottomed flask. Commercial grade solvents were distilled prior to use. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I₂ chamber. ¹H NMR, ¹³C NMR and ¹⁵N NMR spectra were recorded with a JEOL JNM-ECZ-600R/M1 600 MHz spectrometer at 600.17, 150.9, and 60.81 MHz, respectively. The chemical shift values (ppm) are expressed relative to the chemical shift of [D]solvent or to the external standard Liq.NH₃ without correction (¹⁵N). Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; br s = broad singlet; d = doublet; br d = broad doublet, t = triplet; br t = broad triplet; q = quartet; m = multiplet), coupling constants, *J*, in (Hz), and integration. Data for ¹³C NMR was reported in terms of chemical shift (ppm). IR spectra were recorded on a Bruker Tensor II FT-IR spectrometer and reported in cm⁻¹. Melting points and decomposition temperatures (DTA) were determined by DSC-TGA measurements. X-ray data was collected at 298K on a Bruker APEX-III CCD Mo-K α radiation (0.71073 Å).

Materials: Unless otherwise noted all the reagents and intermediates were obtained commercially and used without purification. All the starting compounds were purchased from Spectrochem, Avra Synthesis Pvt Ltd and used as received. 100% HNO₃ was prepared by the distillation of potassium nitrate and 98% sulfuric acid.

Caution! DNPP and ONPP are energetic materials and it tends to explode under certain conditions unpredictably. However, none of the compounds described herein has exploded or detonated in the course of this research. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided. Ignoring safety precautions can lead to serious injuries.

2. Experimental Procedures

Synthesis of 3,6-dinitropyrazolo-[4,3-c]-pyrazole (DNPP) 1

DNPP synthesized from multi step (seven steps) organic reactions from modified procedure of Shreeve *et.al.*^[1] The detailed synthetic route and reaction conditions are shown in Scheme S1.

 $T_d = 331 \text{ °C}$; ¹H NMR (500 MHz, [D₆] Acetone): $\delta 15.2$ (bs, 2H), ¹³C NMR (127 MHz, [D₆] Acetone): $\delta 139.6$, 133.1.



Scheme S1: Synthetic scheme of synthesis of 3,6-dinitropyrazolo-[4,3-c]-pyrazole (DNPP). Synthesis of 4,4-(3, 6-dinitropyrazol [4, 3-c] pyrazole-1,4-diyl)bis-(butane-2-one) 2



Compound 1 (2.0 g, 10.09 mmol) was dissolved in 20.0 mL of water and followed by slow addition of triethylamine (7.14 g, 70.63 mmol) and stirred for 10-15 minutes and later by addition of methylvinylketone (1.5 g, 22.19 mmol) stirred further 2 hours at room temperature. The precipitate in the solution was filtered and washed with water and dried to obtain compound (2) in 58% yield as a light yellow solid (2 g).

m.p. 137 °C; ¹H NMR (600.17 MHz, [D₆] DMSO): δ 4.73 (t, *J* = 6.0 Hz, 4H), 3.15 (t, *J* = 6.0 Hz, 4H), 2.08 (s, 6H), ¹³C NMR (150.91 MHz, [D₆] DMSO): δ 136.8, 131.1, 48.3, 42.5, 30.2; IR (Neat) v = 2992, 2967, 1713, 1548, 1390, 1369, 1302, 1167, 862 cm⁻¹; HRMS (ESI-TOF): calculated for C₁₂H₁₄N₆O₆Na [M+Na]⁺:361.0867, found: 361.0871

Synthesis of 3,6-dinitro-1,4-bis(trinitromethyl)-1,4-dihydropyrazolo[4,3-c]pyrazole (3)



Compound **2** (2.0 g, 5.9 mmol) was added slowly to a mixture of 100% nitric acid (13.0 mL) and 98% H_2SO_4 (12.5 mL) while maintaining temperature at 0-5°C and the reaction was stirred for 18 h at room temperature. Later, reaction mixture was poured into crushed ice, the precipitate was filtered off and washed with cold water and air dried to afford 3,6-dinitro-1,4-bis(trinitromethyl)-1,4-dihydropyrazolo[4,3-c]pyrazole (**3**) in 18% yield as a white solid (0.53 g).

 $T_d = 160 \text{ °C}; {}^{13}\text{C} \text{ NMR} (150 \text{ MHz}, [D_6] \text{ Acetone}): \delta 142.4, 137.8, 118.9; {}^{15}\text{N} \text{ NMR} ([D_6] \text{ Acetone}): 341.1(\text{C-NO}_2), 335.2[\text{C-}(\text{NO}_2)_3], 319.9(\text{N2}), 152.4(\text{N1}) \text{ ppm}; \text{ HRMS} (\text{ESI-TOF}): \text{ calculated for } C_6N_{11}O_{14} [\text{M-NO}_2]^- 449.9632, \text{ found: } 449.9626.$

Theoretical study: All the calculations were performed using the Gaussian 09 program suite.^[2] The geometric optimization of the structures and frequency analyses were carried out using B3LYP functional with $6-311G^{++}(d,p)$ basis set. The zero point energies (ZPEs) and the corresponding thermal corrections (H_T) to the enthalpy at 298.15 K were obtained from frequency calculations and were subsequently added to the electronic energies. The structure of ONPP was optimized and characterized to be true local energy minima on the potential energy. The method of isodesmic reactions has been employed to calculate HOF from total energies obtained from DFT calculations.

Isodesmic Reactions for the Prediction of Heat of Formation:



Scheme S2: Isodesmic reaction of compound 3.

3. X-ray crystallography

X-ray reflections for ONPP was collected on a Bruker APEX-III diffractometer equipped with a graphite monochromator and Mo-K α fine-focus sealed tube ($\lambda = 0.71073$ Å). Data reduction was performed using Bruker SAINT² software.^[3] Intensities for absorption were corrected using SADABS 2014/5.^[4] Structure solution and refinement were carried out using Bruker SHELX-TL.^[5]

CCDC- 2009554 (**3**), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Crystallographic data of compound 3

 Table SI. Crystallographic data for compound 3.

Compound	3
CCDC	2009554
Formula	C ₆ N ₁₂ O ₁₆
M _w	496.18
crystal system	Monoclinic
space group	P21/c
T [K]	298K
a [Å]	9.6672(6)
b [Å]	9.6302(5)
c [Å]	9.0564(6)
α [°]	90
β [°]	101.776(2)
γ [°]	90
Z	2
V [Å ³]	825.38(9)
D _{calc} [g cm ⁻³]	1.997
μ [mm ⁻¹]	0.2
total reflns	2047
unique reflns	2027
observed reflns	2027
$R_1[I > 2\sigma(I)]$	0.0381
wR_2 [all]	0.1077
GOF	1.045
	APEX-III
Diffractometer	CCD

Creation method SHELXL-97

Atomic coordinates

e e e e e e e e e e e e e e e e e e e	<u>л</u> у	L	
4e	0.48309(12)	0.59610(14)	0.12512(12)
4e	0.67180(12)	0.49345(12)	0.59303(12)
4e	0.71011(12)	0.51843(12)	0.45882(13)
4 <i>e</i>	0.66252(14)	0.65841(13)	0.82196(15)
4 <i>e</i>	0.70044(16)	0.24819(12)	0.71506(16)
4 <i>e</i>	0.59650(13)	0.56395(13)	0.20423(13)
4e	0.70825(13)	0.56067(16)	0.16561(13)
4e	0.87453(14)	0.60634(16)	0.93861(14)
4e	0.82170(15)	0.32365(15)	0.92854(15)
4e	0.96455(14)	0.59983(15)	0.66385(16)
4 <i>e</i>	0.76531(13)	0.33465(13)	0.79835(15)
4e	0.97934(14)	0.37404(16)	0.67107(17)
4e	0.77149(13)	0.59274(13)	0.84066(14)
4e	0.92388(13)	0.48453(15)	0.68279(15)
4e	0.59194(14)	0.52962(13)	0.35890(14)
4 <i>e</i>	0.52679(14)	0.48827(13)	0.57489(14)
4e	0.77726(14)	0.47772(14)	0.72411(15)
		$\begin{array}{rcrcr} 4e & 0.48309(12) \\ 4e & 0.67180(12) \\ 4e & 0.71011(12) \\ 4e & 0.66252(14) \\ 4e & 0.70044(16) \\ 4e & 0.59650(13) \\ 4e & 0.70825(13) \\ 4e & 0.87453(14) \\ 4e & 0.82170(15) \\ 4e & 0.96455(14) \\ 4e & 0.76531(13) \\ 4e & 0.97934(14) \\ 4e & 0.77149(13) \\ 4e & 0.59194(14) \\ 4e & 0.52679(14) \\ 4e & 0.77726(14) \\ \end{array}$	4e $0.48309(12)$ $0.59610(14)$ $4e$ $0.67180(12)$ $0.49345(12)$ $4e$ $0.71011(12)$ $0.51843(12)$ $4e$ $0.66252(14)$ $0.65841(13)$ $4e$ $0.70044(16)$ $0.24819(12)$ $4e$ $0.59650(13)$ $0.56395(13)$ $4e$ $0.70825(13)$ $0.56067(16)$ $4e$ $0.87453(14)$ $0.60634(16)$ $4e$ $0.82170(15)$ $0.32365(15)$ $4e$ $0.96455(14)$ $0.59983(15)$ $4e$ $0.77531(13)$ $0.33465(13)$ $4e$ $0.97934(14)$ $0.37404(16)$ $4e$ $0.92388(13)$ $0.48453(15)$ $4e$ $0.52679(14)$ $0.48827(13)$ $4e$ $0.77726(14)$ $0.47772(14)$

Anisotropic displacement parameters (in Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}		
01	0.0447(6)	0.0786(9)	0.0286(5)	0.0063(6)	0.0045(5)	0.0100(5)		
N1	0.0279(5)	0.0418(6)	0.0233(5)	-0.0026(4))	0.0046(4)	0.0029(4)	
N2	0.0329(6)	0.0388(6)	0.0267(6)	-0.0022(4))	0.0086(4)	0.0021(4)	
O7	0.0617(8)	0.0459(6)	0.0567(8)	0.0115(5)	0.0041(6)	-0.0109(5))	
05	0.0780(9)	0.0356(6)	0.0648(8)	-0.0069(6))	0.0122(7)	-0.0005(5)	
N5	0.0388(6)	0.0435(6)	0.0261(5)	-0.0027(5))	0.0098(5)	0.0015(5)	
O2	0.0442(7)	0.0921(10)	0.0386(6)	-0.0009(6))	0.0196(5)	0.0101(6)
08	0.0483(7)	0.0904(10)	0.0401(6)	-0.0141(7))	-0.0024(5)	-0.0175(6)
06	0.0647(8)	0.0727(9)	0.0452(7)	0.0033(6)	-0.0012(6))	0.0262(6)	
O10	0.0510(7)	0.0705(9)	0.0639(8)	-0.0223(6))	0.0171(6)	0.0035(6)	
N7	0.0393(6)	0.0406(6)	0.0405(7)	0.0047(5)	0.0089(5)	0.0100(5)		
09	0.0440(7)	0.0743(9)	0.0715(9)	0.0162(6)	0.0182(6)	0.0015(7)		
N9	0.0398(7)	0.0408(6)	0.0320(6)	-0.0061(5))	0.0050(5)	-0.0025(5)	
N8	0.0306(6)	0.0597(8)	0.0335(6)	-0.0042(6))	0.0046(5)	0.0023(5)	
C1	0.0325(6)	0.0346(6)	0.0246(6)	-0.0014(5))	0.0072(5)	0.0018(5)	
C3	0.0290(6)	0.0357(6)	0.0237(6)	-0.0019(5))	0.0044(5)	0.0018(5)	
C5	0.0285(6)	0.0363(6)	0.0268(6)	-0.0013(5))	0.0027(5)	0.0025(5)	

Selected geometric parameters (Å, °)

O1—N5	1.221(2) O6—N7	1.198(2)
N1—N2	1.362(2) O10—N8	1.202(2)
N1—C3	1.379(2) N7—C5	1.548(2)
N1C5	1.406(2) O9—N8	1.206(2)
N2—C1	1.309(2) N9—C5	1.539(2)
O7—N9	1.211(2) N8—C5	1.539(2)
O5—N7	1.209(2) C1—C3 ⁱ	1.410(2)
N5—O2	1.202(2) C3—C3 ⁱ	1.368(2)
N5-C1	1.449(2) C3—C1 ⁱ	1.410(2)
O8—N9	1.198(2)	
N2—N1—C3	110.79(11)	O10—N8—C5 114.73(13)
N2—N1—C5	119.33(11)	O9—N8—C5 115.58(13)
C3—N1—C5	129.87(12)	N2—C1—C3 ^{i} 111.55(12)
C1—N2—N1	105.87(11)	N2—C1—N5 119.52(11)
O2—N5—O1	126.07(14)	$C3^{i}$ — $C1$ — $N5$ 128.85(12)
O2—N5—C1	118.81(12)	$C3^{i}$ — $C3$ — $N1$ 106.39(11)
O1—N5—C1	115.11(11)	$C3^{i}$ — $C3$ — $C1^{i}$ 105.39(11)
O6—N7—O5	128.80(15)	N1—C3—C1 ^{i} 148.22(13)
O6—N7—C5	116.54(13)	N1—C5—N9 112.33(11)
O5—N7—C5	114.65(12)	N1—C5—N8 109.58(11)
08—N9—07	127.93(14)	N9—C5—N8 107.47(11)
O8—N9—C5	116.45(12)	N1—C5—N7 110.92(11)
O7—N9—C5	115.62(12)	N9—C5—N7 109.05(10)
O10—N8—O9	129.67(16)	N8—C5—N7 107.31(11)

Symmetry codes: (i) 1-x, 1-y, 1-z.

5. Hirshfeld Surface Graphs

The Hirshfeld surface image (Fig. 4, in manuscript) in which, the red spots signify the high contact populations, while blue and white spots are for low contact populations. This suggests that the negative (red) or positive value (blue and white) of d_{norm} depends on the intermolecular contacts being shorter (red) or longer (blue and white) than the van der Waals separations. For each point on the Hirshfeld surface, the normalized contact distance (d_{norm}) was determined by the equation as shown below.

$$[d_{norm} = (d_i - d_i^{vdW})/r_i^{vdW} + (d_e - d_e^{vdW})/r_e^{vdW}]$$

In which d_i is measured from the surface to the nearest atom interior to the surface interior, while d_e is measured from the surface to the nearest atom exterior to the surface interior, where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms.^[6] Hirshfeld surface graphs and two- dimensional fingerprint plots of ONPP were analyzed using Crystalexplorer17.5 software. Individual atomic contacts percentage contributions of 2D-finger print plots were shown below.



Figure S1: All atomic interactions two-dimensional fingerprint plot (percentage 100%)



Figure S2: O...O atomic interactions two-dimensional fingerprint plot (percentage 75.3%)



Figure S3: N...O atomic interactions two-dimensional fingerprint plot (percentage 8.5%)



Figure S4: O...N atomic interactions two-dimensional fingerprint plot (percentage 9.7%)



Figure S5: O...C atomic interactions two-dimensional fingerprint plot (percentage 3.4%)



Figure S6: C...O atomic interactions two-dimensional fingerprint plot (percentage 3.1%)

6. Characterization data



Figure S7: ¹H NMR spectrum of compound 2 in DMSO-d₆.



Figure S8: ¹³C NMR spectrum of compound 2 in DMSO-d₆.



Figure S9: HRMS data of compound 2.



Figure S10: ¹³C NMR spectrum of compound 3 in acetone-d₆.



Figure S11: ¹⁵N NMR spectrum of compound **3** in acetone-d₆ (Liq. NH₃ as reference)



Figure S12: ¹⁵N NMR spectrum of compound **3** in acetone-d₆ (CH₃NO₂ as reference)



Figure S13: HRMS data of compound 3.









Figure S15: TG-DTA data of compound 3 (10 °C min⁻¹)

7. Explo 5 Calculations

Software: Explo 5 ver6.03^[7]

- a) Specific Impulse calculation were performed under isobaric combustion conditions at a chamber pressure of 7MPa bar versus ambient pressure with equilibrium expansion conditions at the nozzle throat. Calculations were also performed with two different formulations and the results are shown in Table SII.
- b) Based on the crystal density and HOF, the detonation velocity (*D*) and detonation pressure (*P*) for the ONPP is calculated.
- c) Oxygen balance based on CO₂. For a compound with the molecular formula of $C_aH_bN_cO_d$, $\Omega CO_2[\%] = 1600 [(d-2a-b/2)/MW]$, where MW is the molecular weight.

ONPP Al (%) (%)		Binder	Specific Impulse (s)	Combustion temperature (K)	nozzle exit velocity (m s ⁻¹)	
60	20	HTPB* (20%)	248	2934	2433	
75	0	HTPB (25%)	232	2327	2274	
60	20	GAP** (20%)	265	3953	2600	
75	0	GAP (25%)	273	3654	2677	

Table SII: Theoretical specific impulse calculated for different propellant formulations.

*Hydroxyl terminated polybutadiene

** Glycidyl azide polymer

d) Specific Impulse calculations were performed under isobaric combustion conditions at a chamber pressure of 7MPa bar versus ambient pressure with equilibrium expansion conditions at the nozzle throat. Calculations were also performed with composite formulation of 60% oxidizer, 20% aluminuum and 20% polymeric binder and the results are shown in Table SII.

Table SIII: Theoretical specific impulse calculated for different propellant formulations with different oxidizers (60% oxidizer, 20% aluminuum and 20% polymeric binder).

	ONPP (3)	AP	ADN	Ι	II	III	IV	V	VI
Formula	C ₆ N ₁₂ O ₁₆	NH ₄ ClO ₄	NH ₄ N(NO ₂) ₂	C ₂ HN ₅ O ₉	$C_4N_8O_{13}$	C ₄ HN ₉ O ₁₂	C ₆ N ₁₀ O ₁₄	C ₈ N ₁₄ O ₂₀	C ₇ N ₁₄ O ₁₇
I _{sp} (s)	248	256	255	254	244	238	234	253	222
(HTPB)									
$I_{sp}(s)$	265	266	276	270	270	260	249	261	243
(GAP)									

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