# Supporting Information

# **Revisiting the Sensitive Nature of H-FOX: Interplay of Nitro and Hydrazine Functionalities to Construct Insensitive Energetic Material**

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#### **Experimental Section:**

**Caution!** The compounds in this work are energetic materials that could potentially explode under certain conditions (e.g., impact, friction, or electric discharge). Appropriate safety precautions, such as the use of shields in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves) should be always taken when handling these materials.

**General.** All reagents were purchased from AKSci or TCI or Merck in analytical grade and were used as supplied. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were recorded JEOL DELTA (ECS) 500 (<sup>1</sup>H, 500 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSOd6) nuclear magnetic resonance spectrometer. Chemical shifts for <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra are given with respect to external (CH<sub>3</sub>)<sub>4</sub>Si (<sup>1</sup>H and <sup>13</sup>C). [D6] DMSO was used as a locking solvent unless otherwise stated. IR spectra were recorded using Zn-Se pellets with a ECO-ATR spectrometer (Bruker Alpha II). A single crystal of suitable dimensions was used for data collection. Diffraction intensities were collected on a Bruker APEX-II CCD diffractometer, with graphite-monochromated Mo Ka (0.71073 Å) radiation at 100(2) K. Density was determined at room temperature by employing Anton Par Ultra5000 gas pycnometer. Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and a heating rate of 5 °C min<sup>-1</sup> on a thermogravimetric differential scanning calorimeter (TGA-DSC (SDT-650)). HRMS was recorded on Agilent mass spectrometer. Impact and friction sensitivity measurements were made using a standard BAM fall hammer and a BAM friction tester.





NMR (126 MHz, DMSO-d6)  $\delta$  159.3, 96.7. IR (ATR ZnSe): 3304, 3181, 3146, 1644, 1575, 1536, 1438, 1341, 1217, 1113, 967, 743, 655 cm<sup>-1</sup>. Elemental Analysis Calcd for C<sub>2</sub>H<sub>7</sub>N<sub>5</sub>O<sub>2</sub>: C, 18.05; H, 5.30; N, 52.61. Found: C, 18.22; H, 5.02; N, 52.49.



Figure S1: Molecular Structure of 2.



Figure S2. a,b,c) Packing diagrams of compound 2 along *a*, *b* and *c*-axis respectively.

CCDC No.	2406898
Empirical formula	$C_2H_7N_5O_2$
Formula weight	133.13

Table S1: Crystallographic data for 2 at 100K.

Temperature/K	100.0
Crystal system	orthorhombic
Space group	Fdd2
a/Å	10.8075(5)
b/Å	27.3498(15)
c/Å	7.4467(5)
α/°	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å3	2201.1(2)
Z	16
pcalcg/cm3	1.607
µ/mm-1	0.138
F(000)	1120.0
Crystal size/mm3	$0.13 \times 0.12 \times 0.11$
Radiation	MoKa ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/°	5.958 to 56.656
Index ranges	$-14 \le h \le 14, -36 \le k \le 33, -9 \le l \le 9$
Reflections collected	8453
Independent reflections	1367 [Rint = 0.0633, Rsigma = 0.0350]
Data/restraints/parameters	1367/1/98
Goodness-of-fit on F2	1.070
Final R indexes [I>= $2\sigma$ (I)]	R1 = 0.0313, wR2 = 0.0839
Final R indexes [all data]	R1 = 0.0316, wR2 = 0.0843
Largest diff. peak/hole / e Å-3	0.19/-0.20
Flack parameter	-0.2(9)



Figure S3: <sup>1</sup>H NMR Spectrum of Compound 2 (recorded in DMSO-d6; 500 MHz).



Figure S4: <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of Compound 2 (recorded in DMSO-d6; 126 MHz).



Figure S5: IR Spectrum of Compound 2.



Figure S6. DSC Plot of Compound 2 at Heating rate 5 °C min<sup>-1</sup>.

#### Heat of Combustion:

The heat of combustion is an essential metric for assessing the energetic properties of explosives. The constant-volume combustion energy of the compounds was measured using high-precision oxygen bomb calorimetry (Parr 6200 calorimeter). About 300 mg of the compound was combined with benzoic acid at a 1:3 mass ratio, sealed in a combustion bomb and ignited in a pure oxygen environment. The internal energy of combustion,  $\Delta cU$ , for compound **2** (C<sub>2</sub>H<sub>7</sub>N<sub>5</sub>O<sub>2</sub>, MW = 133.11 g/mol) was determined to be -1850.87 kJ mol<sup>-1</sup> (-13.90 kJ g<sup>-1</sup>). The enthalpy of combustion, ( $\Delta cH^{\circ}$ ) of compound **2** was calculated to be -1846.53 kJ mol<sup>-1</sup> (-13.87 kJ g<sup>-1</sup>), using the relationship  $\Delta cH = \Delta cU + \Delta nRT$ , where  $\Delta n$  represents the difference in molar quantities of gaseous products and reactants, R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>, T = 298 K.

The combustion equation of the compound 2 is as follows

$$C_2H_7N_5O_2 + 2.75O_2 \rightarrow 2CO_2(g) + 3.5H_2O(l) + 2.5N_2(g)$$
 (1)

The standard enthalpy of formation  $\Delta_{f}H^{\circ}$  of compound **2** was calculated to be 59.11 kJ mol<sup>-1</sup> (0.44 kJ g<sup>-1</sup>), using Hess's Law as shown in equation (2). This calculation was based on the known enthalpies of formation for H<sub>2</sub>O (g) at -285.83 kJ/mol and CO<sub>2</sub> (g) at -393.51 kJ mol<sup>-1</sup>.

$$\Delta_{f}H^{0}[2, s] = 2\Delta_{f}H^{0}[CO_{2}, g] + 3.5\Delta_{f}H^{0}[H_{2}O, l] - \Delta_{c}H^{0}[2, s] \quad (2)$$

#### **Propellant formulations for compound 2:**

To gain more insight, we formulated various composite mixtures based on the recently described Klapötke and Suceska method<sup>2</sup> for calculating specific impulse. These formulations contained 10% glycidyl azide polymer (GAP), 15% nitro-glycerine (NG), 18% aluminium, and a variable proportion (57%) of the oxidizer ammonium perchlorate (AP), along with an energetic filler to achieve an oxygen balance of -33% relative to CO<sub>2</sub>. This composition aligns with modern propellant formulations (70% AP, 16% Al, 12% HTPB, and 2% epoxy) commonly used in practical applications.

The performance of compound **2** was evaluated to determine its potential as a future component of solid rocket propellants. Using the EXPLO-5 (v7.01.01) software, the calculated specific impulse for compound **2** was 272 s, as presented in **Table S2**. This value surpasses that of

FOX-7 and a modern propellant formulation (70% AP, 16% Al, 12% HTPB, and 2% epoxy), which has a calculated specific impulse of 264  $s^2$  and is comparable to benchmark explosives such as RDX and HMX. These findings suggest that compound **2** holds significant promise as a high-performance solid fuel additive for propellants.

**Table S2.** EXPLO5 calculation results using Klapötke and Suceska method for various highenergy composite (HEC) propellant formulations for compound **2** compared with RDX, HMX and FOX-7.

High Energy Explosive Component	RDX	НМХ	FOX-7	2	Pure 2	Pure MMH
Formulation	10% GAP, 15% NG, 18% Al, 45% <b>RDX</b> , 12% AP	10% GAP, 15% NG, 18% Al, 45% <b>HMX</b> , 12% AP	10% GAP, 15% NG, 18% Al, 45% FOX-7, 12% AP	10% GAP, 15% NG, 18% Al, 25% <b>2</b> , 32% AP	100% 2	100% MMH
Specific impulse [s]	275	274	267	272	220	211
Isochoric combustion temperature [K]	3814.6	3806.9	2678.9	3590.6	1624.5	1329.2
Heat of combustion [kJ/kg]	-6110	-6096	-4725	-5921	-2509	-2778
Exhaust velocity [m/s]	2694	2690	2617	2667	2155	2068

#### **BDE, HOMO-LUMO and ESP analysis**

The bond dissociation energies (BDE) of C-NO2 bond in FOX-7, H-FOX and compound **2** were calculated using Gaussian 09 program<sup>3</sup> and detailed data given in **Table S3**. The bond lengths of C-NO<sub>2</sub> bond in FOX-7, H-FOX and compound **2** are 1.4293, 1.4292, and 1.3889 Å, respectively, while their corresponding BDEs are 306.3, 305.1, 378.4 kJ/mol respectively. Compound **2** possess shorter C-NO<sub>2</sub> bond and higher BDE revealing higher bond strength compared to FOX-7 and H-FOX. The energy levels of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) were calculated using M06-2X/def2-TZVPP level of theory. Over the years, a considerable amount of research has focused

on determining the correlation between sensitivity and the HOMO-LUMO energy gap.<sup>38,39</sup> The HOMO-LUMO energy gaps are frequently used to assess the sensitivity of various types of energetic materials, as energy gap value indicates the ease or difficulty of electron excitation, where smaller energy gap indicates greater sensitiveness.<sup>4</sup> The HOMOs and LUMOs of the FOX-7, H-FOX, and compound **2** are presented in **Figure S7**, which reveals that the HOMO of each molecule is localized on all the atoms of these compounds. However, the LUMOs in FOX-7 and H-FOX concentrated on the geminal dinitro groups and hydrazine group, respectively, while covers entire framework in compound **2**. The predicted HOMO-LUMO energy gaps for FOX-7, H-FOX and compound **2** are 10.86, 7.52, and 9.51 eV, respectively. The higher energy gap values in FOX-7 and compound **2** indicate their high stability and consistent with the experimental data.



Figure S7. The HOMO and LUMO orbital plots for FOX-7, H-FOX and compound 2.



**Figure S8**. ESP plots for FOX-7, H-FOX and compound **2**. The minimum and maximum of ESP regions are marked as blue and red areas, respectively.

The sensitivity of energetic materials is closely related to its molecular surface electrostatic potential (ESP).<sup>5,6</sup> Consequently, the ESP values of the newly synthesized compound **2** along with FOX-7 and H-FOX were computed and the related ESP plots and distribution of positive and negative ESP are depicted in **Figure S8**. In all the compounds, positive ESP appeared near the amine and hydrazine functional groups, while negative ESP found on nitro groups. Presence of two geminal nitro groups in FOX-7 and H-FOX create more imbalance in ESP distribution compared to compound **2** and possess more positive ESP region due to their higher electronegativities. The computed values for balance parameter (*v*) between variabilities and strengths of the positive and negative surface potentials of FOX-7, H-FOX and compound **2** are 52.03, 54.38, and 50.38 %, respectively while their corresponding polar surface area region are 80.48, 81.88, and 78.56 %. The less positive ESP region helps to strengthen chemical bonds and thereby improving the molecular stability of energetic compounds.

## **Computational details**

Computations were carried out using the Gaussian 09 program suite.<sup>3</sup> The structure optimizations are performed with M06-2X/def2-TZVPP level of theory and characterized to be true local energy minima on the potential energy surface and no imaginary frequencies were

found. In energetic materials, generally, C–NO<sub>2</sub>, N–NO<sub>2</sub> and O–NO<sub>2</sub> are the weakest bond which easily ruptures on applying external stimuli. In previous reports, evidence indicates that a key initiation step is the rupture of a specific type of bond, a "trigger linkage". Hence, we have calculated the bond dissociation energy (BDE) of longest C–NO<sub>2</sub> bond using following equation (1) at M06-2X/def2-TZVPP level,

$$BDE = [E_{R1} + E_{R2}] - E_{R1-R2}$$
(1)

where  $E_{R1-R2}$ ,  $E_{R1}$ , and  $E_{R2}$  are the total energies with zero-point energy correction of the precursor and the corresponding radicals produced by bond dissociation (see Table S3).

**Table S3.** Calculated total energies ( $E_0$ ) of R–NO<sub>2</sub>, R, and NO<sub>2</sub> at the M06-2X/def2-TZVPP level, used in the prediction of bond dissociation energies.

Compound	E <sub>0</sub> (a.u.)		
	R-NO <sub>2</sub>	R	NO <sub>2</sub>
FOX-7	-598.233189	-393.05209	-205.064437
H-FOX	-653.537123	-448.356472	-205.064437
2	-504.335522	-299.126933	-205.064437

**Table S4**. Optimized Cartesian coordinates for FOX-7 at M06-2X/def2-TZVPP level of theory.

6	1.362323000	0.000238000	-0.000139000
6	-0.048825000	0.000034000	-0.000225000
7	-0.803568000	1.209890000	0.097484000
8	-0.255969000	2.257230000	-0.253957000
8	-1.915903000	1.172502000	0.554134000
7	-0.803083000	-1.210163000	-0.097587000
8	-1.915544000	-1.173291000	-0.553970000
8	-0.254976000	-2.257163000	0.254015000

7	2.064019000	-1.130799000	0.126662000
7	2.063790000	1.131458000	-0.126604000
1	3.048998000	-1.127725000	-0.065692000
1	1.556416000	-1.994020000	0.255969000
1	3.048682000	1.128610000	0.066207000
1	1.555951000	1.994573000	-0.255763000

 Table S5. Optimized Cartesian coordinates for H-FOX at M06-2X/def2-TZVPP level of theory.

6	0.940818000	-0.418563000	0.012463000
6	-0.413412000	0.008547000	0.006287000
7	-0.776389000	1.381113000	0.090240000
8	0.081765000	2.221694000	-0.208980000
8	-1.871062000	1.686537000	0.485225000
7	-1.485593000	-0.931702000	-0.088111000
8	-2.540026000	-0.580084000	-0.549488000
8	-1.264614000	-2.090006000	0.272573000
7	1.282199000	-1.698409000	0.088751000
7	1.945155000	0.471689000	-0.067274000
1	2.266301000	-1.909182000	0.084977000
1	0.555847000	-2.379778000	0.244785000
1	1.691422000	1.442232000	-0.206062000
7	3.261983000	0.018534000	-0.035361000
1	3.732764000	0.273892000	-0.894718000
1	3.749251000	0.439224000	0.746173000

**Table S6**. Optimized Cartesian coordinates for compound 2 at M06-2X/def2-TZVPP level of theory.

6	0.553141000	-0.054752000	-0.007760000
6	-0.650178000	-0.734454000	-0.006289000
7	-1.882252000	-0.093311000	0.000165000
8	-1.943209000	1.150651000	0.005212000
8	-2.887776000	-0.784328000	0.000950000
7	1.730795000	-0.723178000	-0.021124000
7	0.649825000	1.291684000	-0.001613000
1	-0.230757000	1.795334000	0.000297000
7	1.900312000	1.907091000	0.005946000
1	2.004178000	2.485148000	-0.819067000
1	1.988795000	2.493671000	0.826567000
1	-0.689424000	-1.804441000	-0.012130000
7	1.762777000	-2.109376000	0.011282000
1	2.250156000	-2.471236000	-0.797024000
1	2.207100000	-2.438271000	0.858169000
1	2.569861000	-0.165929000	0.015593000

 Table S7. Optimized Cartesian coordinates for FOX-7 at G4 level of theory.

6	1.362323000	0.000238000	-0.000139000
6	-0.048825000	0.000034000	-0.000225000
7	-0.803568000	1.209890000	0.097484000
8	-0.255969000	2.257230000	-0.253957000
8	-1.915903000	1.172502000	0.554134000
7	-0.803083000	-1.210163000	-0.097587000

8	-1.915544000	-1.173291000	-0.553970000
8	-0.254976000	-2.257163000	0.254015000
7	2.064019000	-1.130799000	0.126662000
7	2.063790000	1.131458000	-0.126604000
1	3.048998000	-1.127725000	-0.065692000
1	1.556416000	-1.994020000	0.255969000
1	3.048682000	1.128610000	0.066207000
1	1.555951000	1.994573000	-0.255763000

 Table S8. Optimized Cartesian coordinates for H-FOX at G4 level of theory.

6	0.941845000	-0.442393000	-0.024756000
6	-0.409099000	0.007069000	-0.007646000
7	-0.736015000	1.398432000	0.090415000
8	0.137481000	2.230743000	-0.239318000
8	-1.822787000	1.731007000	0.526653000
7	-1.506459000	-0.910419000	-0.087682000
8	-2.585458000	-0.522410000	-0.496576000
8	-1.298385000	-2.102588000	0.228382000
7	1.244403000	-1.737584000	0.144158000
7	1.955972000	0.414745000	-0.210355000
1	2.162963000	-2.070995000	-0.093081000
1	0.456893000	-2.368947000	0.262456000
1	1.701103000	1.392898000	-0.315461000
7	3.265189000	0.017887000	0.087059000
1	3.818947000	0.045117000	-0.745173000

1 3.655184000 0.638415000 0.767390000

Table S9. Optimized Cartesian coordinates for compound 2 at G4 level of theory.

6	0.611685000	-0.056214000	-0.104652000
6	-0.612753000	-0.779082000	-0.179283000
7	-1.879313000	-0.128347000	-0.021954000
8	-1.933042000	1.105709000	-0.218624000
8	-2.846659000	-0.774904000	0.336079000
7	1.786925000	-0.691711000	0.007363000
7	0.629826000	1.283829000	-0.143938000
1	-0.275232000	1.741523000	-0.208560000
7	1.784018000	1.975310000	0.242964000
1	2.134421000	2.499573000	-0.533158000
1	1.563574000	2.598128000	0.993632000
1	-0.586279000	-1.833858000	-0.357178000
7	1.732231000	-2.090609000	0.017042000
1	2.224597000	-2.448943000	-0.776162000
1	2.155054000	-2.434937000	0.855290000
1	2.652070000	-0.195444000	0.079773000

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