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X-ray Diffraction Studies of Single Crystals at High Pressure using Synchrotron Radiation

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Abstract

X-ray diffraction from single crystals is the most descriptive method of analyzing solid-state structure and convenient experimental methods for analyzing samples under high pressure are still being developed. We have used Cornell University's synchrotron source (CHESS) to develop such experiments using x-rays monochromated to 0.4959 Angstroms. Our samples were small molecular crystals (RDX or 1,3,5-trinitrohexahydro-1,3,5-triazine), loaded in Merrill-Bassett type diamond anvil cells (DACs), mounted on a two-circle diffractometer. The DAC was oscillated over 4° around an axis perpendicular to the x-ray beam. Data were obtained at 1, 2 and 3.5 GPa. An existing data analysis package (DPS/Mosflm, usually used by protein crystallographers) was used for indexing and peak integration. Structure factors were obtained at 1 GPa and a full structural analysis was performed using MaXus crystallographic software. Compared to the ambient pressure structure, significant bond distortions, angular distortions and ring puckering are evident at 1 GPa. The 2 and 3.5 GPa data indicate the existence of two separate phases, or a phase change, indicating that the phase transition previously seen at 3.8 GPa may start occurring at lower pressure.

Introduction

Single-crystal x-ray diffraction, being the most descriptive method of analyzing solid-state structure, will yield not only lattice symmetry but also atomic positions within the unit cell, and thereby the bond lengths, bonding angles etc. Usually, with good data sets, this method is excellent for locating all atoms including hydrogen. In addition, only diffraction studies of single crystals at high pressure can elucidate unknown high-pressure phases. However, compressing single crystals in diamond anvil cells to high pressure is a difficult art. The restricted cone angles on a diamond anvil cell (DAC) severely limit the accessible reflections, especially when Be plates are not used. In addition, materials with small unit cells yield very few reflections per frame in comparison to materials such as proteins.

Despite the difficulties associated with x-ray diffraction of single crystals under pressure, such studies were regularly performed at NIST since their conception of the DAC. [Weir et al. 1965, p. 275; Block et al.1965, p. 947] Subsequently, such work was also performed at Carnegie Institution and other places. [King and Finger 1979, p.374; Hazen and Finger 1989, p. 352; Loveday et al. 1990, p. 392] But all these works use in-lab radiation sources with low intensity, requiring extended periods of exposure and intensive data analysis. Only a few diffraction studies of single crystals in DACs using synchrotron radiation have been done. [Sowa H. et al. 1990, p. 397; Katrusiak and Dauter 1996, p. 607; Allan et al. 2001, p. 10; Fourme et al. 2001, p. 1149;] In particular, we are interested in x-ray diffraction of organic crystals that are sensitive to most of the radiation spectrum. Hence, our intent was to develop a method using monochromatic radiation rather than white incident beam.

The method reported here utilizes x-rays monochromated to 0.4959 Angstroms at the Cornell High Energy Synchrotron Source (CHESS) beam line configured for angle-dispersive diffraction. Our samples were loaded in Merrill-Bassett type DACs that were mounted on a two-circle diffractometer. Image plates were used as detectors, and sufficient diffraction spots were obtained by rocking the DAC (with the crystal inside) within the incident beam. An existing data analysis package (DPS/Mosflm, usually used by protein crystallographers) was used. Structure factors for the 1 GPa dataset were obtained from the data.

The material used in these experiments was a molecular solid 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX). The stable phase of RDX at ambient pressure (α) has orthorhombic symmetry (Pcab), and a unit cell approximately 10x11x13 Å. This material is known to undergo a phase change at 3.8 GPa. [Olinger et al., 1978; Miller et al. 1991, p. 174] This high-pressure phase is speculated to be another orthorhombic phase but a definite structure has not been reported.

Experimental Method

Single crystals (about 0.06-0.1 mm per side) were loaded into Merrill-Bassett diamond anvil cells that had 0.6-1mm culets. Inconel gaskets 0.127 mm thick, drilled with 0.3-0.6 mm holes, were used to contain the sample. Flouro-inert liquid (FC-75) was used as a pressure medium. Pressures were determined from a small ruby sphere (0.01 mm in diameter) added to each sample, and the frequency shift of the ruby R1 line was used as a pressure gauge. [Piermarini et al. 1975, p. 2774]

The DAC was mounted on a two-circle Diffractometer. The crystal was centered in the axis of rotation (χ) by rotating the diffractometer while watching the crystal with an optical microscope. Then the diffractometer was aligned on the beam line (Station B2) by successive rotation of the diffractometer around the axis of oscillation (Ω) by 180° followed by appropriate positioning with micro-alignment screws. Figure 1 shows the orientation of the equipment on the beam line. Station B2 is configured for angle-dispersive x-ray diffraction experiments and radiation monochromated to 0.4959Å. Diffracted x-rays were collected on an x-ray-sensitive image plate for 1-2 minutes per exposure. Images were collected while oscillating the DAC over 4° of Ω, for an Ω range of -12 to +12, for each χ. Data were obtained for χ angles 270°, 225°, 180°, 135°, 90°, at 1 GPa, 2 GPa and 3.5 GPa pressures, from samples with various orientations. The image plates were scanned and digitized.

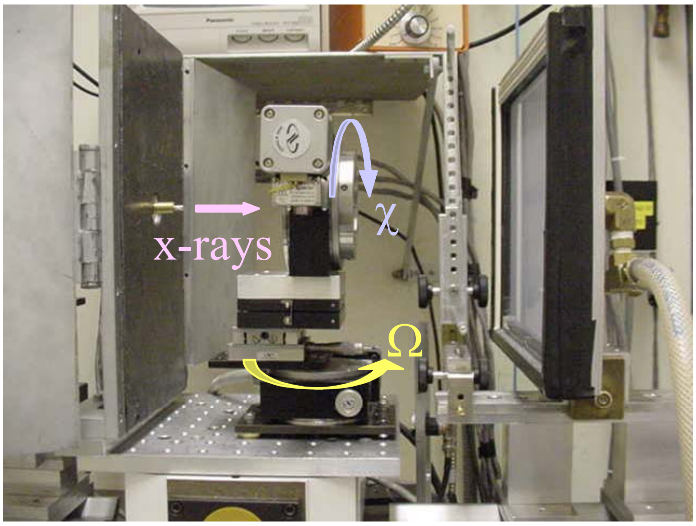

Figure 1: Orientation of Diffractometer with the DAC on the beam line.

Data analysis was performed using DPS/Mosflm software customized for DAC data by restricting the “cone angle” of acceptable data spots, and allowing larger oscillation angles such as 4°-10° degrees (proteins need only 1°-2° degrees) so sufficient numbers of spots/plate could be obtained, depending on the unit cell dimensions.

Results and Discussion

Synchrotron data for RDX at 1 GPa were refined to yield intensity Structure Factors (F) at 1 GPa. F-squared values were then imported into the MaXus crystallographic software. Data were treated in the orthorhombic, space group, Pcab. A total of 1006 reflections were read in and averaged to obtain 199 independent reflections. The R(merge) for the dataset was 8.1 %. The initial attempt to solve the structure via direct methods was successful. All non-hydrogen atoms were obtained. Refinement of the structure was based upon 185 reflections (F-squared > 3). Refinement was carried out with isotropic temperature factors on all non-hydrogen atoms and the inclusion of hydrogen atoms at calculated, idealized positions. The total number of parameters in the model was 61. Since the reflections/parameters ratio was quite low, ~ 3/1, it was decided that the data would not support a more sophisticated model with anisotropic temperature factors. The final agreement factors were R(F) = 17.51% and R(F2) = 44.45 %. These are acceptable values considering that the data were uncorrected for absorption and could only support a model with isotropic temperature factors.

The 1 GPa structure was compared to the ambient pressure structure obtained from neutron data. [Choi and Prince 1972, p. 2857] The neutron dataset is a much more extensive dataset containing 836 independent reflections in contrast to the 199 reflections in the x-ray dataset. The fourfold increase in data allows for more sophisticated modeling for the neutron structure. Anisotropic thermal parameters and secondary extinction were refined in the model derived from the neutron data. Refinement of both types of parameters affects the positions of atoms in the model and, subsequently, the bond distances and angles. Another artifact of neutron data is that scattering of neutrons takes place at the nucleus of an atom, while scattering of X-rays takes place from the electron cloud surrounding the nucleus of an atom. This results in shorter bonds between light atoms, such as carbon and nitrogen, from x-ray datasets since there is some degree of electron density that causes the x-ray refinements to move atoms closer together in an attempt to model density in the bonding region. So, comparison of models from the neutron and high-pressure, x-ray data should be done carefully. In spite of these concerns, there appear to be some major differences between the two models that should be considered significant.

The structure obtained at 1 GPa is shown in Figure 2, and the bond distances are listed in Table 1. There are significant distortions of bonds both in the C-N ring and the N-N nitro attachments. Several bonds are significantly longer while others are shortened. Distortions are not random within the molecule. One side of the molecule appears greatly affected (the N(2) – C(2)- N(3) side) while the other side of the molecule (the C(1) – N(1) – C(3) side) changes to a lesser extent. This degree of change appears to be correlated with the type of nitro attachment to the ring. There are two types of nitro groups in this molecule. The N(5) and N(6) nitro groups have an axial orientation relative to the ring. The N(4) nitro group binds in an equatorial position relative to the ring. The axial groups show the greatest distortions while the equatorial group is essentially the same as in the ambient pressure study. The effect on the N-O bonds appears to be the greatest when there is a subsequent change in the N-N bond to the ring. While N(1) – N(4) remains constant between the two structures, N(4)-O(2) and N(4)-O(1) barely change. However, N(2) – N(5) lengthens by 0.10 Angstroms with lengthening of 0.10 Angstroms in N(5) – O(4) and 0.08 Angstroms in N(5) – O(3). An interesting feature is the change in N(3) – N(6). This bond shortens considerably at 1 GPa from 1.399 Angstroms to 1.22 Angstroms. The N(6) – O(5) bond lengthens by 0.14 Angstroms. The N(6) – O(6) lengthens by 0.26 Angstroms.

When comparing bond angles of the neutron structure and the high-pressure structure, it was found that most of the angles are quite consistent between the two structures. However, the same areas of the molecule that show distortion in bond length exhibit angular distortions. These distortions may be real but the magnitude of such changes may be a result of the limited model used with the high-pressure dataset.

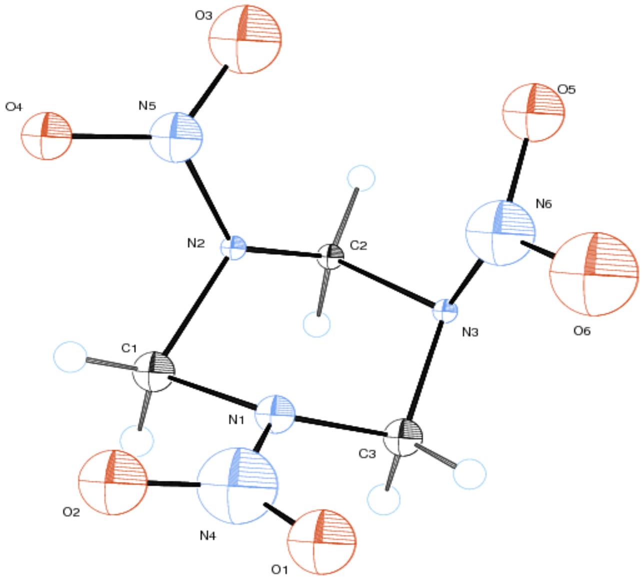

Figure 2: ORTEP diagram of the RDX structure at 1 GPa. The spheres are drawn at the 50% probability level.

Table 1. Bond Distances of RDX at 1 GPa

Atom1	Atom2	Choi and Prince	1 GPa data
		Bond Length	Bond Length
		Angstroms	Angstroms
C(1)	N(1)	1.464(4)	1.56(6)
C(2)	N(2)	1.467(4)	1.25(6)
C(3)	N(1)	1.451(4)	1.45(7)
N(1)	N(4)	1.351(3)	1.35(8)
N(3)	N(6)	1.399(3)	1.22(5)
N(4)	O(2)	1.232(4)	1.29(8)
N(5)	O(4)	1.207(5)	1.30(6)
N(6)	O(6)	1.205(5)	1.46(7)
C(1)	N(2)	1.443(4)	1.55(4)
C(2)	N(3)	1.458(4)	1.63(6)
C(3)	N(3)	1.440(4)	1.45(4)
N(2)	N(5)	1.392(3)	1.49(5)
N(4)	O(1)	1.209(5)	1.19(7)
N(5)	O(3)	1.203(5)	1.28(4)
N(6)	O(5)	1.201(5)	1.34(4)

Non-bonded contacts in both datasets were examined to see if there was any correlation between bond distortions and van-der Waals contacts. Both sets of non-bonded contacts reveal a considerable number of close contacts under 4.0 Angstroms. It is not clear whether the non-bonded contacts can explain the distortions that occur in the bond lengths in the compressed molecule. The one clear result is that the high-pressure structure contains many more non-bonded contacts less than 4.0 Angstroms. This indicates that the crystal has sufficient flexibility to accommodate the increase in pressure by simply increasing the number of non-bonded contacts to remain intact.

Torsion angles for both the neutron dataset and the 1 GPa X-ray data are given in Table 2. Examination of these values shows that the ring structure is more puckered in the high-pressure crystal than at ambient pressure. All five of the ring torsion angles (highlighted) increase with an average change of 17.4 degrees. This indicates that the ring structure accommodates the increase in pressure by puckering, so that the crystal remains intact at 1 GPa.

The dataset from RDX at 2 and 3.5 GPa were examined using the DPS/Mosflm software suite. The 2 GPa datasets had a good signal to background ratio with a number of well defined spots on each frame. The 3.5 GPa datasets were not as promising. They had a number of powder rings with few single crystal spots. Auto indexing of the spots on one or more of the image plate frames was attempted using the auto-indexing routines included with the DPS/Mosflm programs. These programs do not accept manual indices; therefore several spreadsheet routines were written as an attempt to accomplish manual indexing. In spite of these efforts, to date, a consistent indexing of frames from any of the 2 and 3.5 GPa has not been accomplished.

Although acceptable indexing was not obtained at 2 and 3.5 GPa, failed attempts at indexing consistently suggested a monoclinic cell. A monoclinic cell may also account for extra spots that appear on the images. Previous studies of this material have indicated a phase change at 3.8 GPa accompanied by a 1.6% volume change, to a phase labeled γ, thought to also be of orthorhombic symmetry. [Ollinger et al. 1978, Miller et al. 1991, p. 174] They observed that this phase change is rapid and reversible, involving no break up of the single crystal. It is possible that our data also indicated this same phase change seen previously, but that the onset of the high-pressure phase started at lower pressures (2 GPa) than previously seen.

Table 2. Torsion angles for neutron and 1 GPa x-ray datasets.

Atom1	Atom2	Atom3	Atom4	Choi and Prince Torsion Angles Degrees	1 GPa data Torsion Angles Degrees
C(1)	N(2)	N(5)	O(4)	16.2724	31
C(1)	N(2)	C(2)	N(3)	49.4421	77
C(2)	N(3)	N(6)	O(5)	20.5019	38
C(3)	N(3)	N(6)	O(6)	23.1543	35
C(3)	N(3)	C(2)	N(2)	49.162	63
C(3)	N(1)	C(1)	N(2)	57.3802	60
N(1)	C(3)	N(3)	C(2)	51.9413	63
N(1)	C(1)	N(2)	C(2)	52.0888	78
N(2)	C(1)	N(1)	N(4)	145.6191	153
N(2)	C(2)	N(3)	N(6)	91.9035	78
N(3)	C(2)	N(2)	N(5)	92.5702	97
N(3)	C(3)	N(1)	C(1)	57.2246	66
N(4)	N(1)	C(3)	N(3)	146.0667	149
N(5)	N(2)	C(1)	N(1)	89.77	98
N(6)	N(3)	C(3)	N(1)	89.8773	78
O(1)	N(4)	N(1)	C(1)	171.5336	166
O(1)	N(4)	N(1)	C(3)	15.8814	23
O(2)	N(4)	N(1)	C(3)	165.7579	167
O(2)	N(4)	N(1)	C(1)	10.1059	24
O(3)	N(5)	N(2)	C(1)	168.9963	180
O(3)	N(5)	N(2)	C(2)	27.9475	5
O(4)	N(5)	N(2)	C(2)	157.3213	154
O(5)	N(6)	N(3)	C(3)	161.2741	176
O(6)	N(6)	N(3)	C(2)	163.9265	174

Conclusion

Detailed structural descriptions and identification of unknown high pressure phases can only be elucidated by using diffraction studies of single crystals at high pressure. We report here a method for high-pressure single-crystal diffraction experiments using monochromated x-rays, suitable for crystals that are sensitive to white radiation. In this method the diamond anvil cell (loaded with the crystal) was mounted on a 2-circle diffractometer that was rocked (or oscillated) around an axis perpendicular to the x-rays. Image plates were used as detectors and data analysis was performed using DPS/Mosflm software customized for these DAC experiments. Analysis of the 1 GPa dataset revealed a significant distortion from the orthorhombic ambient-pressure structure derived from neutron diffraction. However, the lack of data and lack of absorption correction resulted in very large uncertainties in the final parameters for the model. The 2 and 3.5 GPa x-ray datasets indicated a possibility that the crystal may not be orthorhombic at these pressures.

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