Electronic Supplementary Material (ESI) for RSC Advances.

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

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Table S1. Assignments of Raman modes of β-HMX at ambient pressure, room temperature

Assignments	Experiment (cm^{-1})	Calculation from the reference(cm^{-1})[1]
$\gamma_{NN}(NO_2)$	99	87, 115
σ(CNC)	144	154
	184	
b(NNC), b(CNC)	232	217
b(NNC), b(NCN)	284	270
b(NNC), b(NNO)	317	299
ν(CN), ν(NN), b(NCN)	365	342
b(NNO), b(NNC)	416	399
b(CNC), b(NNC)	438	420
b(NNO)	599	594
b(NNO), ν(NN)	641	625
b(NNO), ν(NN)	663	650
b(ONO), ν(CN)	722	726
σ(ONO)	762	741
$\nu_s(NC_2)$	836	826
$\nu_s(NNC_2)$	885	872
ν(NN), $\rho(CH_2)$	953	925
$\nu_{as}(NNC_2)$	1080	1061
ν_{as}(CNN), $\rho(CH_2)$	1170	1167
$\nu_{as}(NC_2)$	1191	1197
$\nu_{as}(NC_2)$	1250	1238
$\nu_s(NO_2)$	1269	1272
$\omega(CH_2)$	1420	1422

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; $\nu_{s}(XY_2)$: Y-X-Y symmetric stretching vibration; $\nu_{s}(XXY_2)$: X-X-Y_2 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; $\gamma_{NN}(XY_2)$: XY_2 twisting vibration about N-N bond.

Table S2. Assignments of IR modes of β-HMX at 1.0 GPa, room temperature

Assignments	Experiment at 1.0 GPa (cm^{-1})	Calculation from the reference (cm^{-1})[1]
b(NNO)	604	594
b(NNO), ν(NN)	628	622
b(NNO), ν(NN)	660	644
σ(ONO)	752	740
σ(ONO)	761	746
b(NCN),	773	778
$\nu_{s}(NC_2)$	832	828
$\nu_{s}(NNC_2)$	873	862
$\nu_{as}(NNC_2)$	949	922
$\nu_{as}(CNN)$, $\rho(CH_2)$	967	937
ν(NN), $\rho(CH_2)$	1091	1057
$\nu_{as}(CNN)$, $\rho(CH_2)$	1148	1137

$\nu_{as}(NC_2)$	1206	1213
$\nu_{as}(NC_2)$	1240	1236
$\nu_s(NO_2)$	1269	1280
$\nu_s(NO_2)$	1294	1294
γ (CH_2)	1350	1347
$\omega(CH_2)$	1395	1397
$\omega(CH_2)$	1401	1404
b(HCH)	1433	1448
b(HCH)	1465	1464
$\nu_{as}(NO_2)$	1540	1615
$\nu_{as}(NO_2)$	1559	1626
$\nu_s(CH_2)$	2990	2967
ν_s(CH2)	2999	2982
$\nu_{as}(CH_2)$	3031	3046
$\nu_{as}(CH_2)$	3040	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; $\nu_s(XY_2)$: Y-X-Y symmetric stretching vibration; $\nu_s(XXY_2)$: X-X-Y_2 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

P (GPa)	a(Å)	b(Å)	c(Å)	β (°)
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)

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

Atom	x	y	z	Occupancy
C1	0.798032	0.946658	0.773322	1
C2	0.258126	0.879227	0.042925	1
N1	0.376078	0.9972	0.705798	1
N2	0.634423	0.023691	0.807141	1
N3	0.979373	0.869389	0.944138	1
N4	0.88208	0.789296	0.018812	1
O1	0.239499	0.050738	0.748774	1
O2	0.280486	0.914581	0.577143	1
O3	0.005061	0.772039	0.195938	1
O4	0.680925	0.730531	0.909049	1
H1	0.894382	0.001621	0.742948	1
H2	0.68972	0.891705	0.661811	1

H3	0.296567	0.899972	0.948885	1
H4	0.338264	0.798074	0.101542	1

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

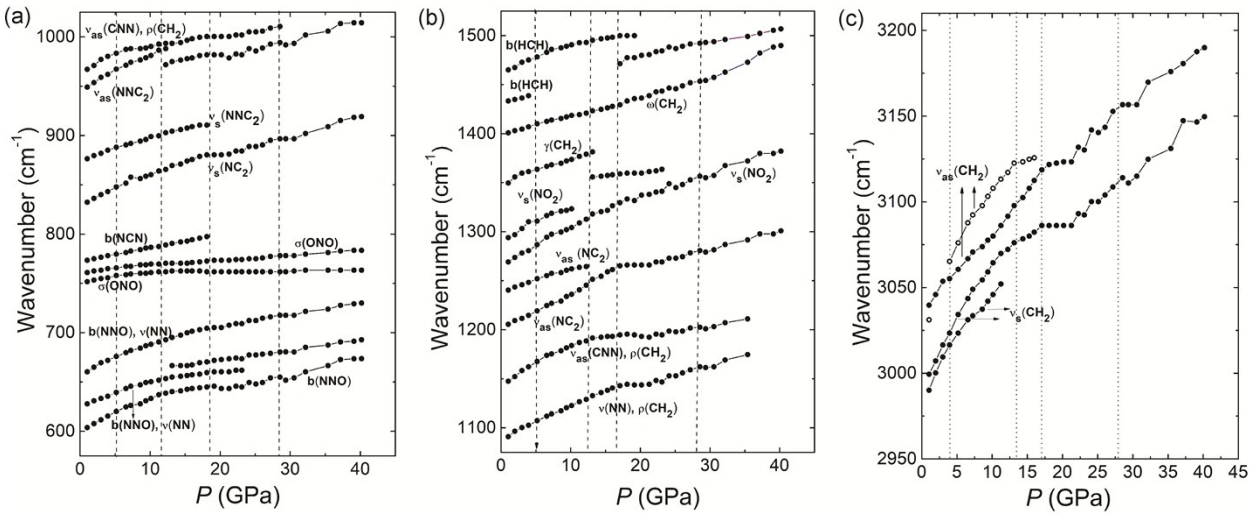

Figure S1. Frequency shifts of *β*-HMX in the IR spectra as a function of pressure in the region of (a) 600-1050, (b) 1050-1650 and (c) 2950-3200 cm^{-1}. The symbol of the different vibration modes can be found in the note of table S2. The dotted lines represent the phase boundaries.

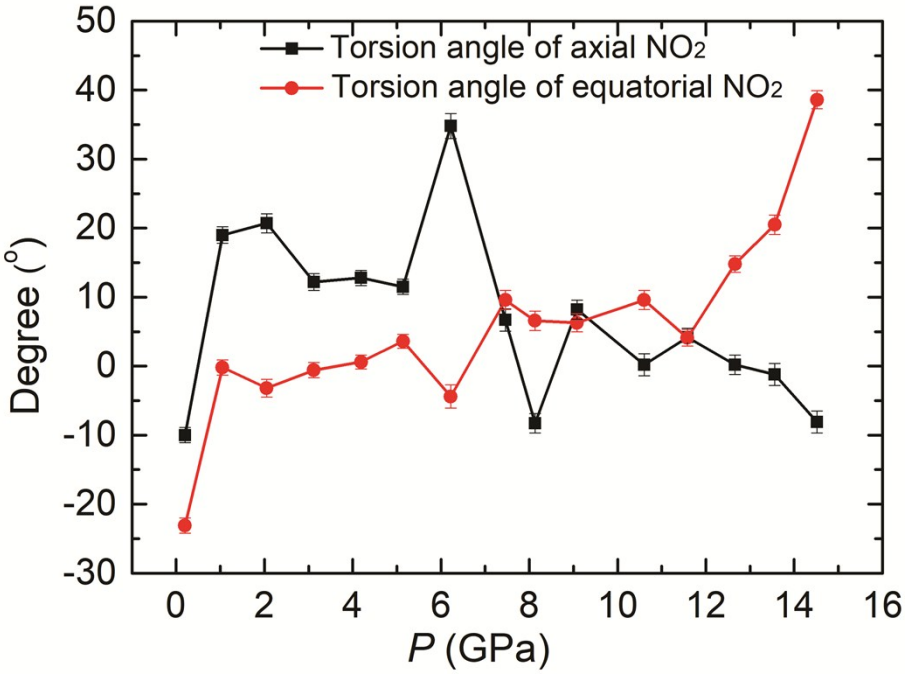

Figure S2. Torsion angles of axial NO_2 (the angle between line C1'-C2 and O3-O4) and equatorial NO_2 (the angle between line C1-C2 and O1-O2) under non-hydrostatic pressure condition. Above 6.2 GPa, the torsion angle abruptly changes by 23.3°.

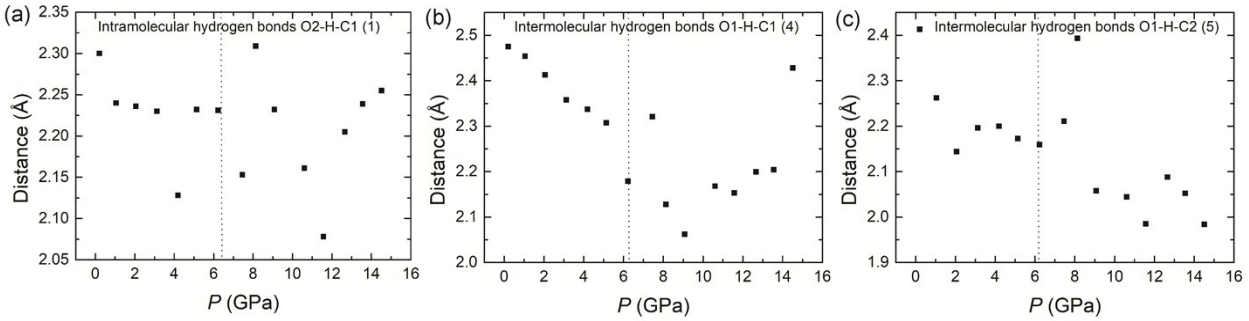

Figure S3. The lengths of hydrogen bonds (O…H) under high pressure. The hydrogen bonds 1, 4 and 5 are indicated in the Figure 7b. (a) is intramolecular hydrogen bond; (b) and (c) are intermolecular hydrogen bonds. The vertical line represents boundary of phase transition.

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.