Shear induced weakening of the hydrogen bonding lattice of the energetic material 5,5'-Hydrazinebistetrazole at high-pressure

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Abstract

5,5'-Hydrazinebistetrazole (HBTA) has been studied by in-situ x-ray diffraction and vibrational spectroscopy to pressures near 25 GPa at room temperature. Analysis of the x-ray diffraction pattern of HBTA collected at ambient pressure and temperature revealed a monoclinic structure consistent with that previously reported. Under compression, the x-ray diffraction reveals little evidence of a phase transition over the pressure range studied. Slight anisotropy in response to compression was noted and the β angle decreased moderately, suggesting geometry modifications occur in the hydrogen bonding lattice and between neighboring HBTA molecules as a result of compression along the *c* axis. Blue shifts in the Infrared active N-H stretching modes were observed, implying a weakening of the hydrogen bond with compression. The weakening of the hydrogen bonding lattice with pressure may lead to an increase in the bending angle of the C-N=N-C bridge between the tetrazole rings and an increased overlap between the π -bonding orbitals. The Raman spectra showed a number of modes associated with HNNH motions of the bridge become more prominent in the spectra under compression. Additionally, the possibility that the increased bend in the angle of the C-N=N-C bridge results from a shearing deformation is discussed.

Introduction

The physical and chemical response of energetic materials at the molecular level to extreme pressure and temperature conditions has been of long standing interest due to the direct similarities experienced by materials under shock loading and initiation processes [e.g. 1-15 and references therein]. Despite the fact that reaction mechanisms for conventional energetic materials, such as RDX and TNT, have been studied for well over a decade, there still is considerable debate about the critical fundamental reaction steps, as well as the importance of including intermolecular interactions, structural rearrangements and phase transitions in these kinetic mechanisms. It has been shown that energetic performance varies widely between polymorphs [13, 16]. As such, measuring the polymorphic phase behavior in response to static high-pressure conditions is necessary to reveal basic details regarding molecular deformation, interactions, and decomposition under pressure, thus yielding a better understanding of the basic chemistry under application of extreme conditions, as is found in detonation. This work is part of a continuing series that focuses on the development of a deeper understanding of the high pressure characteristics of high nitrogen materials [1, 8, 10, 14-15]. In this respect, this report will focus on the structural stability and vibrational behavior of 5,5'-Hydrazinebistetrazole (HBTA), shown in Figure 1.

INSERT FIGURE 1

In recent years, nitrogen-rich energetic materials have attracted interest for applications relating to gas generators, low-signature propellants, and additives to pyrotechnics and explosives. Additionally, explosive formulations which utilize nitrogen-rich energetic materials pose significantly lower environmental and safety hazards than traditional energetic materials such as RDX, as high-nitrogen materials can have high thermal stabilities and a primary decomposition product of molecular nitrogen. Thus, they generate large amounts of gaseous products and are likely environmentally greener than conventional energetic materials. In many cases, detailed chemical and physical characterization of these new high-nitrogen materials has been conducted at ambient conditions, but many are still not fully characterized over a range of thermodynamic conditions.

The molecular structure of HBTA ($C_2H_4N_{10}$), shown in Figure 1, was determined by Klapotke and Sabaté from single crystal x-ray diffraction [17]. The molecule was found to crystallize in the monoclinic space group $C2/c$ with $a = 12.401(3) \text{ \AA}$, $b = 5.513(1) \text{ \AA}$, $c =$

9.835(2) Å and $\beta = 115.57(3)$. In contrast to other azotetrazolates, which have coplanar tetrazole rings, the sp^3 character of the C-N=N-C bridge allows the tetrazole rings to rotate out of plane, which could have important implications for stability at high pressures. The unit cell of HBTA consists of four molecules, each of which form up to eight hydrogen bonds with average distances of 2.93 Å. The extensive hydrogen bonding results in a closely packed structure with a high density of 1.84 g/cm³. It has been postulated this extensive hydrogen bonded network leads to the high thermal stability and low sensitivity of HBTA despite its high nitrogen content [17]; similar effects have been observed in the insensitive hydrogen bonded material, TATB [18]. The mechanical properties and energetic characteristics have been reported [17]. Here, the *in-situ* isothermal x-ray diffraction and vibrational spectroscopic studies of the behavior of HBTA to pressures near 25 GPa are reported. The primary experimental motivations were to examine the structural and chemical response of HBTA under compression, to search for possible structural transitions in the material and determine changes to the vibrational spectra in an effort to better understand the role hydrogen bonding plays in the stabilization of the material to near its detonation pressure of 27.7 GPa [17].

INSERT FIGURE 1

2. Experimental Methods

Polycrystalline 5,5'-Hydrazinebistetrazole (HBTA) was obtained from the laboratory of Dr. Tom Klapötke at the Ludwig-Maximilians-Universität Munich and recrystallized twice in acetone to remove any impurities. Yellow needle shaped crystals were obtained from the recrystallization process, which were gently mechanically ground into a fine powder.

High-pressure conditions were generated in a piston-cylinder type diamond anvil cell (DAC). Approximately 120 micrograms of HBTA and a ruby sphere were loaded into the sample compartment of a stainless steel gasket (thickness ~75 microns, diameter 160 microns), which was then filled with a neon pressure-transmitting medium, using a high-pressure gas loading vessel previously described [19]. The ruby fluorescence method, which correlates the shifts of the R_1 and R_2 lines of ruby to a well-defined equation of state, was used to monitor the *in-situ* pressure [20]. The precision of such measurements at room temperature is estimated to be ± 0.1 GPa. Ruby fluorescence measurements were conducted both prior to and proceeding the spectroscopic or x-ray measurements to ensure pressure stability.

The 514 nm line from a cw diode-pumped solid-state laser was employed for the Raman excitation with an output power less than 100 mW and a laser spot diameter of $\sim 4 \mu\text{m}$. A 460 mm focal length $f/5.3$ imaging spectrograph equipped with an 1800 grooves/mm grating with a resolution of $\pm 0.5 \text{ cm}^{-1}$ was used. Prior to any experimental measurements, a wavelength calibration was performed using a neon lamp; this method of calibration has an accuracy of $\pm 1 \text{ cm}^{-1}$. Synchrotron Infrared (IR) absorption measurements were obtained at beamline U2A of the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (BNL) to near 20 GPa. The spectral resolution of $\pm 4 \text{ cm}^{-1}$ was used for all IR measurements. Room temperature isothermal angle dispersive X-ray diffraction experiments were conducted at beamline 12.2.2 of the Advanced Light Source (ALS) with a 0.049 nm x-ray beam collimated to $15 \mu\text{m} \times 15 \mu\text{m}$; the average collection time per patterns was 180 seconds. In order to limit the sample damage caused by the intense x-ray beam, the beam was strongly attenuated and the beam position was rastered over the entire sample during the course of collection. Structural parameters were determined from the diffraction patterns using Jade software with the LeBail fitting routine. Unit cell parameters at pressure were estimated from lower pressure values and the unit cell parameters were refined based on prominent, clearly identifiable peaks. The refinement of the atomic positions with pressure was not attempted, due to the large number of atoms per unit cell coupled with the need to account for a large number of hydrogen positions and a limited number of diffraction peaks. The resulting volume data was analyzed using a third-order Birch-Murnaghan (BM) equation of state [21].

3. Results and Discussion

Analysis of the x-ray diffraction pattern of HBTA collected at ambient pressure and temperature revealed a $C2/c$ monoclinic structure and the indexing agreed favorably with that of the previously reported crystallographic structure [17], with lattice parameters of $a = 12.415(2) \text{ \AA}$, $b = 5.517(9) \text{ \AA}$, $c = 9.842(3) \text{ \AA}$ and monoclinic angle $\beta = 115.63(2)$. The lattice parameters at ambient pressure refined in this work are marginally larger than those previously reported (Table 1), a trend that can be attributed to thermal expansion. Representative x-ray diffraction patterns of HBTA under compression to near 25 GPa are shown in Figure 2 and reveal no clearly discernable changes that could suggest a phase transition. As such, it can be concluded that the monoclinic phase likely persists up to pressures near where detonation would be observed under

shock impact. At pressures near 3.5 GPa, there is an drop in the intensity of the feature near 13.3°, which can be attributed to several factors, most importantly the increase in random alignment of polycrystalline sample as a result of sample compaction. In general, over the pressure range studied, the peak widths remain fairly uniform, which suggest a nearly hydrostatic pressure distribution within the DAC and a low degree of strain on the polycrystallites. As can be seen in Figure 2, the x-ray diffraction of HBTA collected upon recovery from the compression experiments are similar, although the peaks are notably broader in the recovered sample. This trend is likely due to plastic deformation of the crystal.

INSERT TABLE 1.

INSERT FIGURE 2.

The pressure dependence of the cell parameters are illustrated in Figure 3. The lattice vectors exhibit a slight anisotropy in response to compression, with the smallest lattice deformation noted along the *a* and *b* axes. This observation is not surprising as the tetrazole rings are oriented along these crystallographic axes and any deformation is likely to be small. Higher compressibility of the lattice parameters is observed along the *c* axis, which shows a 3.6% decrease over the pressure range studied. This result is not unexpected as the HBTA stacks primarily occur along this axis and at ambient pressure the gaps between the HBTA molecules is nearly 4 Å [17]. Over the pressure range studied, the β angle decreases moderately from 115.6° to 112.5° which suggests structural changes caused by the compression of HBTA molecules along the *c* axis occurs through shear of the layers. This effect is particularly pronounced within the region from 0.1 GPa to near 6.5 GPa and likely reflects a change in the nature of the interactions between the adjusting HBTA molecules. This suggestion will be discussed further in conjunction with the spectroscopic results in subsequent paragraphs.

INSERT FIGURE 3.

The bulk compressibility was determined by fitting a third-order isothermal Birch-Murnaghan equation of state [21] to the pressure-volume data, shown in Figure 4 and the pressure dependencies of the cell axes using the program EOS-FIT [22]. Analysis of the data collected on HBTA yielded a bulk modulus of 21.8 ± 2.7 GPa with a pressure derivative of 3.8 ± 0.21 . The bulk modulus of HBTA is slightly higher than the structurally and chemically related Dihydrazinium 5, 5'-azotetrazolate dihydrate molecule [23] which was determined to have a bulk modulus of 11.5 GPa using methods similar to the analysis employed herein. In addition to

the azotetrazolate molecule, Dihydrazinium 5, 5'-azotetrazolate dihydrate also consists of dihydrazinium cations and water molecules that are held together by both strong hydrogen bonds as well as weaker van der Waal interactions. In contrast, the HBTA unit cell has a fairly rigid structure due to the moderately strong hydrogen bonding network and the out-of-plane azotetrazolate structure. The density of HBTA increases to near 2.5 g/cm³ over the pressure range studied, as is shown in Figure 5. The most rapid compression occurs between 0 and 15 GPa, and above 15 GPa the density increases only incrementally, indicating near maximum compressibility has been obtained.

INSERT FIGURES 4 and 5

Infrared spectra collected as a function of pressure (Figure 6) show pronounced changes in the spectral regions associated with N-H stretching and bending, signifying modifications to both the intramolecular and intermolecular interactions of HBTA. As pressure increases, the N-H stretching modes, observed between 2600 and 3200 cm⁻¹, show a blue shift, implying a weakening of the hydrogen bond with compression. This trend is in direct contrast to the common observation of a red shift in the stretching frequencies associated with hydrogen bonds, which implies a strengthening of the hydrogen bond [24, 25]. One plausible mechanism that could result in a weakening of the hydrogen bond with pressure is an increase in N-H...N distance. The N-H...N distance is likely to be increased by an increase in the bend of the C-N=N-C bridge between the tetrazole rings. An increase in the angle of the C-N=N-C bridge which is accompanied by a corresponding decrease in the intermolecular distance between the HBTA stacks would result in increased overlap between the π -bonding orbitals and thus a likely increase in the Raman intensity associated with these modes. This suggestion is supported by the Raman spectra (Figure 7) which shows a number of modes associated with HNNH motions of the bridge become more prominent in the spectra under compression, a trend which persists to the highest pressures studied. In particular, modes near 570 cm⁻¹ (H-wag of tetrazole ring), 694 cm⁻¹ (H-N-N-H bend of tetrazole bridge), 735 cm⁻¹ (H-N-N-H wag of tetrazole bridge) and 815 cm⁻¹ (H-N-N-H in phase bend of tetrazole bridge) become clearly resolvable. While the mechanochemical origin of the HBTA bridge bend remains speculative, it is suggested this bending results from an inhomogeneous shearing deformation which likely propagates from the (100) slip plane that lies parallel to the a axis. Compression along this shear axis likely leads to buckling of the C-N=N-C bridge and, as a result, the layers of molecules positioned along this

axis can slip to some extent and create deformations in the geometry of the molecular units. This suggestion is supported by the x-ray diffraction, but conclusive evidence would require a full Reitveld analysis from single crystal diffraction, which is beyond the scope of this paper. The slip of the molecular stacks is likely to result in defects that could potentially aid in the formation of hot-spots. The formation of hot spots has been shown to play an important role in initiation mechanisms (see for example, Ref. 26-29). Upon decompression, there is a slight hysteresis in the location of the N-H frequencies, which could be justified by the slight shift in the slip planes. It is unlikely that plastic deformation in response to stress would be reversible under compression.

INSERT FIGURES 6 and 7

4. Conclusions

In conclusion, x-ray diffraction and vibrational spectroscopic results demonstrate the stability of the monoclinic phase of HBTA under hydrostatic compression to pressures near 25 GPa. HBTA undergoes a weakening of the hydrogen bond which can be attributed to a buckling of the C-N=N-C bridge in response to compression. This is likely accomplished through a shearing deformation along the (100) slip plane, which leads to plastic deformation of the extended structure of HBTA. The activation of the shear axis and the potential generation of defects may be an important factor leading to hot spot formation in the pressure regime close to that of detonation in HBTA.

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Table 1. Crystallographic data and details of measurement for HBTA at ambient pressure, where ρ is the density and T is the temperature

	Klapotke et al. [17]	This study
a (Å)	12.401 (3)	12.415 (2)
b (Å)	5.513(1)	5.517(9)
c (Å)	9.835 (2)	9.842(3)
β (°)	115.57(3)	115.63(2)
V (Å) ³	606.6(9)	607.7(9)
ρ (g/cm ³)	1.84	1.84
T (K)	200	298

Figure 1. (a) Molecular structure of an isolated HBTA molecule. (b) Crystal packing of an HBTA unit cell viewed down the b axis. Hydrogen bonds are shown as dashed blue lines between neighboring molecules (c) the extended network of HBTA shown along the c axis. Hydrogen bonds are shown as dashed blue lines.

Figure 2. Selected X-ray diffraction patterns of HBTA collected as a function of pressure. The patterns are offset for clarity. The pattern collected upon decompression from near 25 GPa is indicated with a 'd' in the pressure labeling.

Figure 3. Pressure dependence of the lattice vectors (left) and monoclinic β -angle (right) of HBTA upon compression (filled markers) and decompression (open markers). Points have been fit to a third-order polynomial to help guide the eye for both the compression (solid) and decompression (dashed) cycles.

Figure 4. Pressure-volume relationship of HBTA upon compression (squares) and decompression (triangles), based on unit cell refinements using x-ray diffraction data. The compression data was fit to a third-order Birch-Murnaghan equation of state (solid line). The decompression data was fit to a third-order polynomial to help guide the eye (dashed line).

Figure 5. The density of HBTA as a function of pressure collected upon compression (squares) and decompression (triangles). Points have been fit to a third-order polynomial to help guide the eye for both the compression (solid) and decompression (dashed) cycles.

Figure 6. Select Infrared spectra shown as a function of pressure. Spectra are offset for clarity. The data collected upon decompression from near 25 GPa is indicated with a 'd' in the pressure labeling.

Figure 6. Select IR spectra shown as a function of pressure. Spectra are offset for clarity.

Figure 7. Select Raman spectra shown as a function of pressure. Spectra are offset for clarity.