ELECTRONIC SUPPLEMENTARY INFORMATION

Unraveling the Mechanical Behaviour of Hydrazine Borane (NH_2-NH_2-BH_3)

Pascal G. Yot,*, [a] Vibhav Yadav,[a] Salem Ould Amara,[b] Jean-Paul Itiè,[c] Umit B. Demirci,[b]

Guillaume Maurin[a]

a. Institut Charles Gerhardt Montpellier (ICGM), UMR 5253 Univ Montpellier CNRS ENSCM, CC 15005, Université de Montpellier, Place Eugène Bataillon, F-34095 Montpellier cedex 05, France. e-mail: pascal.yot@umontpellier.fr; Tel.: +33 4 67 14 32 94; Fax: +33 4 67 14 42 90.
b. Institut Européen des Membranes (IEM), UMR 5635 Univ Montpellier CNRS ENSCM, CC 047, Université de Montpellier, Place Eugène Bataillon, F-34095 Montpellier cedex 05, France
c. Synchrotron Soleil, L'orme des Merisiers, Saint-Aubin - BP 48, F-91192 Gif-sur-Yvette cedex, France.

1. High pressure synchrotron X-ray powder diffraction

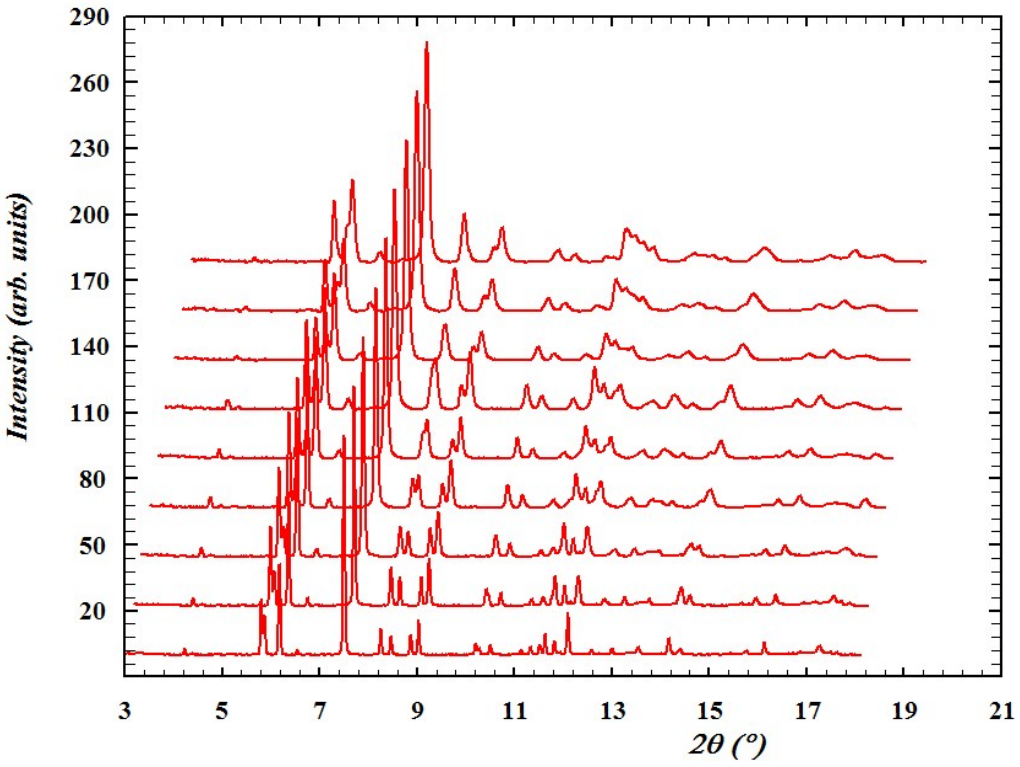


Figure S1. *Waterfall plots of the normalized diffraction patterns of hydrazine borane under increasing pressure (down to up).*

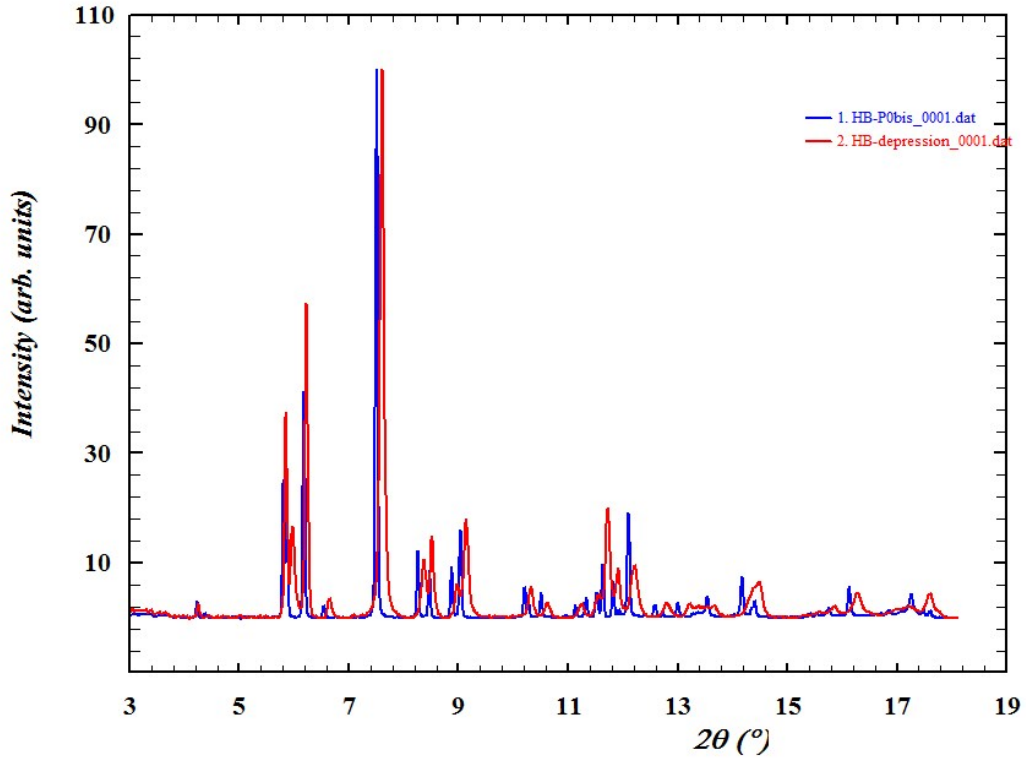


Figure S2. *Comparison of the normalized initial diffraction pattern obtained under atmospheric pressure (in blue) and the diffraction pattern after releasing the pressure (0.44 GPa) (in red).*

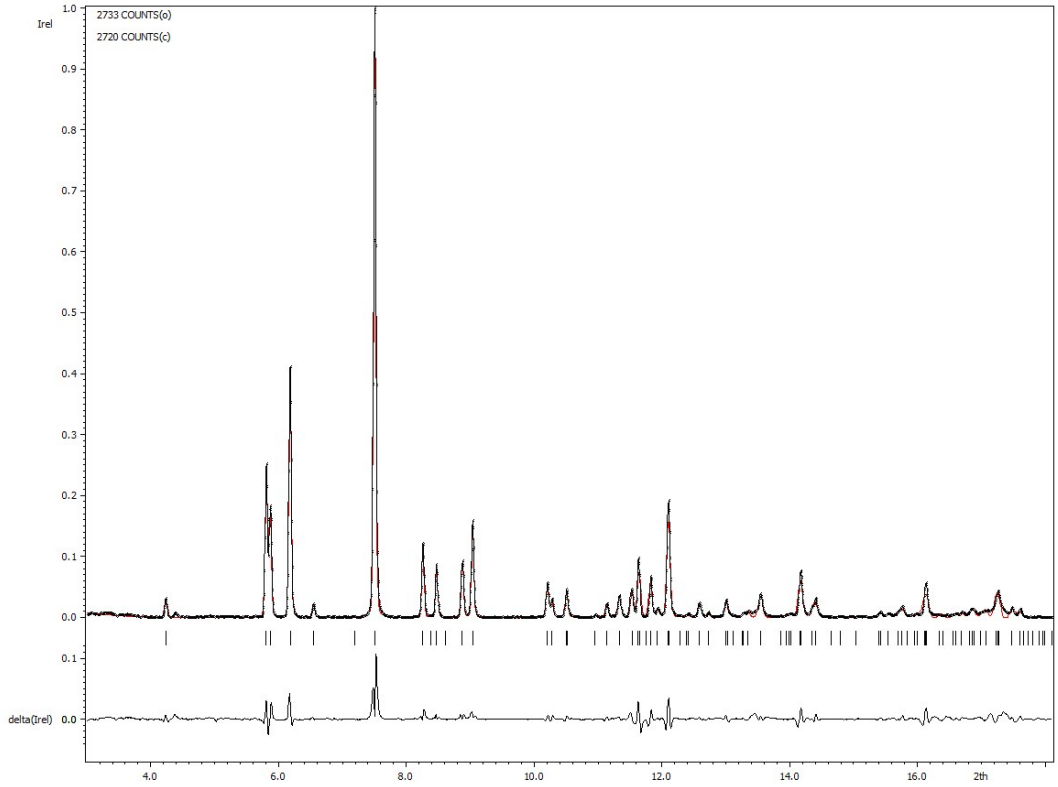


Figure S3. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under atmospheric pressure (GoF = 1.90, Rp = 17.02, wRp = 29.49).*

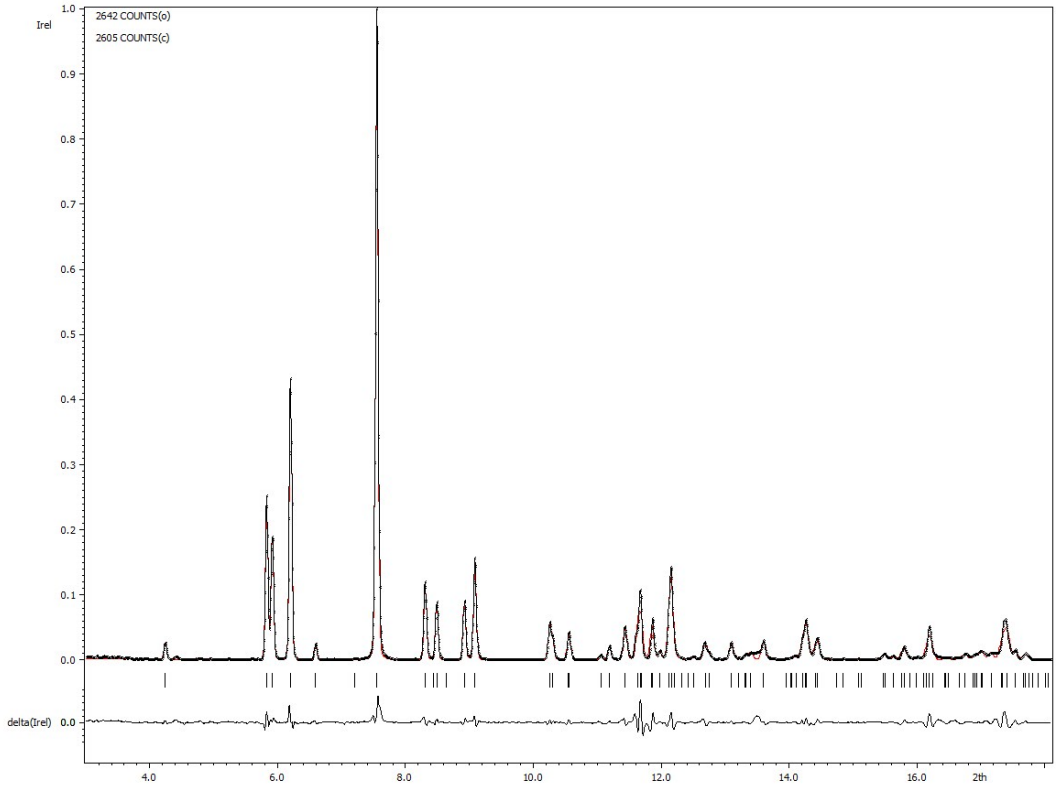


Figure S4. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under ~0.17GPa (GoF = 1.56, Rp = 12.19, wRp = 23.79).*

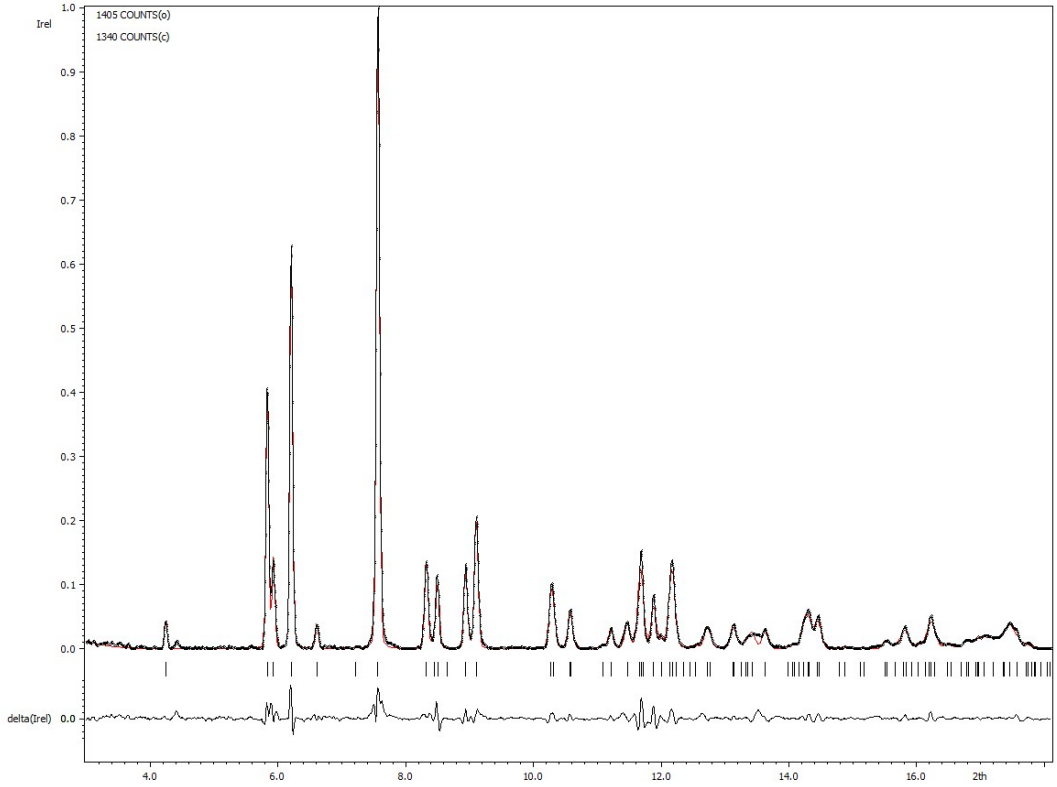


Figure S5. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under ~0.29 GPa (GoF = 1.41, Rp = 12.48, wRp = 23.91).*

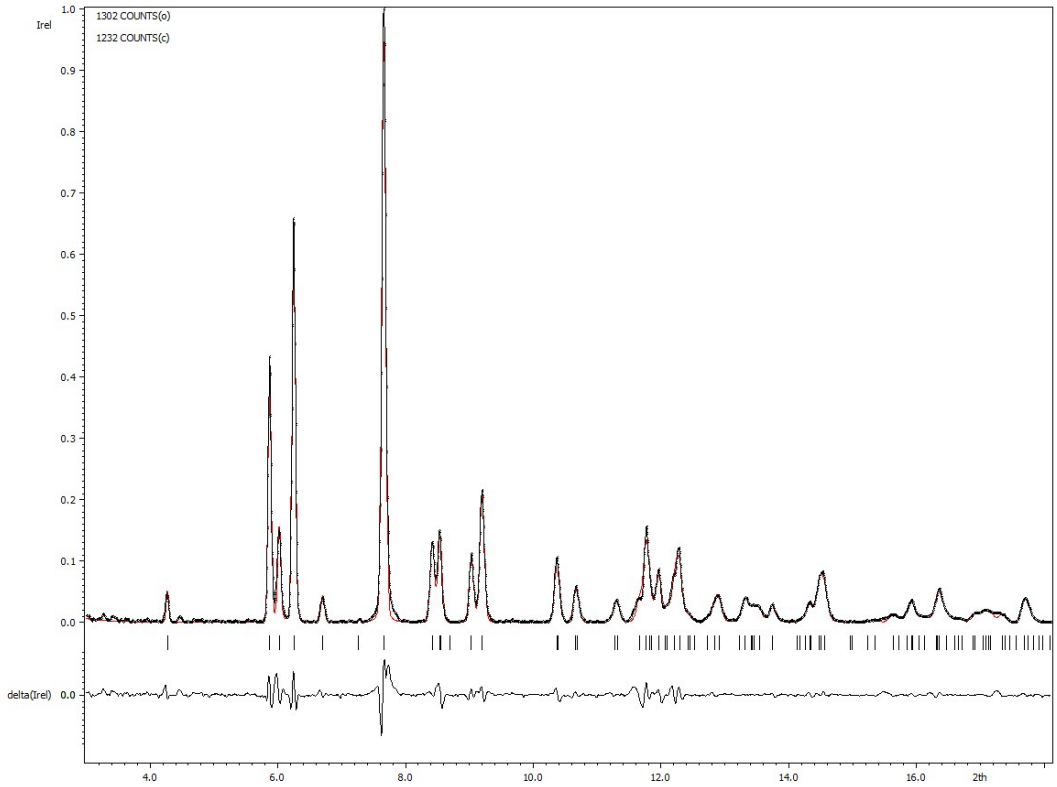


Figure S6. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under ~0.73 GPa (GoF = 1.33, Rp = 11.90, wRp = 21.95).*

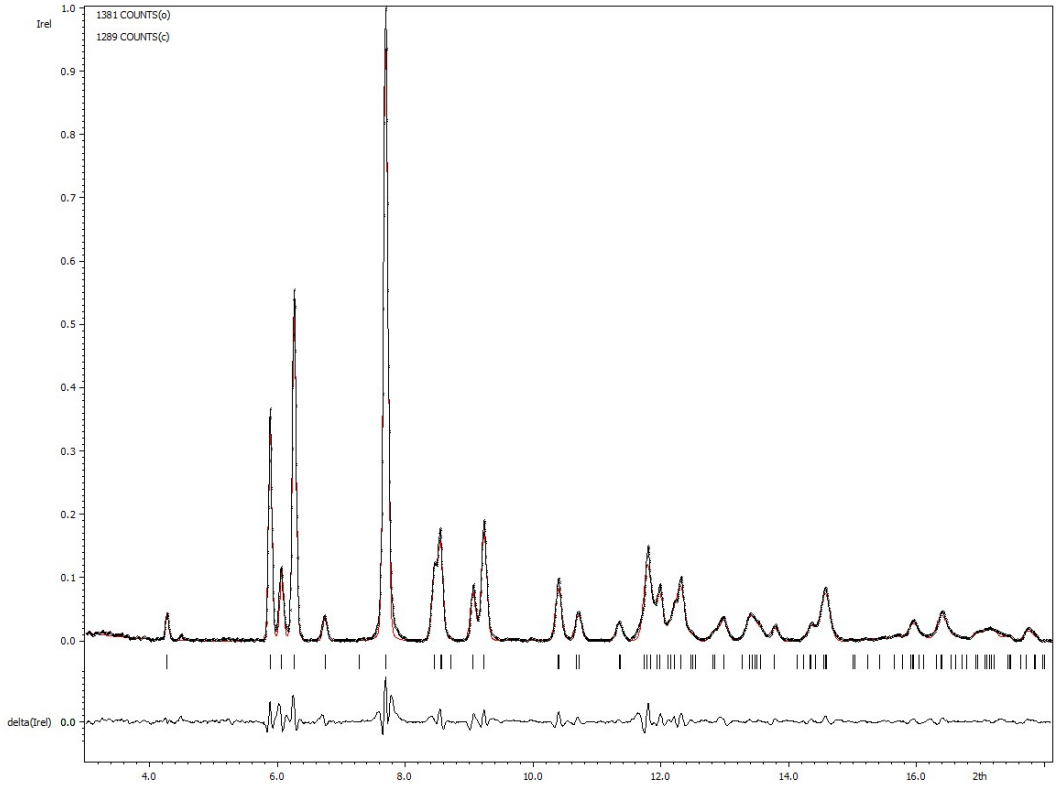


Figure S7. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under ~0.94 GPa (GoF = 1.42, Rp = 11.96, wRp = 22.71).*

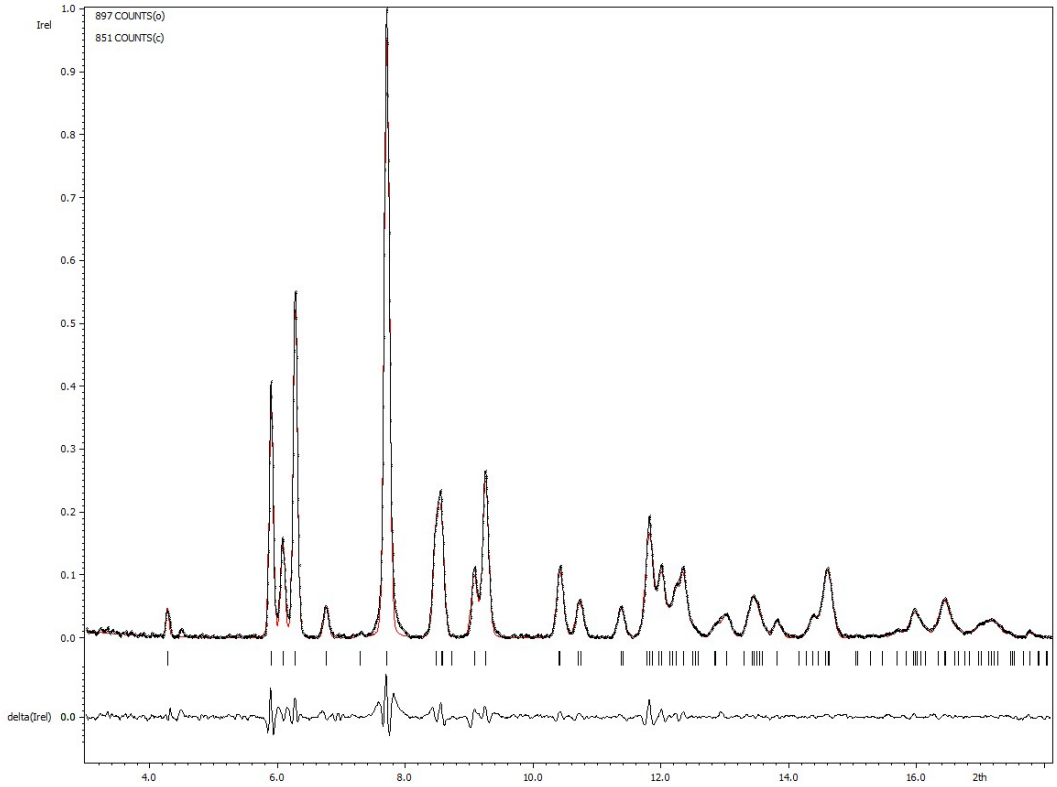


Figure S8. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under~0.99 GPa (GoF = 1.09, Rp = 9.60, wRp = 18.85).*

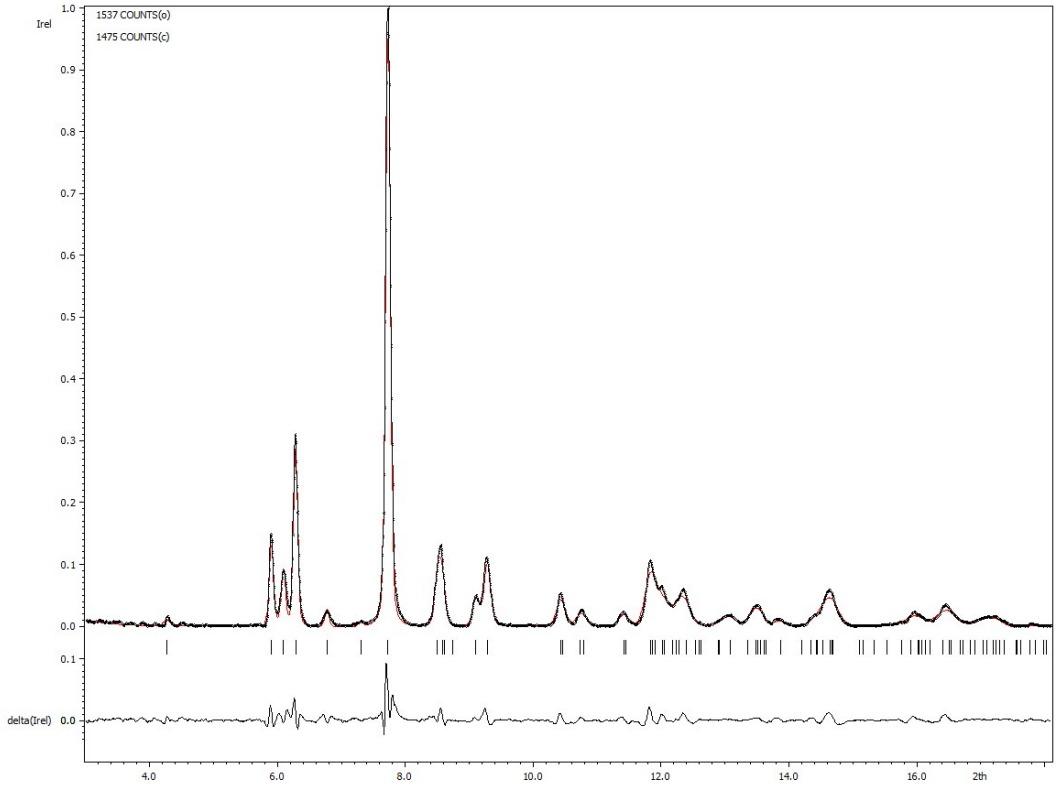


Figure S9. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under ~1.50 GPa (GoF = 1.45, Rp = 13.65, wRp = 23.70).*

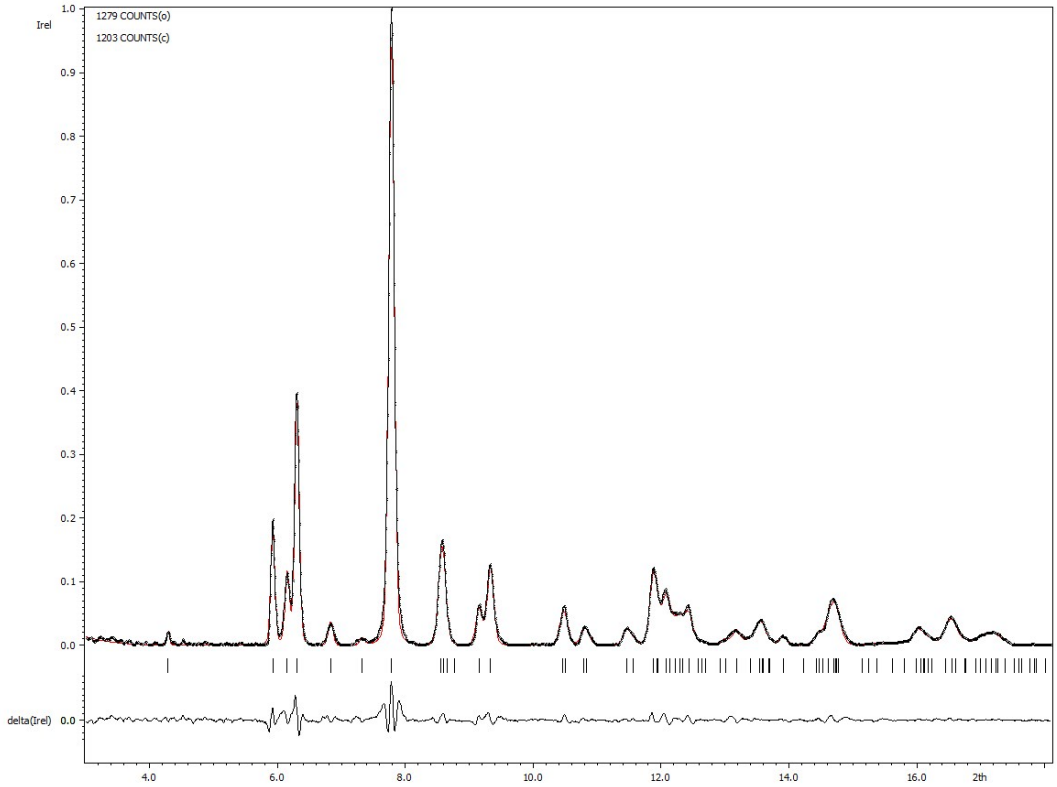


Figure S10. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under~1.17 GPa (GoF = 1.40, Rp = 12.48, wRp = 23.60).*

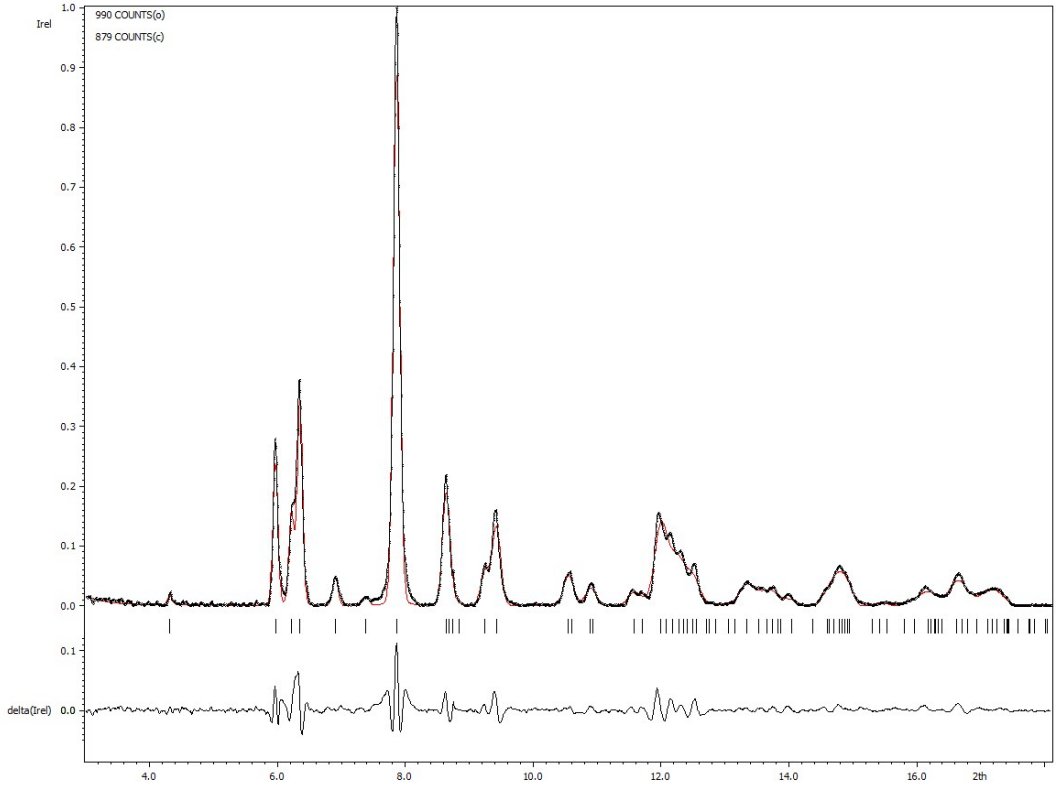


Figure S11. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under ~2.04 GPa (GoF = 1.48, Rp = 14.96, wRp = 24.99).*

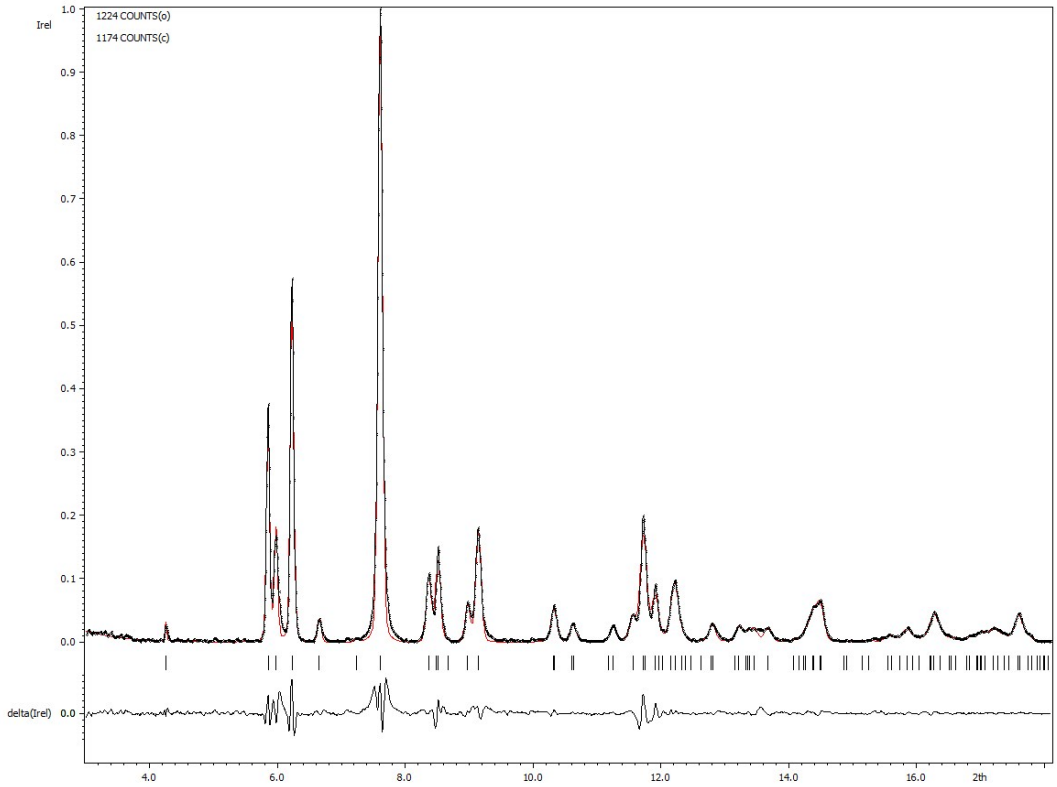
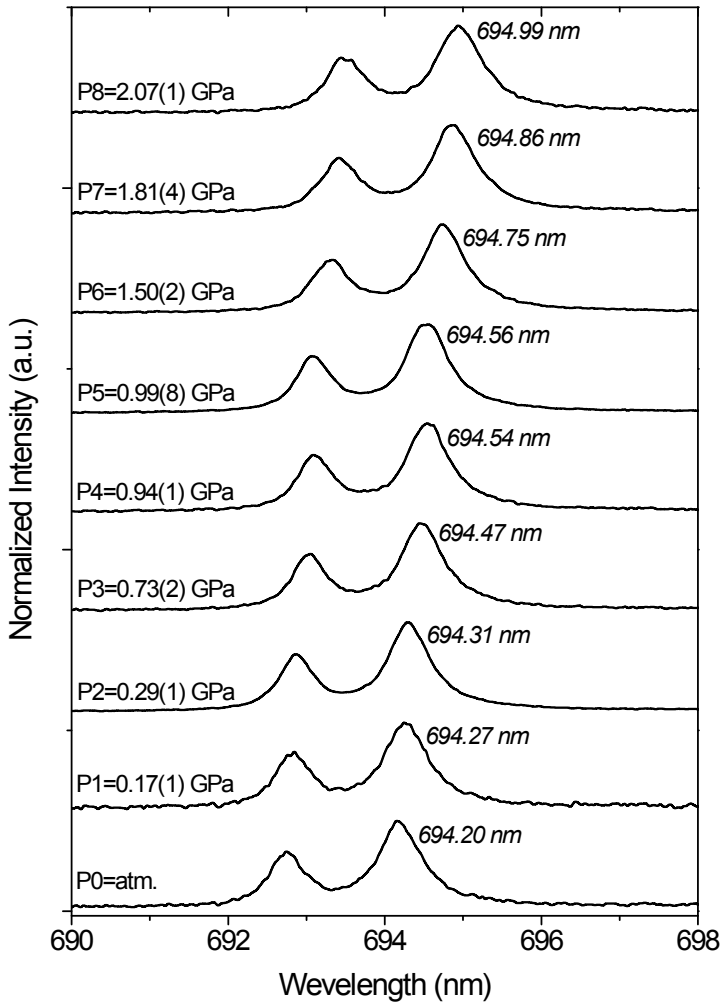


Figure S12. *Structure-independent refinement of the unit cell of the diffraction pattern obtained for hydrazine borane (orthorhombic, S.G. Pbcn) under ~0.44 GPa recorded after releasing the pressure (GoF = 1.44, Rp = 12.37, wRp = 24.22).*

2. Pressure determination by ruby florescence



<u>Figure S13.</u> *Evolution of the R1-ruby fluorescence as a function of the applied pressure in the MDAC. The values of the pressure were determined using the work of Mao et al. [1].*

3. Equation of state determination

The equations of state parameters where determined using EosFit7c software form R. J. Angel [2] using the Birch-Murnaghan model [3, 4].
The third-order Birch-Murnaghan isothermal equation of state is given by the following expression:

$$P(V)=\frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}}-\left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1+\frac{3}{4}(K_P-4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]\right\}$$

where P is the pressure, V_0 is the reference volume, V is the deformed volume, K_0 is the bulk modulus, and K_P is the derivative of the bulk modulus with respect to pressure. The bulk modulus and its derivative are defined as:

$$K_0=-V\left(\frac{\partial P}{\partial V}\right)_{P=0} \text{ and } K_P=-V\left(\frac{\partial K}{\partial P}\right)_{P=0}.$$

In addition a_0, b_0 and c_0 are the reference unit cell parameters, M_0 the compressibility and M_P the derivative of the compressibility along the crystallographic axes.

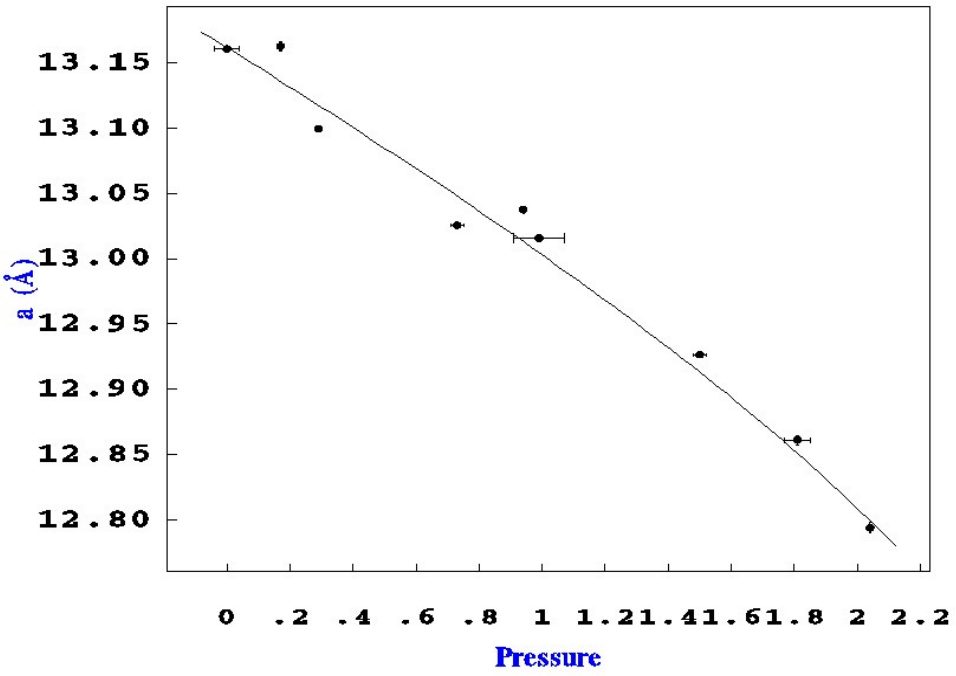


Figure S14. *Evolution of the a-unit cell parameter as a function of the applied pressure.*

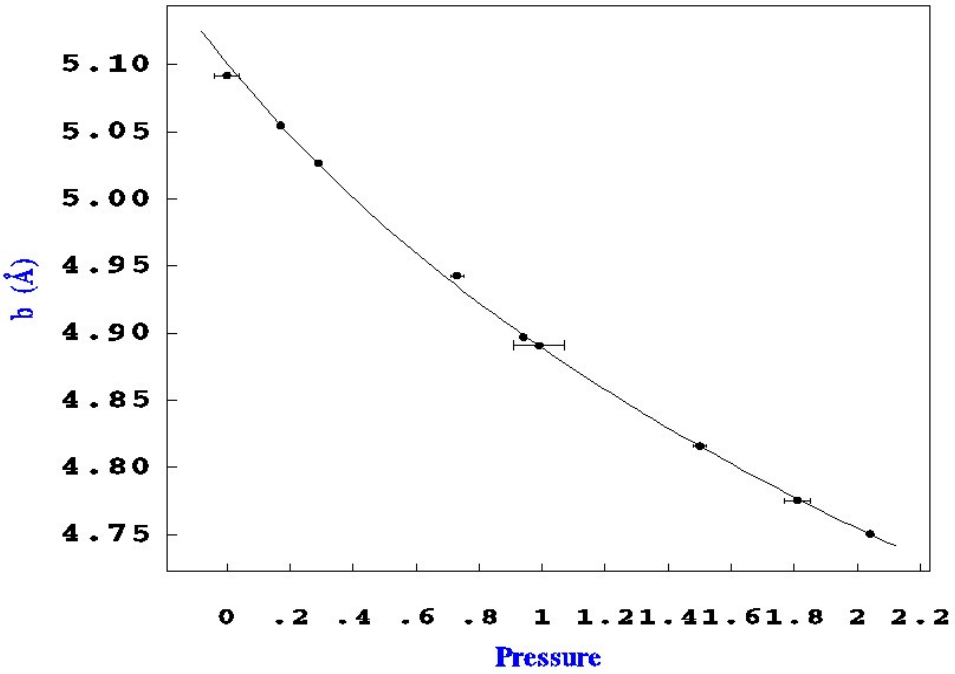


Figure S15. *Evolution of the b-unit cell parameter as a function of the applied pressure.*

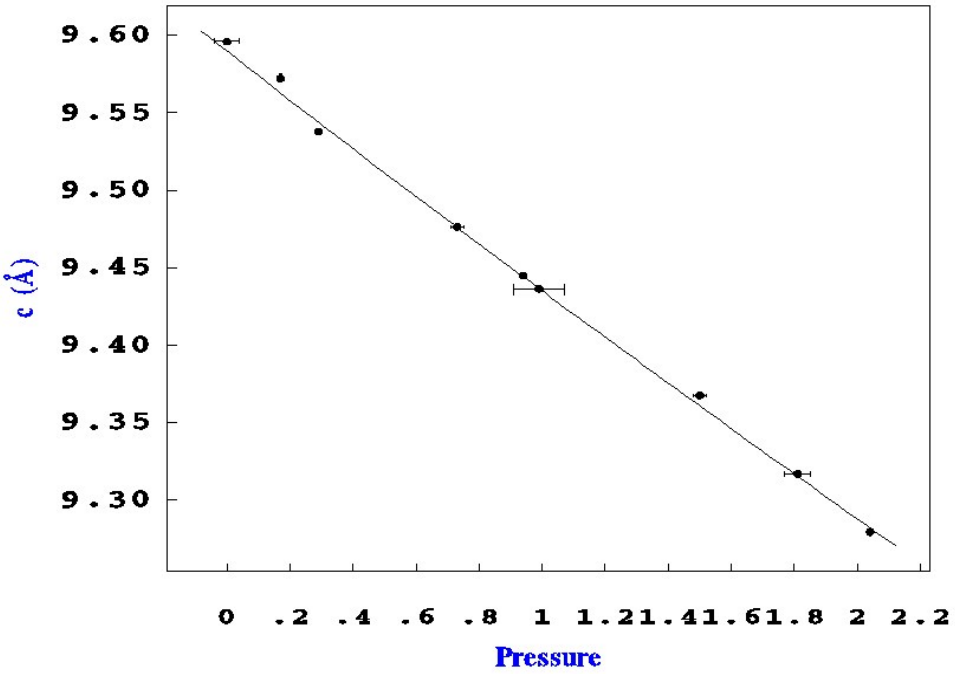


Figure S16. *Evolution of the c-unit cell parameter as a function of the applied pressure.*

4. Molecular Simulation

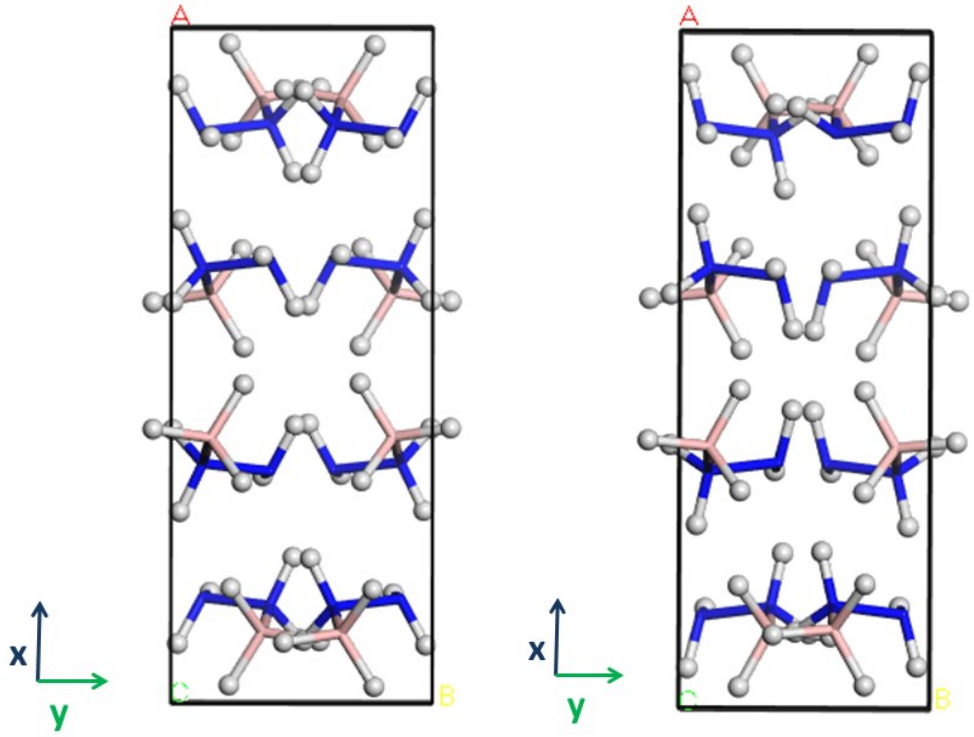


Figure S17. *Comparison between 0 GPa (left) and 2.04 GPa (right) of the pressure induced contraction of the a axisin the corresponding DFT-optimized structures.*

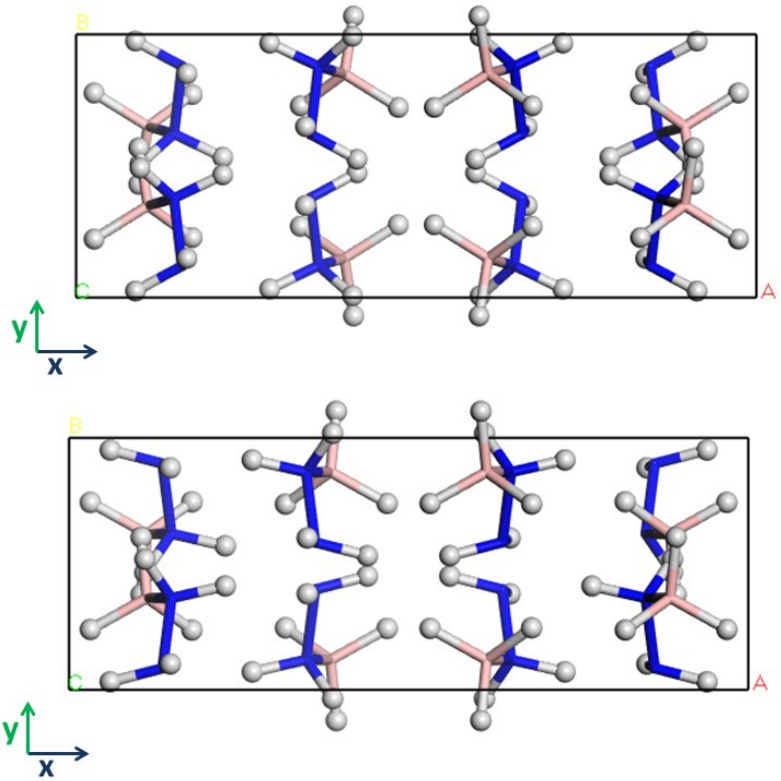


Figure S18. *Comparison between 0 GPa (left) and 2.04 GPa (right) of the pressure induced contraction of the b axis in the corresponding DFT-optimized structures.*

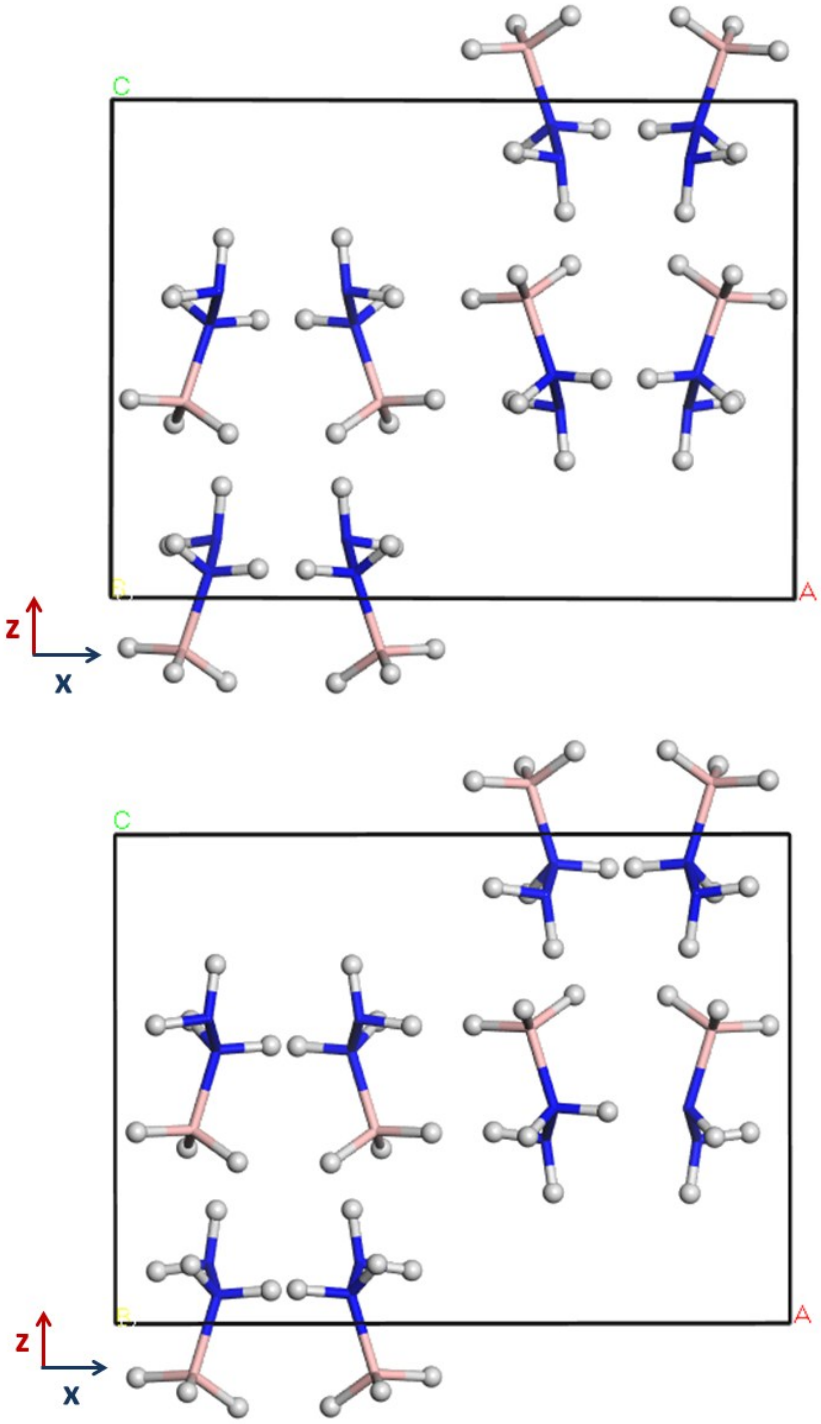


Figure S19. *Comparison between 0 GPa (left) and 2.04 GPa (right) of the pressure induced contraction of the c axis in the corresponding DFT-optimized structures.*

Table S1. *Total and relative electronic energies of the pressure-induced DFT-optimized structures.*

Pressure (GPa)	Energy (kJ.mol^{-1})	ΔE ($E_p - E_{min}$) (kJ.mol^{-1})
0.00	-564800.9154	6.786703
0.17	-564800.822	6.880135
0.29	-564805.9571	1.744989
0.73	-564806.9957	0.706377
0.94	-564804.676	3.026171
0.99	-564804.7655	2.936574
1.50	-564807.7021	0
1.81	-564805.8218	1.880295
2.04	-564803.4701	4.231988

E_p = Energy at given Pressure (kJ/mol) E_{min} = Minimum Energy (at 1.5GPa) (kJ/mol)

Table S2. *N_1-N_2-B-H torsion angle of the hydrazine borane chains averaged over the whole DFT-optimized unit cell.*

Pressure (GPa)	Torsion Angle (°)
0.00	62.0
0.17	62.0
0.29	64.5
0.73	65.0
0.94	66.0
0.99	66.0
1.50	71.5
1.81	72.5
2.04	72.5

Table S3. *Intermolecular N_1-N_1 distances between two neighbor hydrazine borane chains averaged over the whole DFT-optimized unit cell.*

Pressure (GPa)	N_1 - N_1 (Å)
0.00	3.56
0.17	3.55
0.29	3.63
0.73	3.60
0.94	3.60
0.99	3.59
1.50	3.71
1.81	3.70
2.04	3.73

Table S4. *Intermolecular B-B and N_2-N_2 distances between two neighbor hydrazine borane chains averaged over the whole DFT-optimized unit cell.*

Pressure (GPa)	B - B (Å)	$N_2 – N_2$ (Å)
0.00	4.57	3.78
0.17	4.56	3.76
0.29	4.51	3.73
0.73	4.47	3.69
0.94	4.44	3.67
0.99	4.42	3.67
1.50	4.26	3.48
1.81	4.20	3.46
2.04	4.20	3.48

Table S5. *Intermolecular B-N_2 and H-H distances between two neighbor hydrazine borane chains averaged over the whole DFT-optimized unit cell.*

Pressure (GPa)	B – N_2 (Å)	H – H (Å)
0.00	3.61	2.10
0.17	3.59	2.10
0.29	3.56	2.05
0.73	3.51	1.98
0.94	3.49	1.96
0.99	3.48	1.95
1.50	3.45	1.91
1.81	3.41	1.89
2.04	3.37	1.85

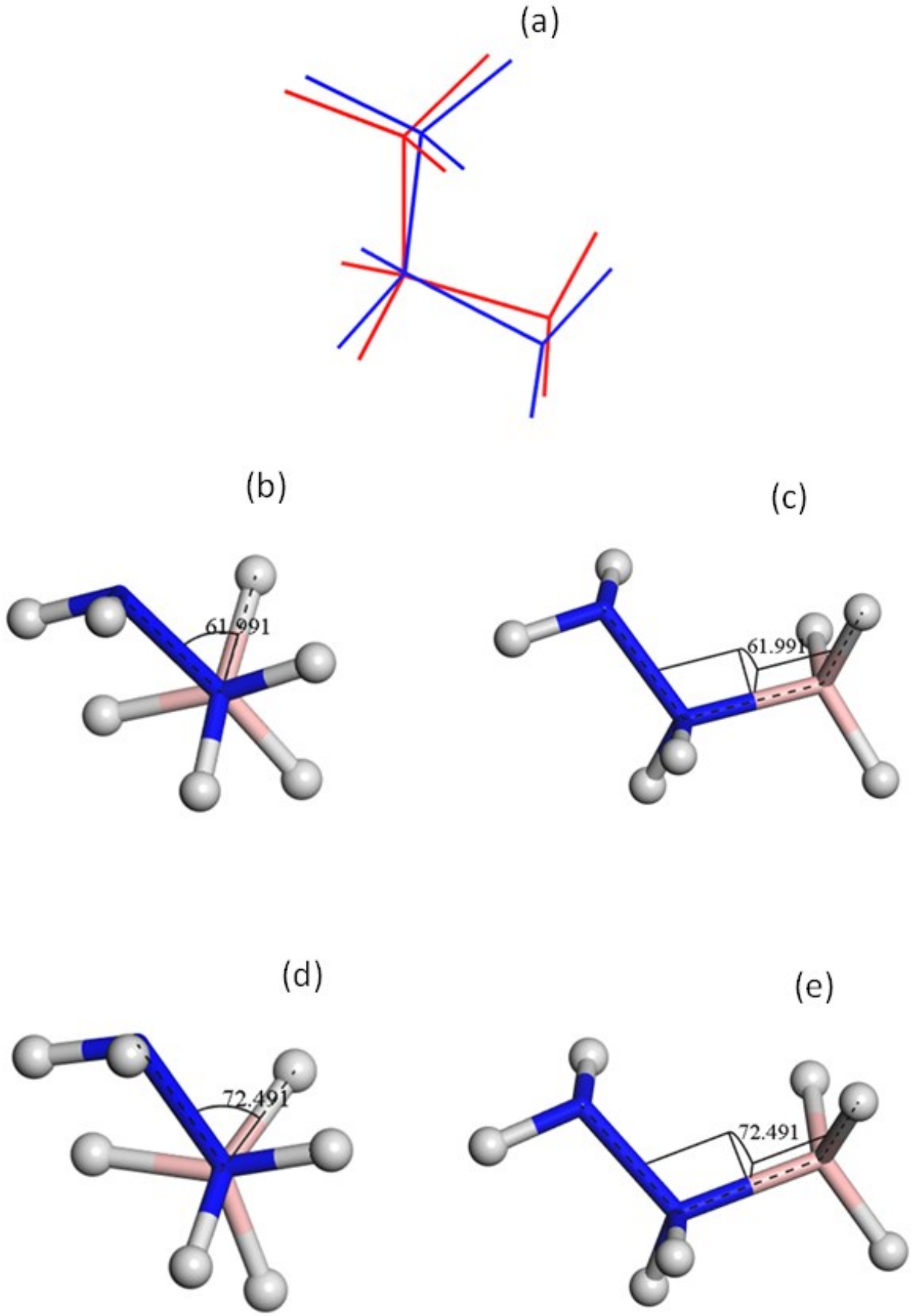


Figure S20. *(a) Superimposed hydrazine borane chains (blue and red correspond to the DFT-optimized structure under 0 and 2.04 GPa respectively). (b, d) and (c, e) corresponds to the N_1-N_2-B-H torsion angle for the HB chains under 0 GPa and 2.04 GPa respectively.*

References

[1] H. K. Mao, J. Xu, P. M. Bell, *J. Geophys. Res.*, **1986**, 91, 4673-4676.
[2] R. J. Angel, M. Alvaro, J. Gonzalez-Platas, *Z. Kristallogr.*, **2014**, 229, 405-419.
[3] F. Birch, *Phys. Rev.*, **1947**, 71, 809-824.
[4] F. D. Stacey, B. J. Brennan, R. D. Irvine, *Geophysical Surveys*, **1981**, 4, 189-232.