

Supporting information for

Pressure induced phase transition of 1,5-diamino-1H-Tetrazole (DAT) under high pressure

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Fig. S1 plots the X-ray powder diffraction (XRPD) pattern under ambient pressure and the simulated X-ray diffraction (XRD) peaks of DAT. Fig. S2(a) plots the lattice parameters and Beta angle as a function of pressure, which were obtained by LeBail fitting by using GSAS-II software package¹. The ambient pressure phase is $P2_1/c$ with a volume of 423.2 \AA^3 from cif file in Ref. 2. Fig. S2(b) displays a fitting to the Second-order Birch–Murnaghan (BM) equation of state (EOS)³ of the ambient pressure phase,

$$P = \frac{3B_0}{2} \left[\left(\frac{V}{V_0} \right)^{\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} \left(B_0' - 4 \right) \left[\left(\frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right] \right\}$$

where V_0 is the ambient volume per formula unit, V is the volume per formula unit at pressure P given in GPa, B_0 is the bulk modulus, and B_0' is the derivative of bulk modulus. It gives the bulk modulus $B_0 = 23(3)$ GPa at a fixed $B_0' = 4$ and fixed ambient volume $V_0 = 423.2 \text{ \AA}^3$. Fig. S3 (a) and Fig. S3(b) plot the LeBail method refinement of XRD patterns at 0.6 GPa and 2.3 GPa for the ambient phase, and the refinement at 0.6 GPa show a good agreement with the structure in Ref. 2. $R_{wp} = 2.47\%$, $R_p = 1.11\%$ at 0.6 GPa and $R_{wp} = 1.23\%$, $R_p = 0.95\%$ at 2.3 GPa. Fig. S4 and Fig. S5 display the Raman and infrared-ray (IR) spectra of DAT at near ambient pressure (0.03 GPa) and decompression to ambient pressure, which consist of external and internal vibrational modes. The external vibrations usually contain lattice vibrations, hydrogen bond modes, and other interactions among individual molecules. The internal modes are typically vibrations of the single molecule itself, which can be tuned by some of the external vibrations. The newfound external vibrations 147 cm^{-1} , 138 cm^{-1} , 104 cm^{-1} , 90 cm^{-1} , 77 cm^{-1} and 60 cm^{-1} in the Raman spectra are lattice modes. The details of the external and internal vibration modes at ambient conditions are listed in Table S1, the results are compared with the IR spectra modes in Ref. 4 and Ref. 5. Some modes are recognized according to Ref. 6 and Ref. 7. In the molecular modes, the modes located in $200\text{-}1000 \text{ cm}^{-1}$ and $3000\text{-}3500 \text{ cm}^{-1}$ are related to NH_2 stretching ($\nu(\text{NH}_2)$) or N-H wagging ($\nu(\text{N-H})$). The modes in $1000\text{-}1800 \text{ cm}^{-1}$ are mostly connected with heterocycle vibrations, plus the N-H bending modes ($\beta(\text{N-H})$) at 1545 cm^{-1} in Raman and at 1636 cm^{-1} , 1659 cm^{-1} in IR^{6,8}. The two typed of DAT polymorphs coexist in the sample because of the existing of their unique vibrational modes. For better clarification in Fig. S4 and Fig. S5, the unique vibrational modes of structure I are marked in

green, the unique vibrational modes of structure II are marked in red, and the other common modes in both are marked in blue. More specifically, the unique modes in the molecular structure I^{4,7} are the in-phase or out-of-phase $\nu_{\text{endo}}(\text{C}=\text{N})$ at 1473 cm^{-1} , 1490 cm^{-1} , 1622 cm^{-1} , the $\nu(\text{N}5\text{H}_2)$ mode at 3323 cm^{-1} , 3193 cm^{-1} in Raman spectra and the in-phase or out-of-phase $\nu_{\text{endo}}(\text{C}=\text{N})$ at 1470 cm^{-1} , 1489 cm^{-1} , 1578 cm^{-1} , the $\nu(\text{N}5\text{H}_2)$ mode at 3317 cm^{-1} in the IR spectra. While the $\gamma(\text{N-H})(\text{ring})$ modes at 937 cm^{-1} , 955 cm^{-1} , the $\nu_{\text{exo}}(\text{C}=\text{N})$ mode at 1669 cm^{-1} , the $\nu(\text{N-H})(\text{ring})$ at 3154 cm^{-1} in the Raman spectra and the $\gamma(\text{N-H})(\text{ring})$ mode at 937 cm^{-1} , the $\nu_{\text{exo}}(\text{C}=\text{N})$ mode at 1730 cm^{-1} , the $\nu(\text{N-H})(\text{ring})$ at 3160 cm^{-1} in the IR spectra can only exist in molecular structure II⁴. At last, almost all the modes recover when decompressed to ambient pressure.

Table S1 Vibrational modes of DAT at near ambient pressure.

| Description | Raman (cm^{-1}) | IR (cm^{-1}) | IR (cm^{-1}) [4] | IR (cm^{-1}) [5] |
|--|----------------------------|-------------------------|-----------------------------|-----------------------------|
| $\nu(\text{N}5\text{H}_2)[6]$ | 3323 | 3317 | 3325 | 3300 |
| $\nu(\text{N}6\text{H}_2)[6]$ | 3271 | | | |
| $\nu(\text{N}6\text{H}_2) [6]$ | 3246 | 3240 | 3240 | 3215 |
| $\nu(\text{N}5\text{H}_2)[6]$ | 3193 | | | |
| $\nu(\text{N-H}) (\text{ring})$ | 3154 | 3160 | 3160 | 3125 |
| $\nu_{\text{exo}}(\text{C}=\text{N})^a$ | 1669 | 1730 | 1685 | |
| $\beta(\text{N-H})$ | | 1659 | 1660 | |
| $\beta(\text{N-H})$ | | 1636 | 1635 | 1642 |
| $\nu_{\text{endo}}(\text{C}=\text{N})^a (\text{out-of-phase})$ | 1622 | | | 1629 |
| $\nu_{\text{endo}}(\text{C}=\text{N})^a (\text{out-of-phase})$ | | 1578 | 1580 | |
| $\beta(\text{N-H})$ | 1545 | | | 1547 |
| $\nu_{\text{endo}}(\text{C}=\text{N})^a (\text{in-phase})$ | 1490 | 1489 | 1490 | |
| $\nu_{\text{endo}}(\text{C}=\text{N})^a (\text{in-phase})$ | 1473 | 1470 | | |
| $\nu(\text{N}=\text{N})$ | | | | 1458 |
| $\nu(\text{ring})$ | | 1332 | 1330 | |
| $\nu(\text{ring})$ | | 1305 | | |
| $\nu_{\text{exo}}(\text{C}=\text{N})^a$ | | | | 1327 |
| $\nu(\text{ring})$ | 1134 | 1134 | | 1130 |
| $\nu(\text{ring})$ | 1105 | 1110 | 1105 | 1105 |
| $\nu(\text{ring})$ | 1078 | 1080 | 1065 | 1071 |
| $\nu(\text{ring})$ | 998 | 1002 | ~1000 | |
| $\gamma(\text{N-H})(\text{ring})$ | 955 | | | |
| $\gamma(\text{N-H})(\text{ring})$ | 937 | 937 | 935 | |
| $\nu(\text{NH}_2)$ | 791 | 790 | 670-800 | |
| | 747 | 747 | | 743 |
| | 697 | 708 | | |
| | 687 | 688 | | |
| | 676 | | | |
| $\nu(\text{C-NH}_2) [7]$ | 495 | | | |
| $\nu(\text{Ring-NH}_2) [7]$ | 370 | | | |

| | | | | |
|--------------|-----|--|--|--|
| | 328 | | | |
| | 322 | | | |
| | 307 | | | |
| | 239 | | | |
| | 230 | | | |
| Lattice mode | 147 | | | |
| Lattice mode | 138 | | | |
| Lattice mode | 104 | | | |
| Lattice mode | 90 | | | |
| Lattice mode | 77 | | | |
| Lattice mode | 60 | | | |

^aexo refers to the stretching mode attached to the five-membered nitrogen heterocycle; ^aendo refers to the stretching mode inside the five-membered nitrogen heterocycle. ν refers to stretching of bond. β refers to bending of bond. γ refers to wagging of bond. The ring with bracket behind modes, such as $\gamma(\text{N-H})(\text{ring})$, means that H is attached to the heterocycle directly.

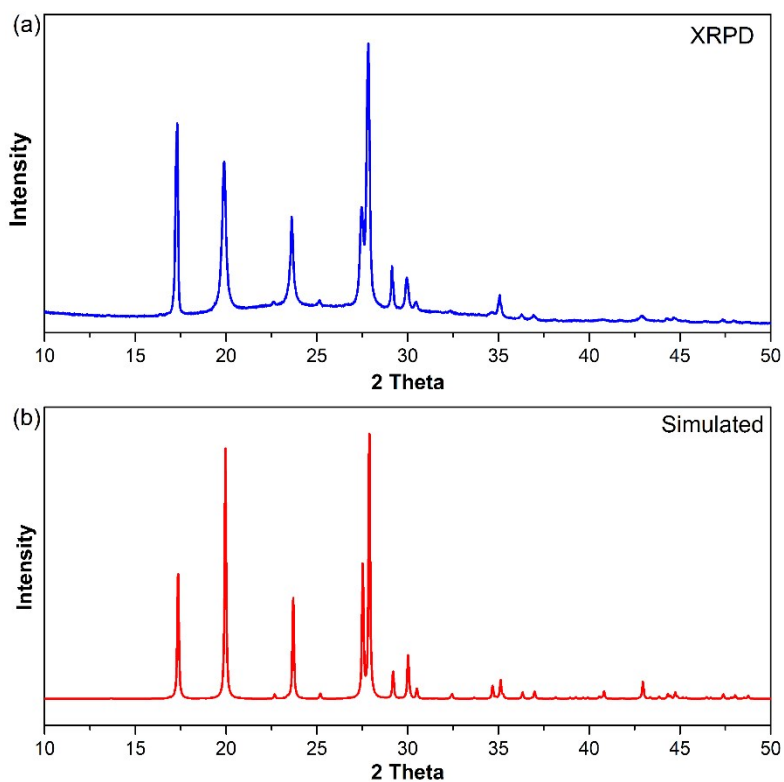


Figure S1 The (a) XRPD (blue) and (b) simulated (red) curve of DAT.

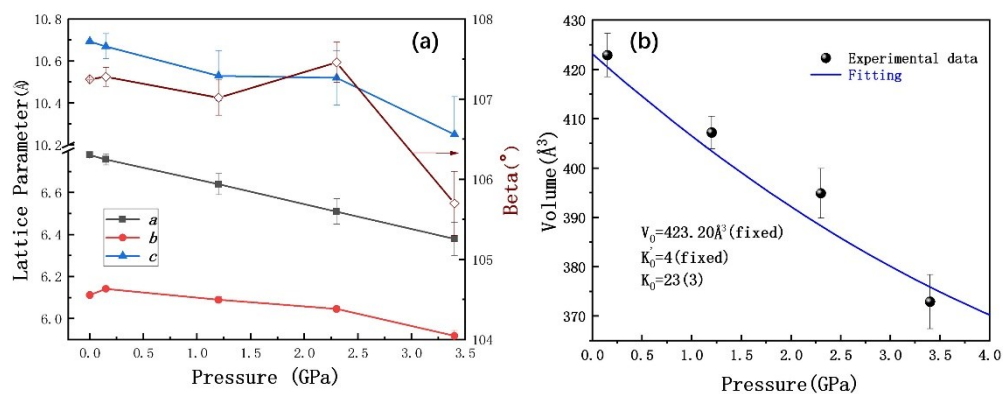


Figure S2 (a) Lattice parameters and Beta angle evolutions as a function of pressure, which were obtained by LeBail fitting by using GSAS-II software package¹. The ambient pressure phase is $P2_1/c$ with a volume of 423.2 \AA^3 from cif file in Ref. 2; (b) A fit to the Second-order Birch–Murnaghan EOS³ of the ambient pressure phase gives the bulk modulus $B_0 = 23(3) \text{ GPa}$ at a fixed $B_0' = 4$ and fixed ambient volume $V_0 = 423.2 \text{ \AA}^3$.

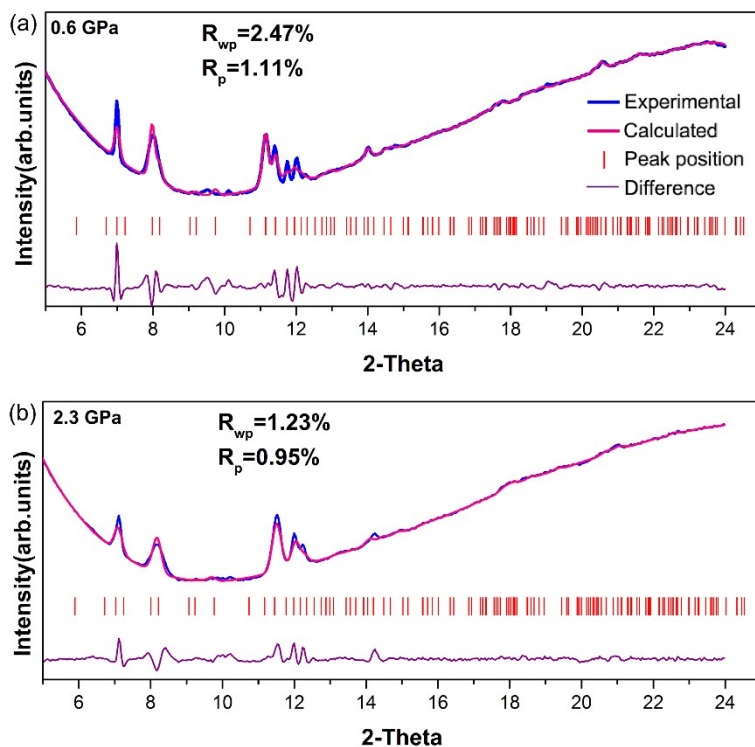


Figure S3 LeBail method refinement of XRD pattern for the ambient phase at (a) 0.6 GPa and (b) 2.3 GPa. $R_{wp} = 2.47\%$, $R_p = 1.11\%$ at 0.6 GPa and $R_{wp} = 1.23\%$, $R_p = 0.95\%$ at 2.3 GPa. The blue, pink and purple lines represent experimental pattern, calculated pattern and the difference between experimental and calculated patterns. The vertical red line stands for the expected positions of diffraction peaks.

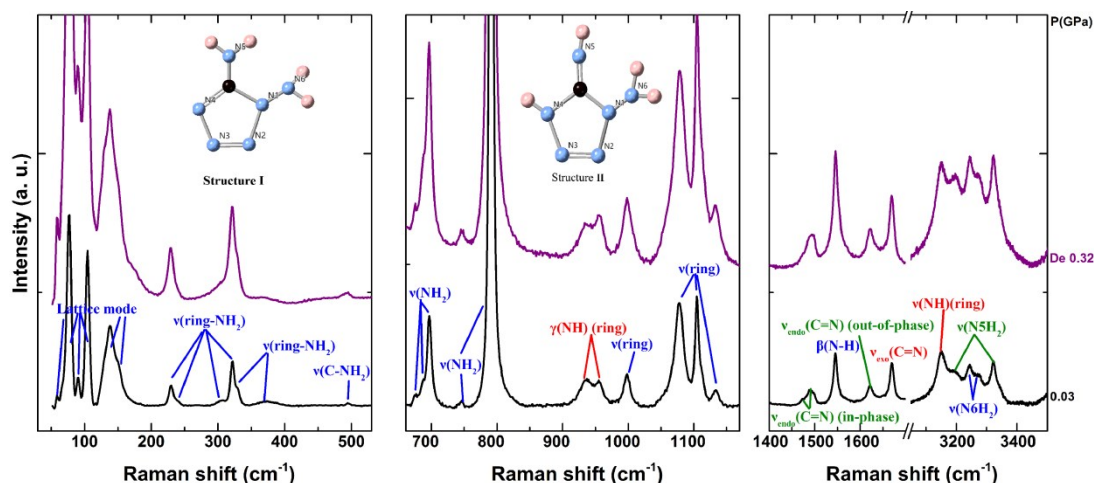


Figure S4 Vibrational modes at ambient pressure (black) and decompression to ambient pressure (purple) in Raman spectra. Inset is two molecular structures of DAT. The blue characters stand for the common modes existing in both of the molecular structures, the green characters stand for the unique modes in structure I, the red characters stand for the unique modes in structure II. The “ring” with bracket behind modes, such as $\gamma(\text{N-H})(\text{ring})$, means that H is attached to the heterocycle directly.

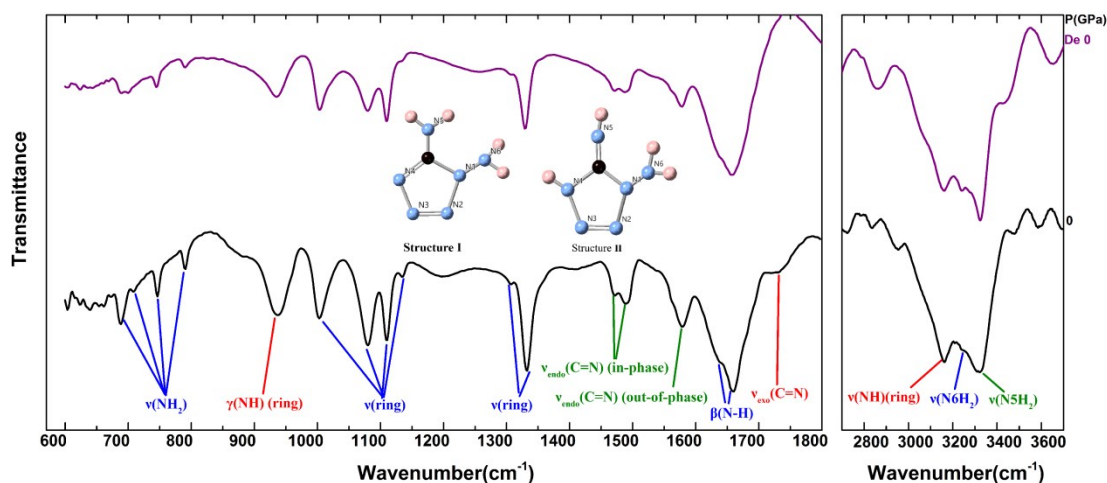


Figure S5 Vibrational modes at ambient pressure (black) and decompression to ambient pressure (purple) in IR spectra. Inset is two molecular structures of DAT. The blue characters stand for the common modes existing in both of the molecular structures, the green characters stand for the unique modes in structure I, the red characters stand for the unique modes in structure II. The “ring” with bracket behind modes, such as $\gamma(\text{N-H})(\text{ring})$, means that H is attached to the heterocycle directly.

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