Electronic Supplementary Information

N-Functionalized nitroxy/azido fused-ring azoles as high-performance energetic materials

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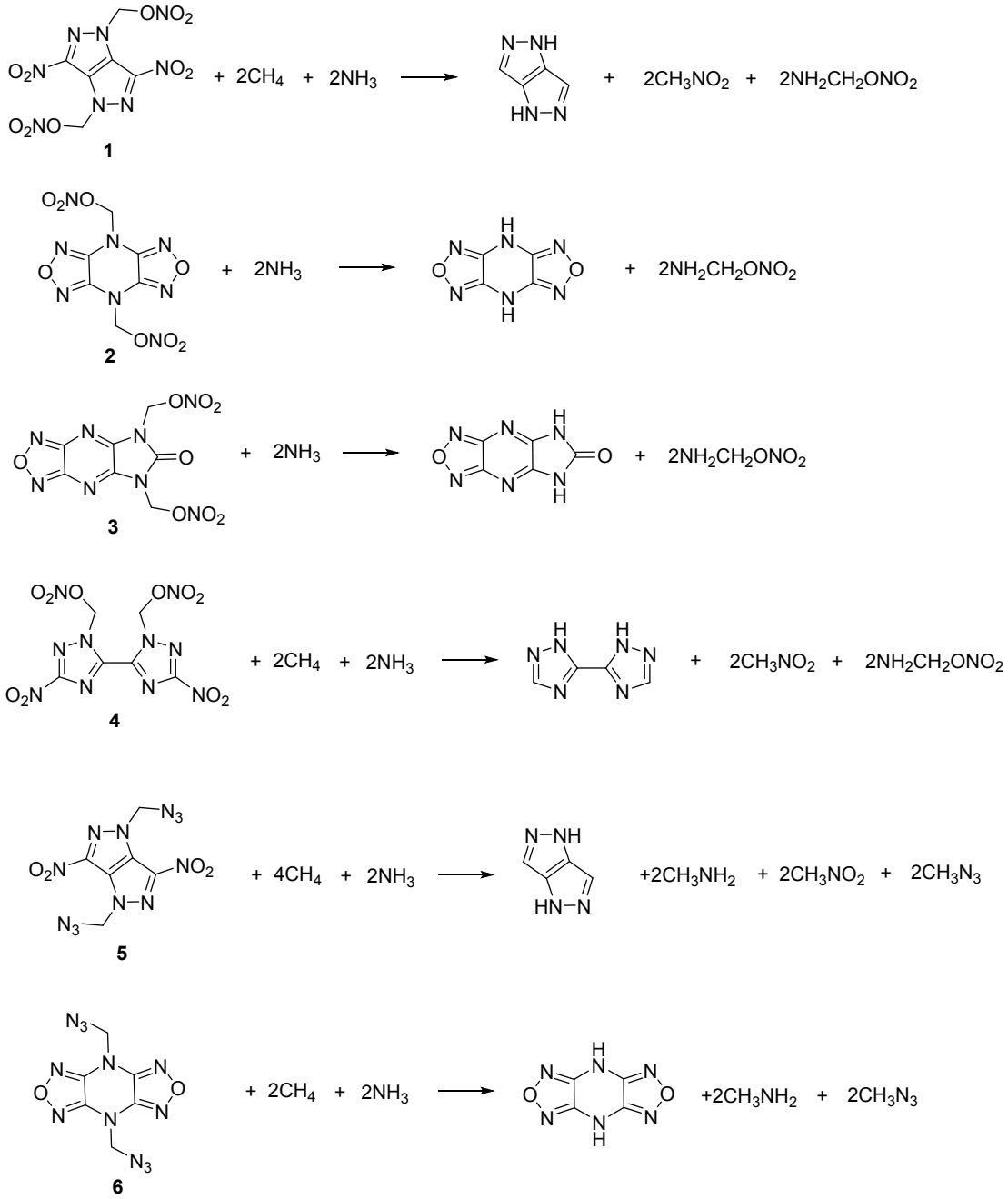
Theoretical calculations

The heats of formation for **1** – **6** were determined using the isodesmic reaction approach (**Scheme S1**). The calculations were carried out using Gaussian 03 (Revision D.01) suite of programs.[1] The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level,[2] and single energy points were calculated at the MP2/6-311++G** level.[3] The heats of formation for 1,4-dihydropyrazolo[4,3-c]pyrazole, 4H,8H-bis([1,2,5]oxadiazolo)[3,4-b:3',4'-e]pyrazine, 5H-imidazo[4,5-b][1,2,5]oxadiazolo[3,4-e]pyrazin-6(7H)-one, 2H,2'H-3,3'-bi(1,2,4-triazole), and aminomethyl nitrate were obtained by atomization approach using G2 ab initio method (**Table S1**).[4] The heats of formation for other build block molecules were obtained from the NIST WebBook.[5] Thus, the gas phase enthalpy of the species being investigated can be readily extracted. The enthalpy of sublimation was calculated by using Trouton's rule.[6] Solid state heats of formation of the resulting compounds were calculated with equation (1) in which $T_{m/d}$ is the melting temperature or decomposition temperature.

$$\Delta H_{f(solid)} = \Delta H_{f(g)} - \Delta H_{sub} = \Delta H_{f(g)} - 188[\text{J mol}^{-1}\ \text{K}^{-1}] * T_{m/d} \quad (1)$$



Scheme S1. Isodesmic reactions for calculating heats of formation for **1-6**.

Table S1. Enthalpies of the gas-phase building block molecules.

M	ΔH_f° (kJ mol^{-1})
1,4-dihydropyrazolo[4,3-c]pyrazole	422.17
4H,8H-bis([1,2,5]oxadiazolo)[3,4-b:3',4'-e]pyrazine	518.47
5H-imidazo[4,5-b][1,2,5]oxadiazolo[3,4-e]pyrazin-6(7H)-one	241.10
2H,2'H-3,3'-bi(1,2,4-triazole)	381.40

aminomethyl nitrate	-119.27
methane	-74.60
ammonia	-45.90
nitromethane	-81.00
methanamine	-23.50
azidomethane	296.54

Crystal sructure analysis

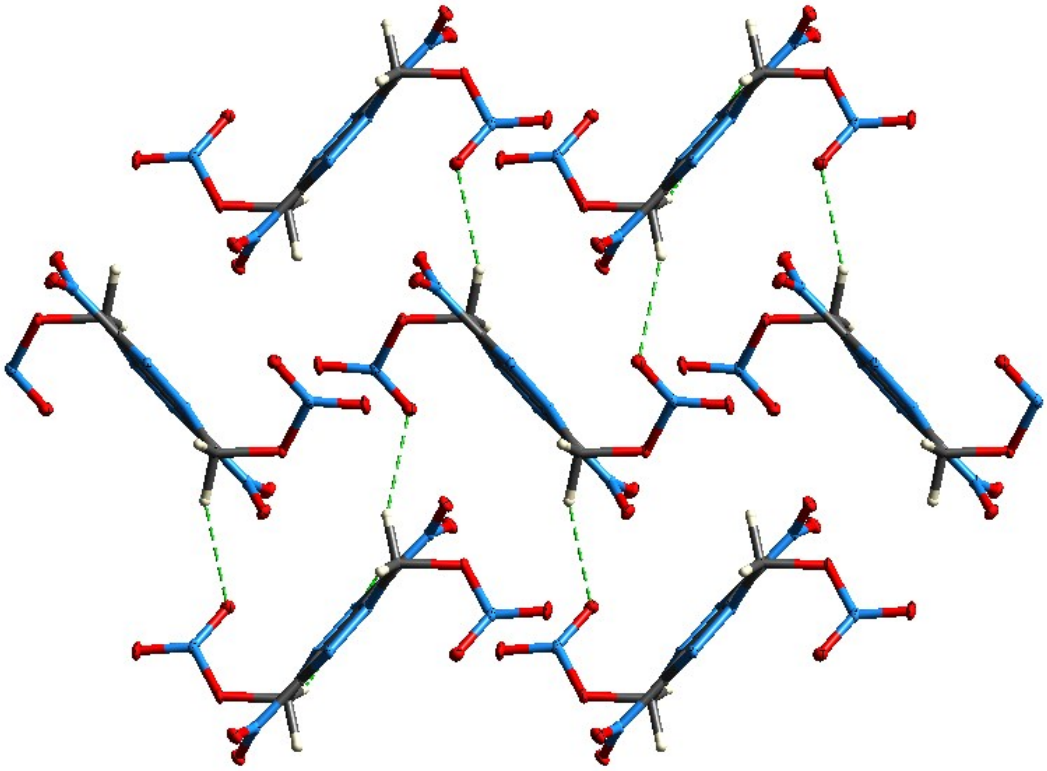


Figure S1. Unit cell view of **1** along *a* axis; hydrogen bonds are indicated as dotted lines.

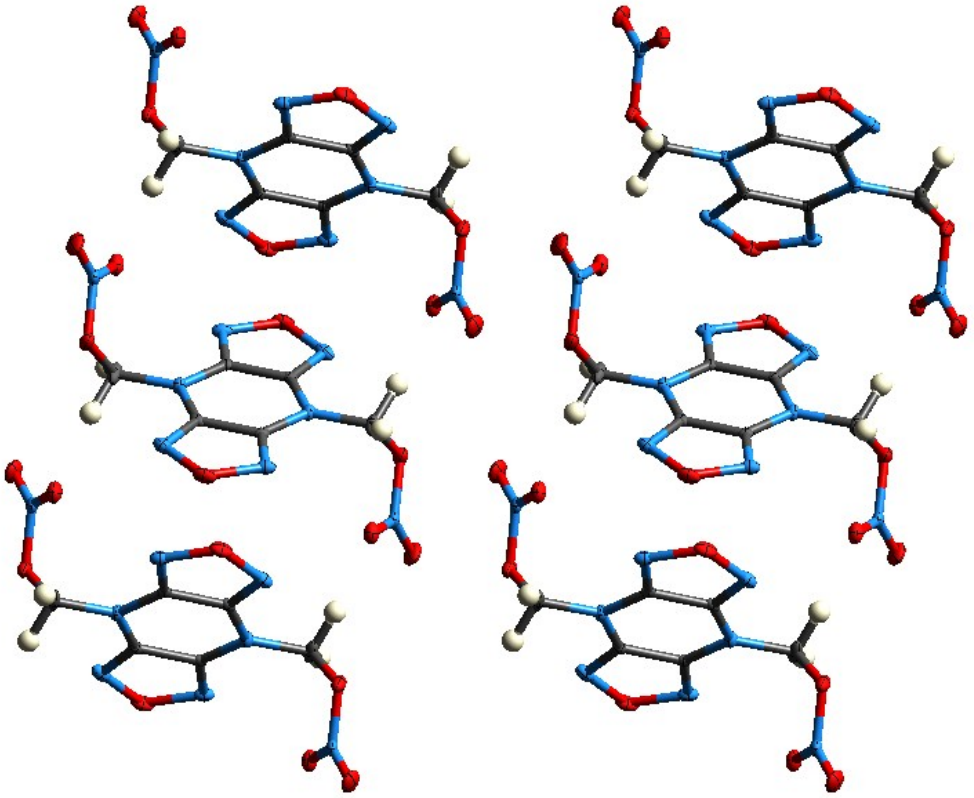


Figure S2. Unit cell view of **2** along *b* axis.

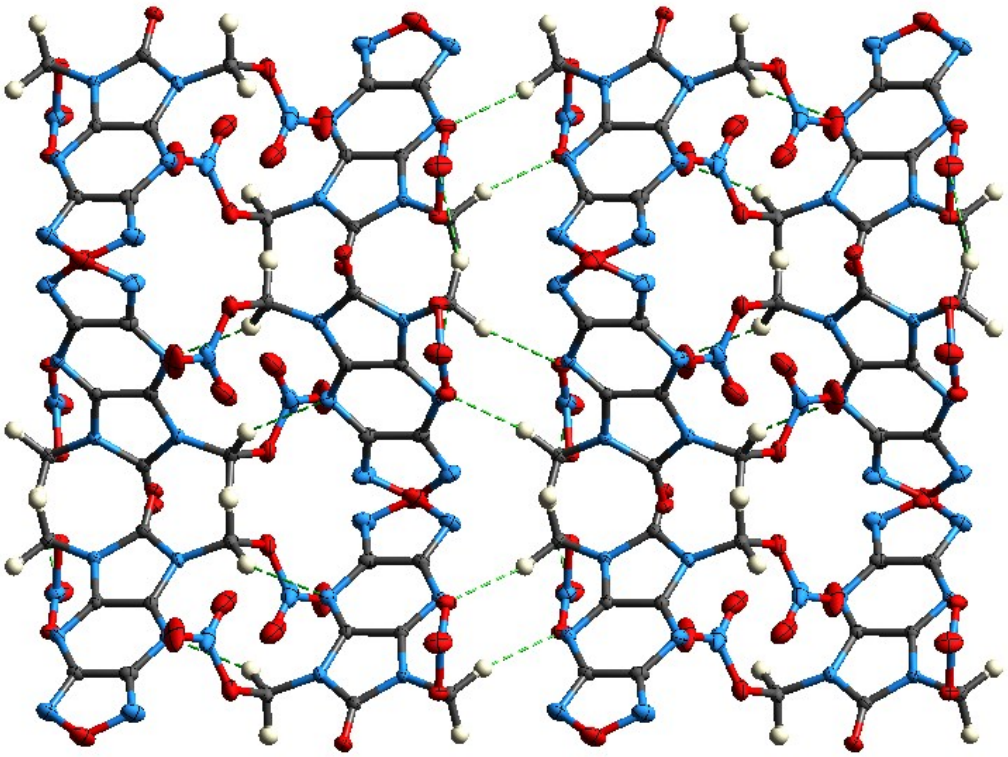


Figure S3. Unit cell view of **3** along *c* axis; hydrogen bonds are indicated as dotted lines.

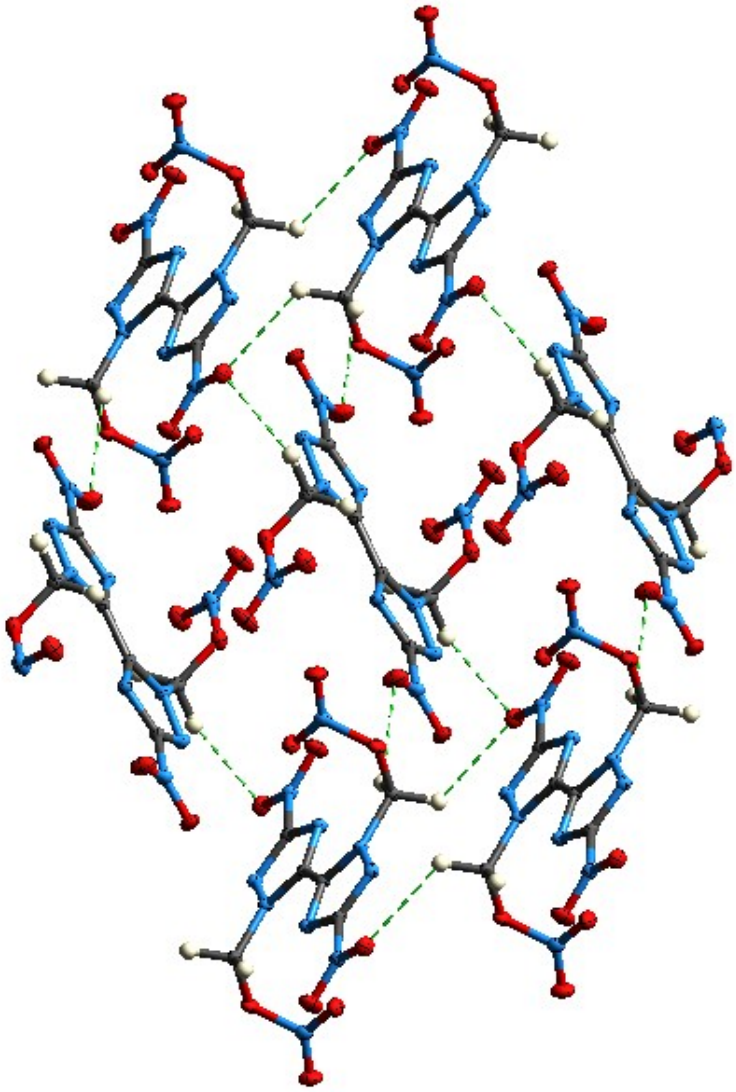


Figure S4. Unit cell view of **4** along *b* axis; hydrogen bonds are indicated as dotted lines.

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