*Article*

# Computational Design of High Energy RDX-based Derivatives: Property Prediction, Intermolecular Interactions, and Decomposition Mechanisms

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**Table S1.** Calculated total energy ($E_0$), zero-point energy (*ZPE*), thermal correction ($H_T$), and HOFs of the reference compounds.[1.]

| Compound | $E_0$(a.u) | *ZPE*(a.u) [1] | $H_T$(kJ/mol) [1] | HOF(kJ/mol) [2] | HOF(kJ/mol) [3] |
|---|---|---|---|---|---|
| $NH_3$ | -56.5826 | 0.0342 | 10.05 | -45.90 | -45.10 |
| $NH_2NO_2$ | -261.1248 | 0.0392 | 12.39 | -3.20 | -1.90 |
| $NH_2NH_2$ | -111.8976 | 0.0527 | 12.23 | 95.40 | 110.66 |

[1] The scaling factor for *ZPE* was 0.98 and the scaling for $H_T$ was 0.96 [48]. [2] The experimental values were taken from Ref. [31]. [3] The calculated values were calculated at the G2 level.

**Table S2.** Calculated total energy ($E_0$), zero-point energy (*ZPE*), thermal correction ($H_T$), gas-phase HOFs ($\Delta H_{f,gas}$), heat of sublimation ($\Delta H_{sub}$), and solid-phase HOFs ($\Delta H_{f,solid}$) for the designed compounds.

| Compound | $E_0$(a.u) | *ZPE*(a.u) [1] | $H_T$(kJ/mol) [2] | $\Delta H_{f,gas}$(kJ/mol) | $\Delta H_{sub}$(kJ/mol) | $\Delta H_{f,solid}$(kJ/mol) |
|---|---|---|---|---|---|---|
| R1 | -1455.15 | 0.19 | 56.04 | 1250.84 | 164.82 | 1086.01 |
| R2 | -1155.98 | 0.14 | 44.18 | 1118.18 | 98.16 | 1020.03 |
| R3 | -971.37 | 0.12 | 36.44 | 699.88 | 103.83 | 596.05 |
| R4 | -1564.62 | 0.20 | 58.74 | 1445.52 | 131.05 | 1314.48 |
| R5 | -1713.76 | 0.18 | 62.33 | 1556.46 | 132.49 | 1423.97 |
| R6 | -1453.93 | 0.16 | 52.92 | 1334.44 | 116.90 | 1217.54 |
| R7 | -1529.15 | 0.17 | 54.78 | 1150.88 | 118.54 | 1032.34 |

[1] The correction factor for *ZPE* was 0.98.

[2] The correction factor for $H_T$ was 0.96.

**Table S3.** Bond type and bond cutoff radius in the fragment analysis of the AIMD trajectory.

| Bond type | Cutoff radius(Å) | Bond type | Cutoff radius(Å) |
|---|---|---|---|
| C-C | 2.31 | H-O | 1.50 |
| C-H | 1.63 | H-N | 1.61 |
| C-O | 2.15 | O-O | 2.22 |
| C-N | 2.20 | O-N | 2.10 |
| H-H | 1.11 | N-N | 2.17 |

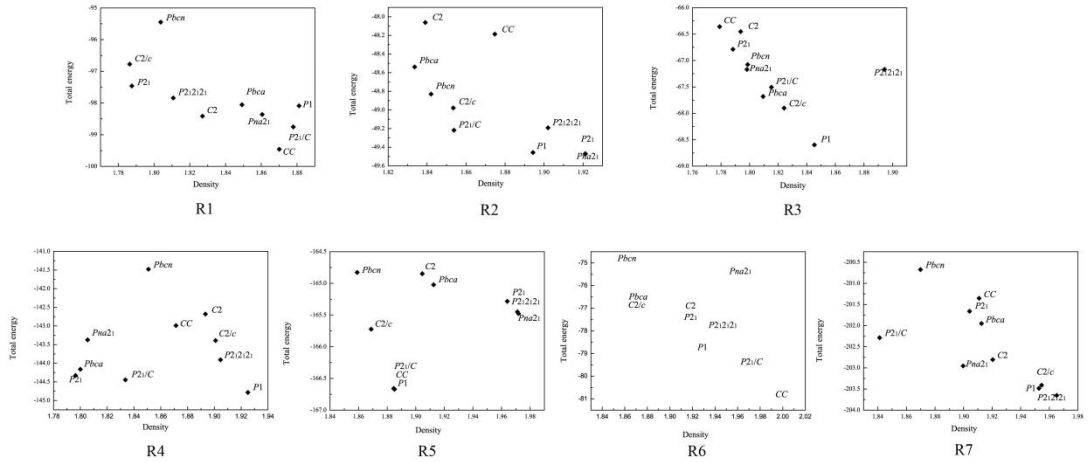


**Figure S1.** Relationship between crystal density and total energy of the packing for R1-R7.

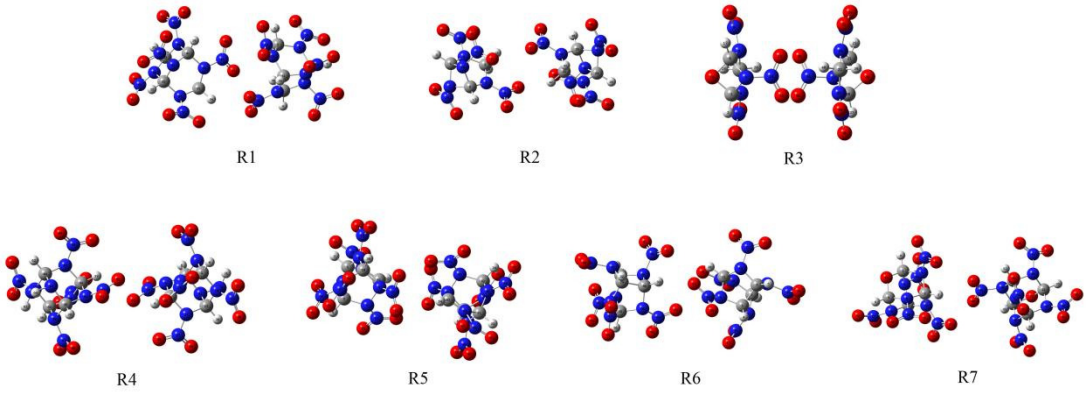


**Figure S2.** Optimized bimolecular structures and atom numbers.

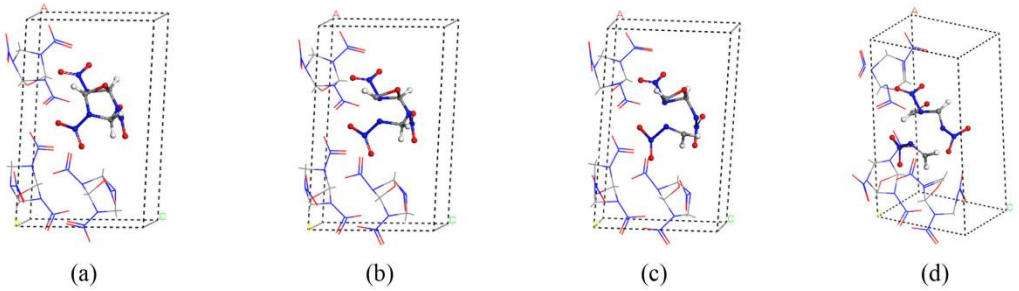


**Figure S3.** Snapshots of the decomposition mechanisms of (i).

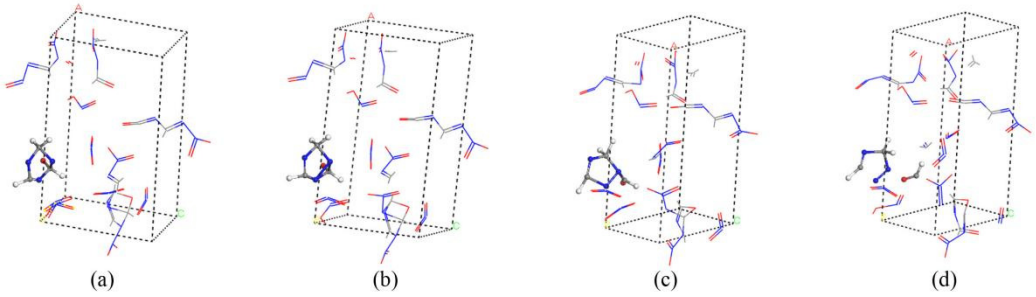


**Figure S4.** Snapshots of the decomposition mechanisms of (iii).

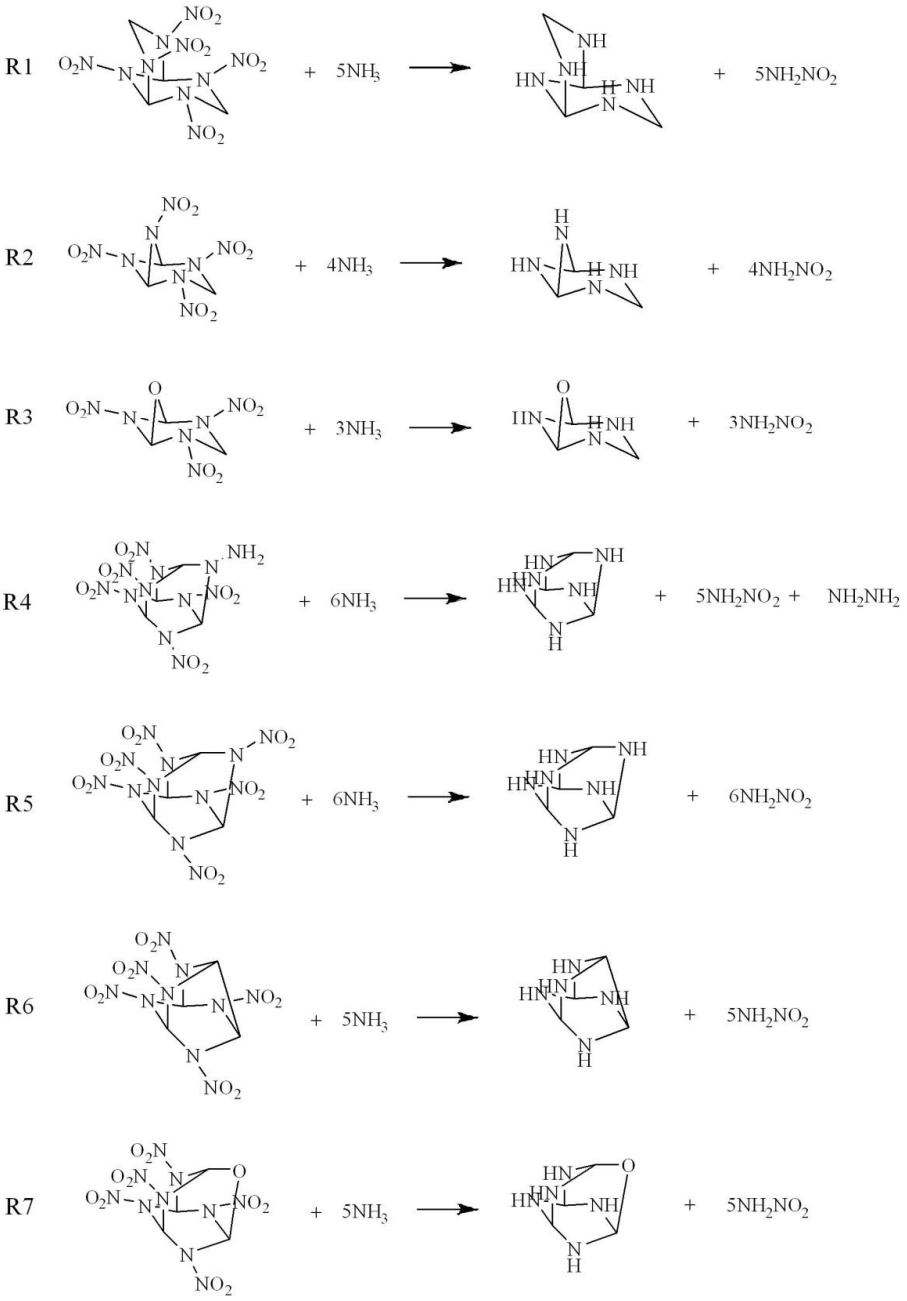


**Figure S5.** The corresponding isodesmic reactions of seven designed compounds (R1−R7).

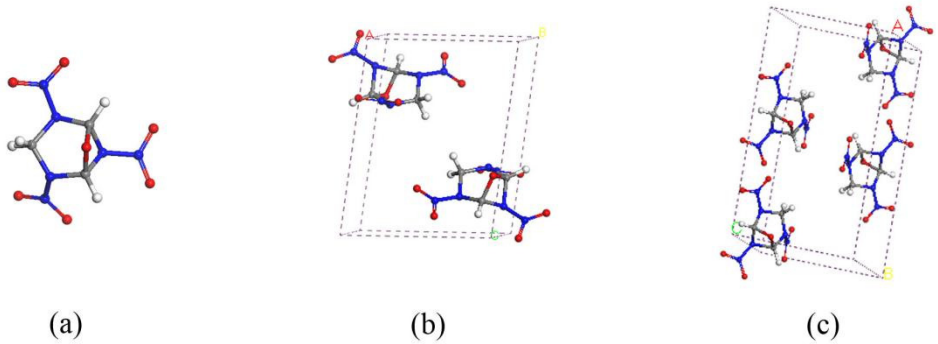


**Figure S6.** Molecular structures of R3 (a) and a unit cell (b) and a 2 × 1 × 1 supercell (c) of R3 crystal. Gray, blue, red, and white spheres stand for carbon, nitrogen, oxygen, and hydrogen atoms, respectively.