Carbon-Free Energetic Materials: Computational Study on Nitro-substituted BN-cage Molecules with High Heat of Detonation and Stability

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Table S1 The calculated densities for some compounds at the M06-2X/6-311++G** level with their experimental data

Figure S1 The color-filled map and curve map of ELF for B-N bond paths of the designed BN-cage at the M06-2X levels of theory

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Table S4 Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the trinitro-substituted BN-cage compounds and their isomers at the M06-2X, oB97XD and B3LYP level.

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**Table S5** Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the tetrinitro-substituted BN-cage compounds and their isomers at the M06-2X, ωB97XD and B3LYP level.

**Figure S9** Optimized geometries (bond lengths in Å) at the M06-2X level for the pentanitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol$^{-1}$) at M06-2X level are indicated in parentheses

**Table S6** Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the pentanitro-substituted BN-cage compounds and their isomers at the M06-2X, ωB97XD and B3LYP level.

**Figure S10** The color-filled map and curve map of ELF for B3-N7 bond path of NO$_2$-5-1 at the M06-2X levels of theory

**Figure S11** Optimized geometries (bond lengths in Å) at the M06-2X level for the hexanitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol$^{-1}$) at M06-2X level are indicated in parentheses

**Table S7** Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the hexanitro-substituted BN-cage compounds and their isomers at the M06-2X, ωB97XD and B3LYP level.

**Table S8** Total energies (E), zero point energies (ZPE), thermal correction values (H$_T$), heat of formation (kJ/mol), molecular surface properties (As, v6tot2), enthalpy of sublimation (ΔH$_{sub}$) and solid phase enthalpy of formation (ΔH$_o(s)$) of the NO$_2$-substituted BN-cage compounds at the M06-2X /6-311++G** level.

**Table S9** Total energies (E), zero point energies (ZPE), thermal correction values (H$_T$), heat of formation (kJ/mol), molecular surface properties (As, v6tot2), enthalpy of sublimation (ΔH$_{sub}$) and solid phase enthalpy of formation (ΔH$_o(s)$) of the NO$_2$-substituted BN-cage compounds at the ωB97XD/6-311++G** level.

**Table S10** Total energies (E), zero point energies (ZPE), thermal correction values (H$_T$), heat of formation (kJ/mol), molecular surface properties (As, v6tot2), enthalpy of sublimation (ΔH$_{sub}$) and solid phase enthalpy of formation (ΔH$_o(s)$) of the NO$_2$-substituted BN-cage compounds at the B3LYP/6-311++G** level.
Table S1 The calculated densities for some compounds at the M06-2X/6-311++G** level with their experimental data

| compounds | Experiment (g/cm^3) | Calculated (g/cm^3) |
|-----------|---------------------|---------------------|
| TNT       | 1.654               | 1.647               |
| RDX       | 1.816               | 1.800               |
| HMX       | 1.902               | 1.877               |
| PETN      | 1.732               | 1.656               |
| CL-20     | 2.040               | 1.954               |
Figure S1 The color-filled maps and curve maps of ELF for B-N bond paths of the designed BN-cage at the M06-2X levels of theory
Figure S2 Optimized geometries (bond lengths in Å) at the M06-2X level for the mononitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol\(^{-1}\)) at M06-2X level are indicated in parentheses.

Table S2 Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the mononitro-substituted BN-cage compounds and their isomers at the M06-2X, ωB97XD and B3LYP level.

|        | M06-2X       | ωB97XD      | B3LYP        |
|--------|--------------|-------------|--------------|
| E      | -685.871906  | -685.870761 | -685.868852  |
| ΔE     | 0            | 20.3        | 0.0          |
| symmetry | C1          | Cs          | C1           |

Figure S3 The color-filled map and curve map of ELF for B3-N7 bond path of NO\(_2\)-1-3 at the M06-2X levels of theory.
**Figure S4** Optimized geometries (bond lengths in Å) at the M06-2X level for the dinitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol⁻¹) at M06-2X level are indicated in parentheses.

**Table S3** Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the dinitro-substituted BN-cage compounds and their isomers at the M06-2X, ωB97XD and B3LYP level.

|           | 2-1         | 2-2         | 2-3         | 2-4         | 2-5         |
|-----------|-------------|-------------|-------------|-------------|-------------|
| M06-2X    | -890.392507 | -890.382149 | -890.343073 | -890.334532 | -890.319916 |
| ΔE        | 0           | 27.2        | 129.9       | 152.3       | 190.7       |
| symmetry  | Cs          | C1          | C1          | C1          | Cs          |
| ωB97XD    | -890.397972 | -890.390197 | -890.350567 | -890.340891 | -890.326487 |
| ΔE        | 0           | 20.4        | 124.5       | 149.9       | 187.8       |
| symmetry  | Cs          | C1          | C1          | C1          | Cs          |
| B3LYP     | -890.389855 | -890.382626 | -890.341921 | -890.331176 | -890.318839 |
| ΔE        | 0           | 18.8        | 126.0       | 154.0       | 186.7       |
| symmetry  | Cs          | C1          | C1          | C1          | Cs          |
**Figure S5** Optimized geometries (bond lengths in Å) at the M06-2X level for the trinitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol\(^{-1}\)) at M06-2X level are indicated in parentheses.

**Table S4** Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the trinitro-substituted BN-cage compounds and their isomers at the M06-2X, ωB97XD and B3LYP level.

|        | 3-1                              | 3-2                              | 3-3                              | 3-4                              |
|--------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| **M06-2X** | E = -1094.897765                | E = -1094.849808                 | E = -1094.840454                 | E = -1094.836407                 |
| ΔE     | 0                               | 126.0                            | 150.5                            | 161.2                            |
| symmetry | Cs                              | Cs                               | C1                               | C1                               |
| **ωB97XD** | E = -1094.913044              | E = -1094.863675                 | E = -1094.856440                 | E = -1094.856044                 |
| ΔE     | 0                               | 129.7                            | 148.7                            | 149.7                            |
| symmetry | Cs                              | Cs                               | C1                               | C1                               |
| **B3LYP** | E = -1094.898515              | E = -1094.846713                 | E = -1094.840291                 | E = -1094.839262                 |
| ΔE     | 0                               | 136.0                            | 152.8                            | 155.7                            |
| symmetry | Cs                              | Cs                               | C1                               | C1                               |
**Figure S6** Optimized geometries (bond lengths in Å) at the M06-2X level for the tetranitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol\(^{-1}\)) at M06-2X level are indicated in parentheses.

**Table S5** Total energies (\(E\) in hartree), relative energies (\(\Delta E\) in kJ/mol) and symmetries for the tetranitro-substituted BN-cage compounds and their isomers at the M06-2X, \(\omega\)B97XD and B3LYP level.

|        | 4-1               | 4-2               | 4-3               |
|--------|-------------------|-------------------|-------------------|
| **M06-2X** |                   |                   |                   |
| \(E\)  | -1299.351602      | -1299.348266      | -1299.279785      |
| \(\Delta E\) | 0                 | 8.8               | 188.6             |
| symmetry | Cs                | C1                | Cs                |
| **\(\omega\)B97XD** |               |                   |                   |
| \(E\)  | -1299.385229      | -1299.386115      | -1299.308946      |
| \(\Delta E\) | 0                 | -2.3              | 200.4             |
| symmetry | Cs                | C1                | Cs                |
| **B3LYP** |                   |                   |                   |
| \(E\)  | -1299.351958      | -1299.351286      | -1299.283357      |
| \(\Delta E\) | 0                 | 1.7               | 180.0             |
| symmetry | Cs                | C                 | Cs                |
**Figure S7** The color-filled map and curve map of ELF for B3-N7 bond path of NO$_2$-4-2 at the M06-2X levels of theory

**Figure S8** The color-filled map and curve map of ELF for B3-N7 bond path of NO$_2$-4-3 at the M06-2X levels of theory
**Figure S9** Optimized geometries (bond lengths in Å) at the M06-2X level for the pentanitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol\(^{-1}\)) at M06-2X level are indicated in parentheses.

**Table S6** Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the pentanitro-substituted BN-cage compounds and their isomers at the M06-2X, \(\omega\)B97XD and B3LYP level.

|            | 5-1                  | 5-2                  |
|------------|----------------------|----------------------|
| M06-2X E   | -1503.799129         | -1503.718869         |
| ΔE         | 0                    | 210.8                |
| symmetry   | C1                   | Cs                   |
| \(\omega\)B97XD E | -1503.829668   | -1503.750364         |
| ΔE         | 0                    | 208.3                |
| symmetry   | C1                   | Cs                   |
| B3LYP E    | -1503.781134         | -1503.709551         |
| ΔE         | 0                    | 188.0                |
| symmetry   | C1                   | Cs                   |

**Figure S10** The color-filled map and curve map of ELF for B3-N7 bond path of NO\(_2\)-5-1 at the M06-2X levels of theory.
Figure S11 Optimized geometries (bond lengths in Å) at the M06-2X level for the hexanitro-substituted BN-cage compounds and their isomers. Relative energies (kJ mol\(^{-1}\)) at M06-2X level are indicated in parentheses.

Table S7 Total energies (E in hartree), relative energies (ΔE in kJ/mol) and symmetries for the hexanitro-substituted BN-cage compounds and their isomers at the M06-2X, ωB97XD and B3LYP level.

|          | E     | ΔE   | symmetry |
|----------|-------|------|----------|
| M06-2X   | -1708.236006 | 0    | Cs       |
| ωB97XD   | -1708.272682 | 0    | Cs       |
| B3LYP    | -1708.209609 | 0    | Cs       |
Table S8 Total energies (E), zero point energies (ZPE), thermal correction values ($H_T$), heat of formation (kJ/mol), molecular surface properties (As, $\nu_b^{tot2}$), enthalpy of sublimation ($\Delta H^o_{sub}$) and solid phase enthalpy of formation ($\Delta fH^o(s)$) of the NO$_2$-substituted BN-cage compounds at the M06-2X/6-311++G** level.

| compounds | E (Hartree) | ZPE (kJ/mol) | $H_T$ (kJ/mol) | As | $\nu_b^{tot2}$ | $\Delta H^o_{sub}$ (kJ/mol) | $\Delta fH^o(s)$ (kJ/mol) |
|-----------|-------------|---------------|----------------|----|----------------|-----------------------------|-----------------------------|
| NO2-1-1   | -685.872    | 332.772       | 362.968        | 195.450 | 102.097 | 124.900 | -289.545 |
| NO2-2-1   | -890.393    | 343.310       | 380.750        | 222.400 | 88.958  | 132.842 | -449.511 |

Table S9 Total energies (E), zero point energies (ZPE), thermal correction values ($H_T$), heat of formation (kJ/mol), molecular surface properties (As, $\nu_b^{tot2}$), enthalpy of sublimation ($\Delta H^o_{sub}$) and solid phase enthalpy of formation ($\Delta fH^o(s)$) of the NO$_2$-substituted BN-cage compounds at the $\omega$B97XD/6-311++G** level.

| compounds | E (Hartree) | ZPE (kJ/mol) | $H_T$ (kJ/mol) | As | $\nu_b^{tot2}$ | $\Delta H^o_{sub}$ (kJ/mol) | $\Delta fH^o(s)$ (kJ/mol) |
|-----------|-------------|---------------|----------------|----|----------------|-----------------------------|-----------------------------|
| NO2-1-1   | -685.871    | 331.089       | 361.455        | 195.563 | 99.072  | 123.909 | -269.297 |
| NO2-2-1   | -890.398    | 342.447       | 379.931        | 222.788 | 92.823  | 134.435 | -413.859 |

Table S10 Total energies (E), zero point energies (ZPE), thermal correction values ($H_T$), heat of formation (kJ/mol), molecular surface properties (As, $\nu_b^{tot2}$), enthalpy of sublimation ($\Delta H^o_{sub}$) and solid phase enthalpy of formation ($\Delta fH^o(s)$) of the NO$_2$-substituted BN-cage compounds at the B3LYP/6-311++G** level.

| compounds | E (Hartree) | ZPE (kJ/mol) | $H_T$ (kJ/mol) | As | $\nu_b^{tot2}$ | $\Delta H^o_{sub}$ (kJ/mol) | $\Delta fH^o(s)$ (kJ/mol) |
|-----------|-------------|---------------|----------------|----|----------------|-----------------------------|-----------------------------|
| NO2-1-1   | -685.869    | 325.331       | 355.989        | 198.391 | 101.246 | 125.908 | -274.313 |
| NO2-2-1   | -890.390    | 333.32        | 371.382        | 227.201 | 95.520  | 137.619 | -554.623 |