Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

For

A DFT Study on Five-membered Nitrogen-containing Fused Heterocycles for Insensitive High Energetic Materials

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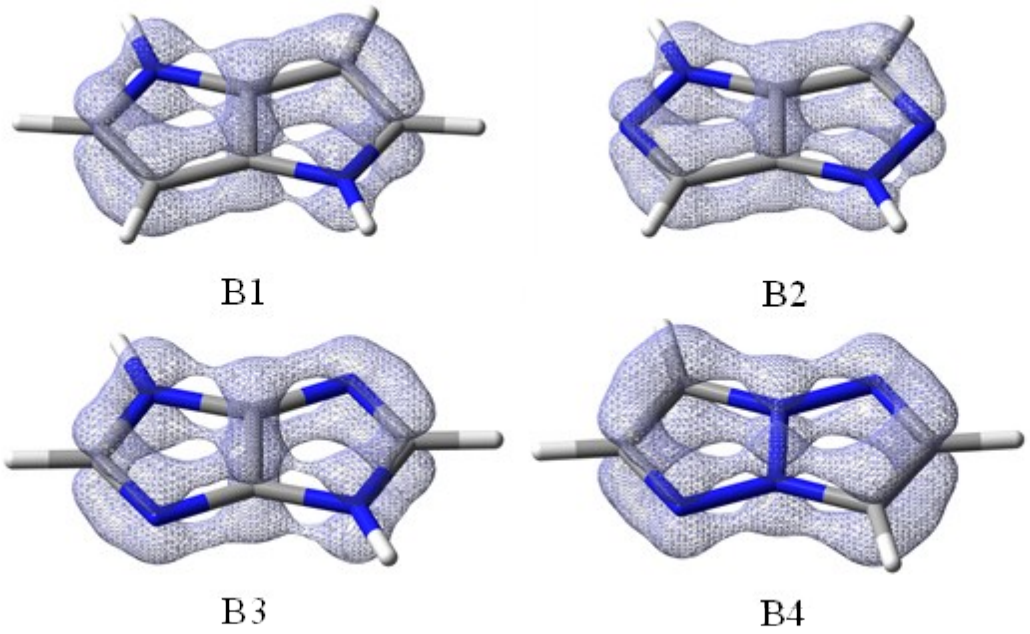


Fig S1 Isosurface of localized orbital locator for π-elections with the isovalues of 0.46 (B1), 0.45 (B2 and B3), 0.43 (B4).

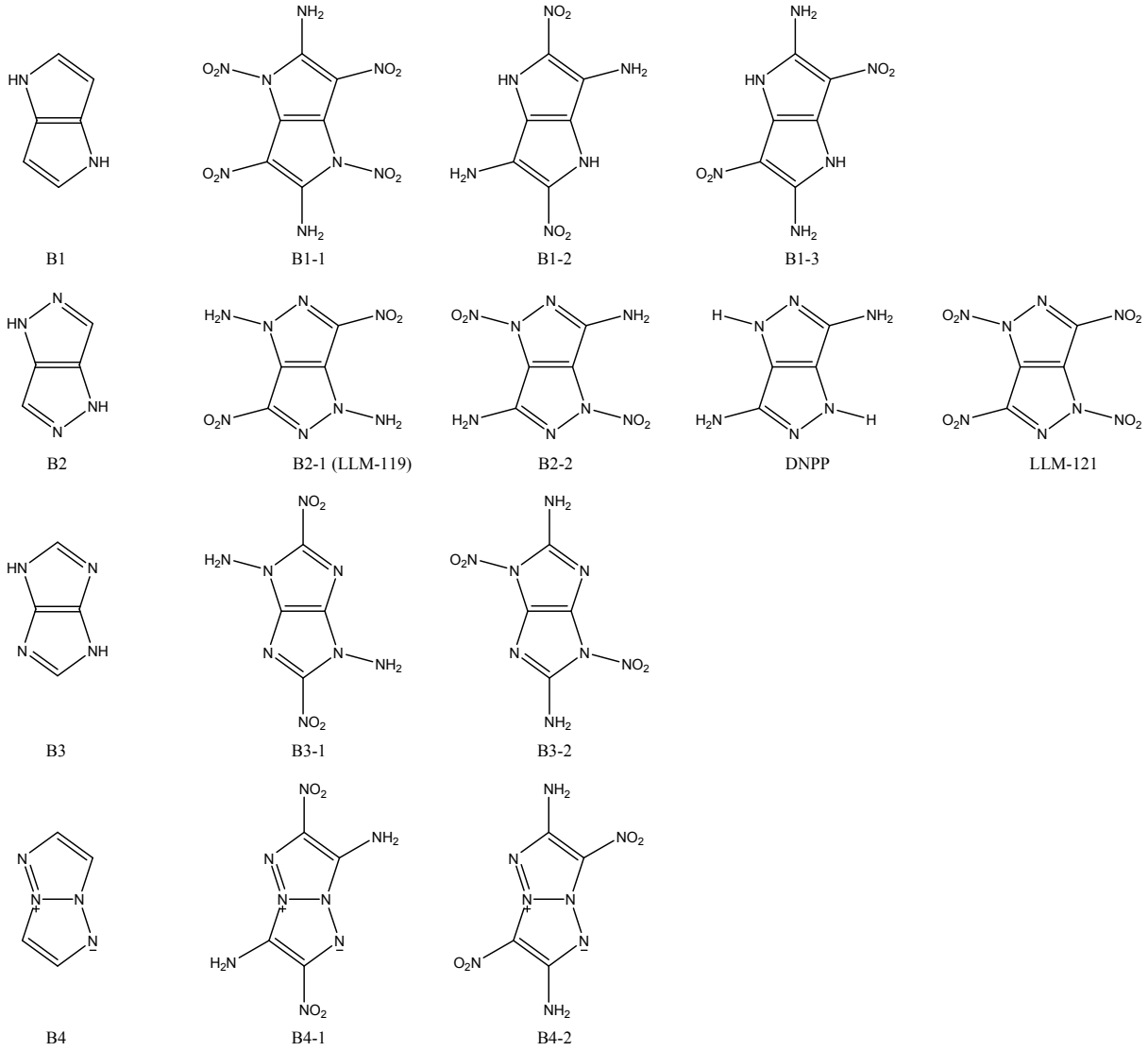


Fig S2 The structures of the compounds derived from four backbones with $–NH_2$ and $–NO_2$ groups, DNPP, and LLM-121. Among them, **B1-3** and **B3-2** have not been studied with the no planar structures.

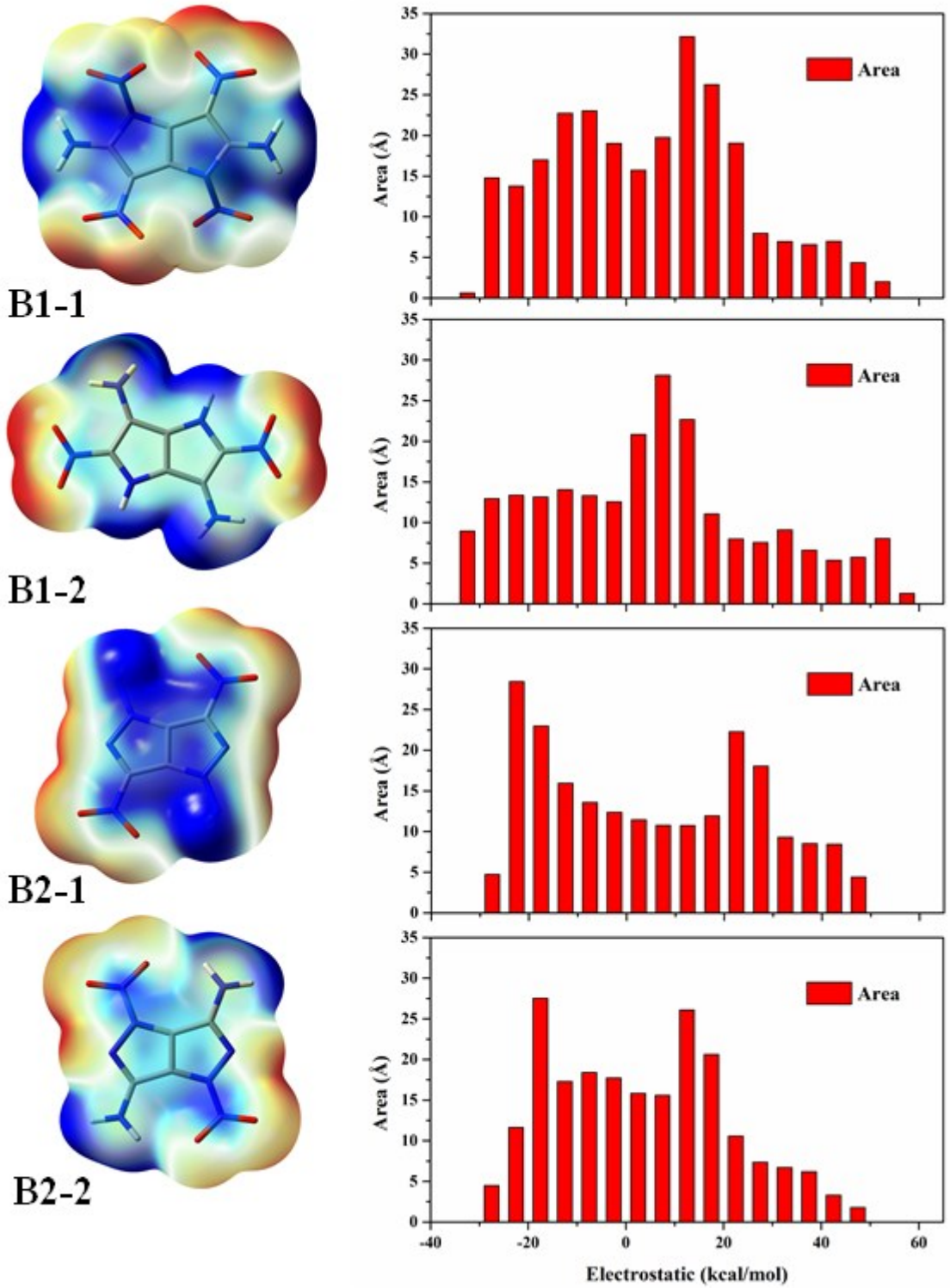


Fig S3 MEPs for compound **B1-1**, **B1-1, B2-1** and **B2-2**, and the surface areas in each MEP range.

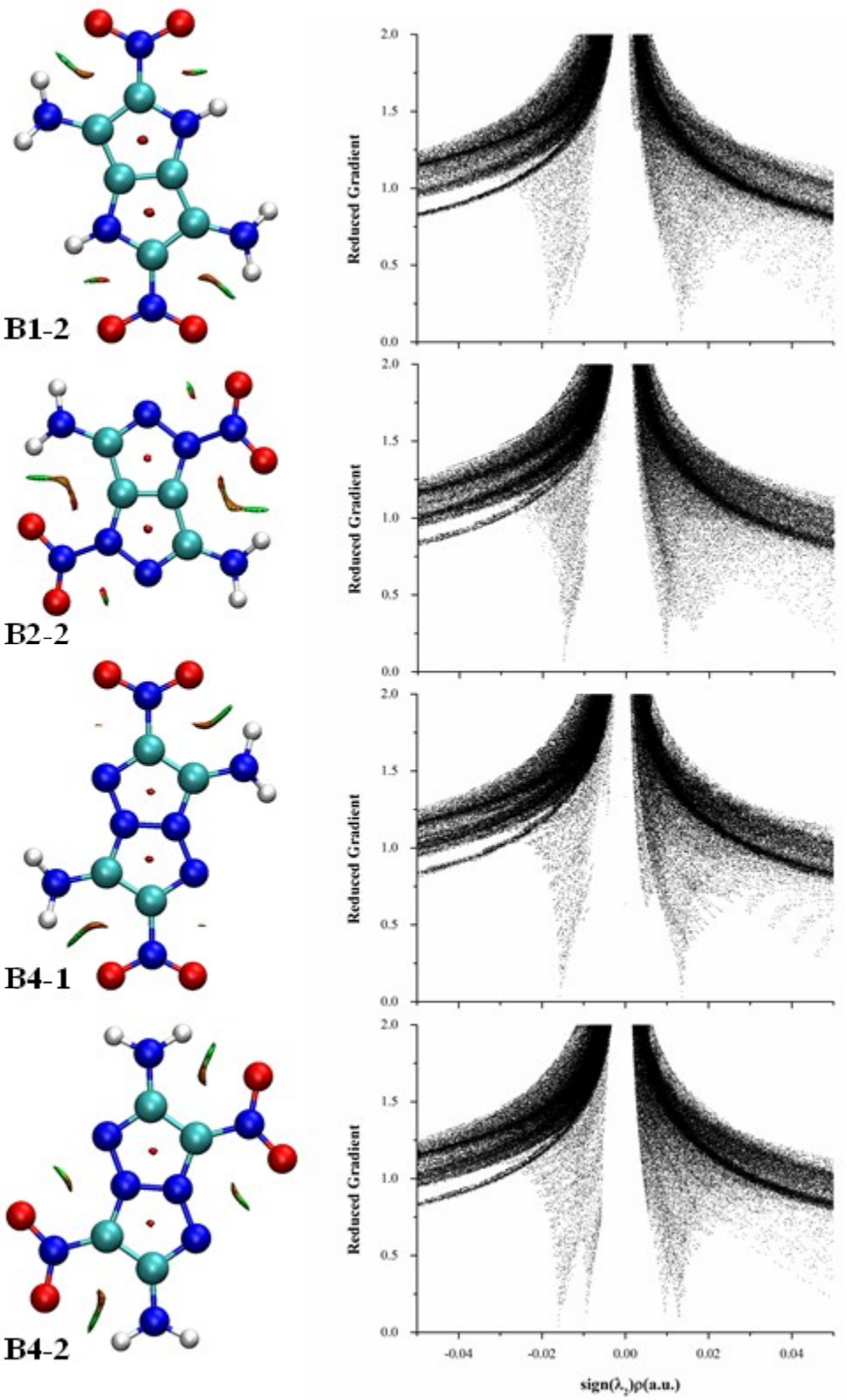
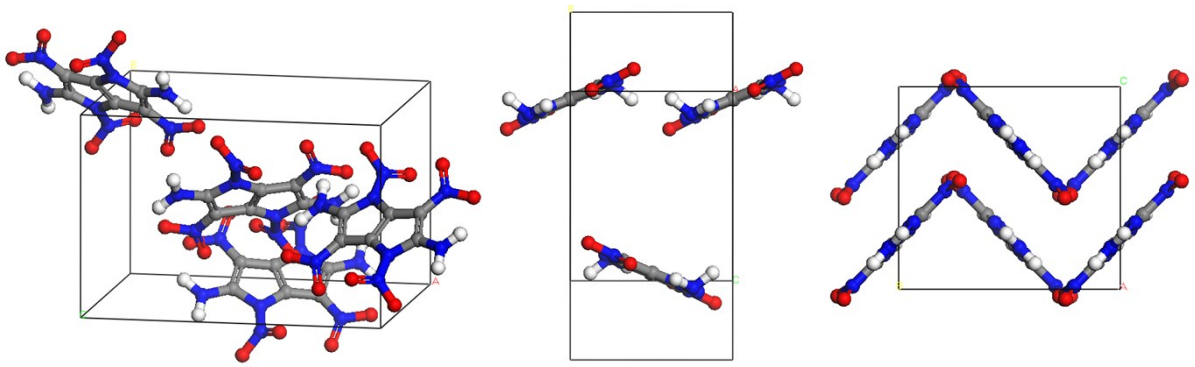


Fig. S4 The hydrogen bonds (depicted by an interaction surface around the critical point) and the graphs of the reduced electron density gradient vs sign(λ_2)ρ for **B1-2**, **B2-2**, **B4-2** and **B4-2**.

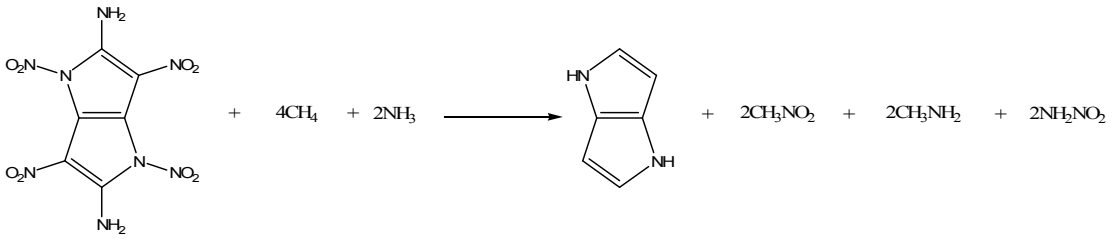


B1-1 **B2-1** **B4-2**

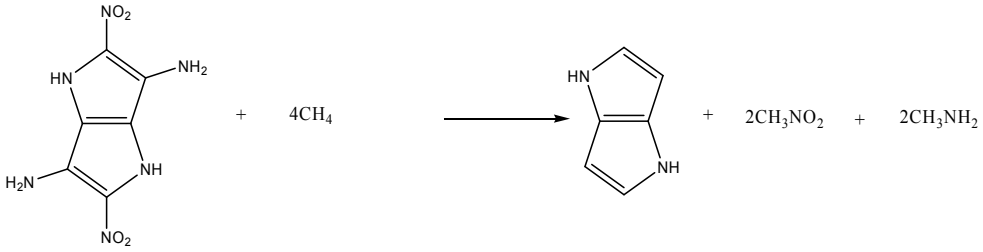
Fig. S5 The cell structures of **B1-1**, **B2-1**, and **B4-2**.

Scheme S1 The isodesmic reactions designed for target compounds

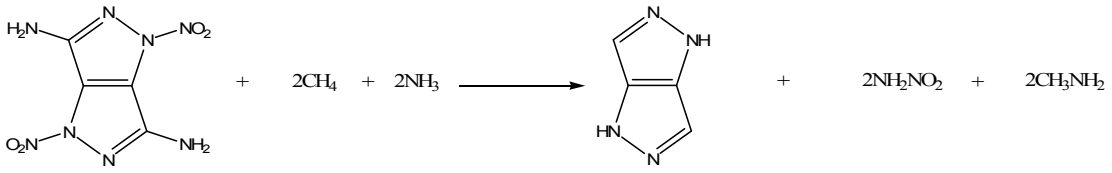
B1-1:



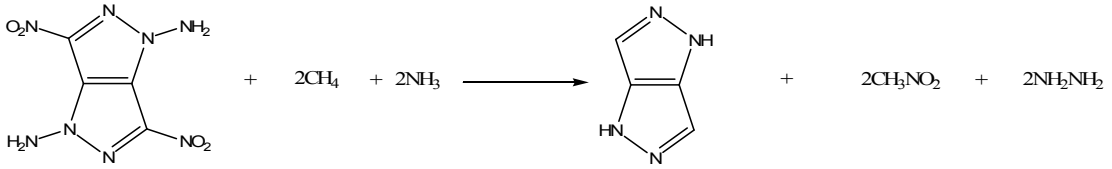
B1-2:



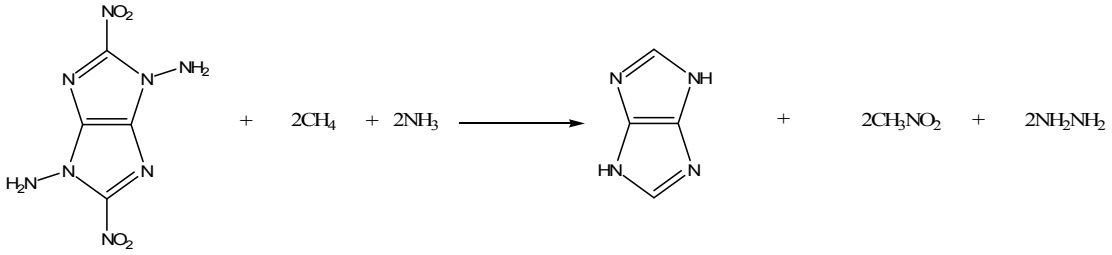
B2-1:



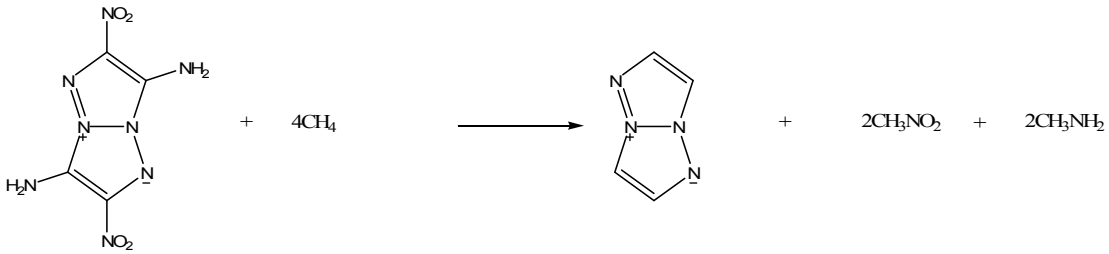
B2-2:



B3-1:



B4-1:


NO2
NH2
N
N
N
N
H2N
NO2
+ 4CH4
N
N
N
N
+ 2CH3NO2 + 2CH3NH2

B4-2:

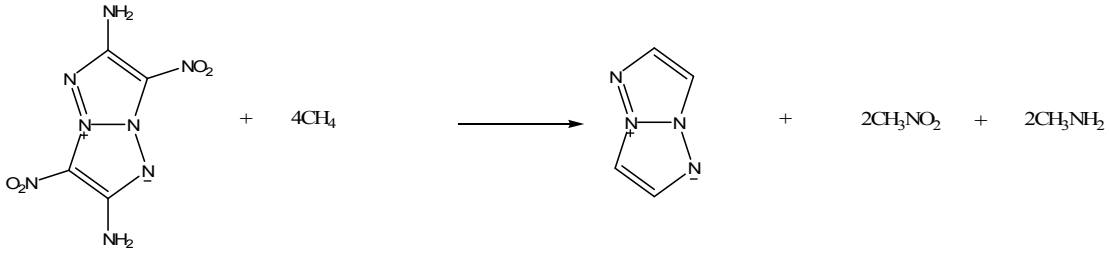

NH2
NO2
N
N
N
N
O2N
NH2
+ 4CH4
N
N
N
N
+ 2CH3NO2 + 2CH3NH2

Table S1 the densities predicted with the parameters fitted by Politzer et al (ρ(2009))[a] and Rice et al (ρ')[b], the densities (ρ) predicted using crystal packing with the Dreiding force field, and the experimental densities (g/cm^3).

	ρ(2009)	ρ'	ρ	ρ(EXP)
B1-1	1.898	1.901	2.017	
B1-2	1.747	1.709	1.886	
B2-1	1.742	1.734	1.917	1.845
B2-2	1.755	1.750	1.926	
B3-1	1.765	1.754	1.889	
B4-1	1.762	1.750	2.192	
B4-2	1.790	1.773	2.263	
DNPP	1.776	1.772	1.842	1.865
TNT	1.685	1.686	1.688	1.654
TATB	1.758	1.756	1.931	1.937

a Mol. Phys. 2009, 107, 2095-2101

b J. Comput. Chem. 2013, 34, 2146–2151.

As shown in **Table S1**, ρ are indeed higher than ρ(2009) and ρ'. But for B2-1(LLM-119), DNPP and TATB, ρ are much closer to experimental measures compared with ρ(2009) and ρ'. The mode introduced by Politzer et al tends to underestimate the density for the systems containing strong intermolecular interaction (Mol. Phys. 2009, 107: 2095-2101). In this work, the compounds are similar with DNPP and LLM-119, and characterized with hydrogen bonds. From this aspect, ρ should be more suitable for these structures. Therefore, the mode with the parameters fitted by Rice et al was just used to calculate the density as a reference.