Supporting information for

Phase Transitions and Chemical Reactions of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine under High Pressure and High Temperature

Dexiang Gao, a Jin Huang, a Xiaohuan Lin, a Dongliang Yang, b Yajie Wang, a,* Haiyan Zheng a,*

a Center for High Pressure Science and Technology Advanced Research, 100094, Beijing, China
b Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

*E-mail: Yajie Wang: yajie.wang@hpstar.ac.cn; Haiyan Zheng: zhenghy@hpstar.ac.cn
**Table S1.** Assignments of Raman modes of $\beta$-HMX at ambient pressure, room temperature

| Assignments          | Experiment (cm$^{-1}$) | Calculation from the reference(cm$^{-1}$)$^1$ |
|----------------------|------------------------|---------------------------------------------|
| $\gamma_{NN}(NO_2)$  | 99                     | 87, 115                                     |
| $\sigma$(CNC)        | 144                    | 154                                         |
|                      |                        | 184                                         |
| $b$(NNC), $b$(CNC)   | 232                    | 217                                         |
| $b$(NNC), $b$(NCN)   | 284                    | 270                                         |
| $b$(NNC), $b$(NNO)   | 317                    | 299                                         |
| $v$(CN), $v$(NN), $b$(NCN) | 365                   | 342                                         |
| $b$(NNO), $b$(NNC)   | 416                    | 399                                         |
| $b$(CNC), $b$(NNC)   | 438                    | 420                                         |
| $b$(NNO)             | 599                    | 594                                         |
| $b$(NNO), $v$(NN)    | 641                    | 625                                         |
| $b$(NNO), $v$(NN)    | 663                    | 650                                         |
| $b$(ONO), $v$(CN)    | 722                    | 726                                         |
| $\sigma$(ONO)        | 762                    | 741                                         |
| $v_s$(NC$_2$)        | 836                    | 826                                         |
| $v_s$(NNC$_2$)       | 885                    | 872                                         |
| $v$(NN), $\rho$(CH$_2$) | 953                  | 925                                         |
| $v_{as}$(NNO$_2$)    | 1080                   | 1061                                        |
| $v_{as}$(CNN), $\rho$(CH$_2$) | 1170                | 1167                                        |
| $v_{as}$(NC$_2$)     | 1191                   | 1197                                        |
| $v_{as}$(NC$_2$)     | 1250                   | 1238                                        |
| $v_s$(NO$_2$)        | 1269                   | 1272                                        |
| $\omega$(CH$_2$)     | 1420                   | 1422                                        |
| Assignments | Experiment at 1.0 GPa (cm$^{-1}$) | Calculation from the reference (cm$^{-1}$)$^1$ |
|-------------|----------------------------------|-----------------------------------------------|
| b(HCH)      | 1438                             | 1446                                          |
| b(HCH)      | 1455                             | 1461                                          |
| $\nu_{as}(NO_{2})$ | 1526                           | 1611                                          |
| $\nu_{as}(NO_{2})$ | 1559                           | 1624                                          |
| $\nu_{as}(NO_{2})$ | 1570                           | 1626                                          |
| $\nu_s(CH_{2})$ | 2993                           | 2983                                          |
| $\nu_{as}(CH_{2})$ | 3028                           | 3046                                          |
| $\nu_{as}(CH_{2})$ | 3036                           | 3049                                          |

Note: b(XYZ): X-Y-Z bending vibration; $\nu_{as}(XY_{2})$: Y-X-Y asymmetric stretching vibration; $\nu_{as}(XXY_{2})$: X-X-Y$_2$ asymmetric stretching vibration; $\nu_s(XXY_{2})$: X-X-Y$_2$ symmetric stretching vibration; $\rho(XXY_{2})$: XY$_2$ rocking vibration in XY$_2$ plane; $\sigma(XXY_{2})$: X atom rocking vibration out of XY$_2$ plane; $\omega(XXY_{2})$: Y$_2$ rocking vibration out of XY$_2$ plane; $\gamma_{NN}(XY_{2})$: XY$_2$ twisting vibration about N-N bond.

**Table S2.** Assignments of IR modes of $\beta$-HMX at 1.0 GPa, room temperature
| P (GPa) | a(Å)        | b(Å)        | c(Å)        | θ (°)       |
|--------|-------------|-------------|-------------|-------------|
| 0.2    | 6.5400(53)  | 11.022(2)   | 8.7012(25)  | 124.371(74) |
| 1.0    | 6.370(3)    | 10.892(5)   | 8.5699(57)  | 124.100(75) |
| 2.0    | 6.345(4)    | 10.771(5)   | 8.4963(55)  | 124.174(88) |
| 3.1    | 6.282(5)    | 10.629(5)   | 8.430(7)    | 124.3(1)    |
| 4.2    | 6.252(5)    | 10.548(5)   | 8.3760(69)  | 124.5(1)    |

**Note:** b(XYZ): X-Y-Z bending vibration; v_\text{as}(XY_2): Y-X-Y asymmetric stretching vibration; v_\text{as}(XXY_2): X-X-Y asymmetric stretching vibration; v_\text{s}(XY_2): Y-X-Y symmetric stretching vibration; v_\text{s}(XXY_2): X-X-Y symmetric stretching vibration; \(\rho(XY_2)\): XY_2 rocking vibration in XY_2 plane; \(\sigma(XY_2)\): X atom rocking vibration out of XY_2 plane; \(\omega(XY_2)\): Y_2 rocking vibration out of XY_2 plane; \(\gamma(XY_2)\): XY_2 twisting vibration about bisector of Y-X-Y angle.

**Table S3.** The refined cell parameters under non-hydrostatic pressure conditions
| Pressure (GPa) | x      | y      | z      | Occupancy |
|---------------|--------|--------|--------|-----------|
| 5.1           | 6.233(6) | 10.474(5) | 8.3691(76) | 124.49(12) |
| 6.2           | 6.215(18) | 10.417(5) | 8.2724(78) | 124.88(26) |
| 7.5           | 6.183(4)  | 10.240(4)  | 8.2993(63) | 124.902(97) |
| 8.1           | 6.182(8)  | 10.146(5)  | 8.29(1)    | 124.92(17)  |
| 9.1           | 6.126(7)  | 10.083(4)  | 8.2746(75) | 124.75(14)  |
| 10.6          | 6.146(8)  | 10.037(5)  | 8.2593(93) | 124.94(16)  |
| 11.6          | 6.125(6)  | 9.978(6)   | 8.2570(73) | 124.93(12)  |
| 12.6          | 6.130(7)  | 9.846(5)   | 8.2578(88) | 125.06(15)  |
| 13.6          | 6.130(9)  | 9.763(6)   | 8.282(11)  | 125.19(19)  |
| 14.5          | 6.109(8)  | 9.672(5)   | 8.3097(95) | 124.96(17)  |

**Table. S4** Atomic coordinates of HMX at 6.2 GPa
### Table. S5 Atomic coordinates of HMX at 12.6 GPa

| Atom | x       | y       | z       | Occupancy |
|------|---------|---------|---------|-----------|
| C1   | 0.777669| 0.957574| 0.756563| 1         |
| C2   | 0.257581| 0.883921| 0.009341| 1         |
| N1   | 0.359191| 0.99604 | 0.719635| 1         |
| N2   | 0.621561| 0.029659| 0.813958| 1         |
| N3   | 0.973534| 0.865065| 0.911512| 1         |
| N4   | 0.891796| 0.779844| 0.996675| 1         |
| O1   | 0.208721| 0.079615| 0.720349| 1         |
| O2   | 0.265464| 0.910467| 0.587171| 1         |
| O3   | 0.058757| 0.732505| 0.160045| 1         |
| O4   | 0.664538| 0.793308| 0.950863| 1         |
| H1   | 0.659531| 0.907335| 0.637082| 1         |
| H2   | 0.867345| 0.022405| 0.727194| 1         |
| H3   | 0.289201| 0.923013| 0.918064| 1         |
| H4   | 0.344492| 0.797062| 0.045582| 1         |
Figure S1. Frequency shifts of β-HMX in the IR spectra as a function of pressure in the region of (a) 600-1050, (b) 1050-1650 and (c) 2950-3200 cm\(^{-1}\). The symbol of the different vibration modes can be found in the note of table S2. The dotted lines represent the phase boundaries.

Figure S2. Torsion angles of axial NO\(_2\) (the angle between line C1'-C2 and O3-O4) and equatorial NO\(_2\) (the angle between line C1-C2 and O1-O2) under non-hydrostatic pressure condition. Above 6.2 GPa, the torsion angle abruptly changes by 23.3°.
Figure S3. The lengths of hydrogen bonds (O…H) under high pressure. The hydrogen bonds 1, 4 and 5 are indicated in the Figure 7b. (a) is intramolecular hydrogen bond; (b) and (c) are intermolecular hydrogen bonds. The vertical line represents boundary of phase transition.

Reference

1 V. B. Holmann, L. R. Ronald, J. F. David, D. Irina, P. Peter and K. L. Thomas, *J. Phys. Chem. B.*, 2002, **106**, 10594-10604.