The high-pressure phase stability of 2,4,6-trinitrotoluene (TNT)

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Abstract. 2,4,6-trinitrotoluene (TNT) is a widely used explosive that is relatively insensitive to initiation by shock loading. While the detonation properties of TNT have been extensively reported, the high pressure-temperature (P-T) stability of TNT has not been investigated in detail. At ambient conditions, TNT crystallizes in a monoclinic lattice (space group P21/a), and our previous X-ray diffraction (XRD) measurements at room temperature suggested a phase transition to orthorhombic (space group Pca21) at ~20 GPa. In this work, we have performed in-situ synchrotron XRD and vibrational spectroscopy measurements along the room temperature isotherm to investigate phase stabilities up to 18 GPa. While our Raman spectroscopy measurements indicate spectral changes at ~2 GPa, careful XRD measurements reveal that the monoclinic phase persists up to 10 GPa.

1. Introduction
Static compression experiments are important for defining material compressibility, presence/absence of phase transitions, and fundamental thermodynamic properties defining equations of state (EOS). Previous works have investigated the high pressure properties of 2,4,6-trinitrotoluene (TNT), a widely used explosive, and have determined the pressure sensitivities of vibrational modes [1-3], and unit cell lattice parameters as a function of compression [4].

TNT is known to exist in two distinct crystal structures at ambient conditions, monoclinic (P21/a) and orthorhombic (Pca21). Both are obtained through preferential crystallization as observed by Vrcelj et al. [5]; the orthorhombic phase is metastable at ambient pressure/temperature and was observed at high pressure [4]. Both crystal structures are comprised of a 50/50 mixture of two conformers (A and B) which differ from one another by slight rotations of the methyl group and 2- and 6-NO2 groups [6]. Previously reported X-ray diffraction (XRD) of TNT in diamond anvil cells (DAC) was used to determine the room temperature isotherm and fitting to a Murnaghan semi-empirical equation of state resulted in calculation of the zero-pressure room-temperature isothermal bulk modulus (K0, 298) and first pressure derivative (K0, 298'). Raman spectra as a function of pressure previously indicated [1] a phase transition at ~ 2 GPa. Herein, the room temperature isotherm is refined with the use of three non-hydrostatic data sets and comparison is made among all available data (Raman and XRD) regarding the proposed 2 GPa phase transition [1].
2. Experimental

TNT was re-crystallized from acetone, and determined to be in the monoclinic phase (space group \(P2_1/\alpha\)) by the observed absence of a pre-melt solid-solid phase transition by differential scanning calorimetry (DSC) [5]. The high-purity TNT single crystals were gently crushed into smaller crystallites, and loaded into the sample chambers of high pressure diamond anvil cells (DAC).

For angle-dispersive X-ray diffraction measurements, TNT was loaded into an easyLab Diacell® HeliosDAC (www.almax-easylab.com) with 300 μm culet type IIa diamonds (D’Anvils and Technodiamant), and gaskets (stainless steel or rhenium) with dimensions of 100 μm diameter and 50-60 μm thickness. Au powder was used as an internal pressure marker using the \(P-V-T\) equation of state reported by Fei et al. [7]. These measurements were made in non-hydrostatic environments, i.e. no pressure medium was used, at the 16-ID-B (HPCAT) beam line at the Advanced Photon Source, Argonne National Laboratory as described previously [8].

The Raman spectroscopy experiments used TNT loaded into symmetrical DACs with 800 μm culet (0 to 5.8 GPa) and 300 μm culet (6.0 to 10.0 GPa) Type IIa diamonds; stainless steel gasket dimensions were 600 μm diameter and 200 μm thickness (0 to 5.8 GPa) and 150 μm diameter and 55 μm thickness (6.0 to 10.0 GPa). Ruby fluorescence was used to monitor internal pressure via the \(R_1\) line [9]. The Raman spectroscopy and ruby fluorescence were measured on the same Raman system as described previously [10] using an excitation wavelength of 532 nm. Spectral resolution was about 1.5 cm\(^{-1}\) and pressure was estimated to +/- 0.5 GPa; no pressure medium was used.

3. Results and Discussion

3.1. X-Ray Diffraction

Three non-hydrostatic room-temperature isothermal compression experiments, up to 10 GPa, were performed on TNT. The unit cell parameters at each pressure increment were obtained by LeBail refinement [11] using the EXPGUI graphical interface [12] version of General Structure Analysis System (GSAS) [13]. These data sets, in addition to previously reported XRD data [4] were analyzed to refine zero-pressure isothermal bulk modulus (\(K_{0,298}\)) and first pressure derivative (\(K'_{0,298}\)), and examine values obtained by various semi-empirical equations of state (Murnaghan [14] and Vinet [15]) as shown in table 1.

| Table 1. | Bulk modulus (\(K_{0,298}\)) and first pressure derivative (\(K'_{0,298}\)) obtained by fitting the data sets to both Murnaghan and Vinet semi-empirical equations of state using \(V_0 = 1828.8 \, \text{Å}^3\). |
|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|           | Murnaghan                       | Vinet                           |                                 |                                 |
|           | \(K_{0,298}\) (GPa)             | \(K'_{0,298}\) (GPa)            | \(K_{0,298}\) (GPa)             | \(K'_{0,298}\) (GPa)            |
| Experiment 1 | 10.8 ± 0.6                      | 6.6 ± 0.4                       | 8.8 ± 0.7                       | 9.5 ± 0.7                       |
| Experiment 2 | 9.8 ± 0.4                       | 8.2 ± 0.3                       | 7.8 ± 0.5                       | 11.9 ± 0.5                      |
| Experiment 3 | 9.6 ± 0.9                       | 8.0 ± 0.6                       | 7.2 ± 1.6                       | 12.1 ± 1.7                      |
| Non-Hydro [4] | 7.3 ± 0.5                       | 9.6 ± 0.4                       | 7.1 ± 0.5                       | 12.0 ± 0.5                      |
| Hydrostatic (N\(_2\) medium) | 12.8 ± 1.4                      | 7.1 ± 0.8                       | 9.0 ± 1.3                       | 11.6 ± 1.2                      |

The previously reported \(K_{0,298} = 8.52 \, \text{GPa}\) and \(K'_{0,298} = 8.0\), respectively [4], for TNT were obtained by a Murnaghan fit to \(P-V/V_o\) data up to 20 GPa with \(V_0 = 1828.8 \, \text{Å}^3\), the ambient pressure/temperature unit cell volume reported by Golovina et al. [16]. This value was also used for each of the current data sets. Figure 1(a) plots the following data sets in \(P-V/V_o\) space: Stevens et al. non-hydrostatic compression data [4], a hydrostatic (\(N_2\) pressure medium) experiment to 10 GPa, three new non-hydrostatic experimental data sets to 10 GPa and Vasil’ev et al.’s data for TNT [17]; Murnaghan fits to \(P-V/V_o\) data from Experiments 1 and 2 are also shown. Using EXPGUI, all data sets were fit to the monoclinic space group. Errors in measured pressure were determined by calculating
the difference between the pressure obtained for the Au (111) and Au (200) reflections using Fei et al.'s Au EOS [7]; differences were determined to be ≤ 0.8 GPa. Errors in V/V₀ were estimated to be 0.005. As noted in [18], using semi-empirical equations of state fitted to isothermal data results in considerable variability in calculated $K_{0,298}$ and $K'_{0,298}$ between fitting forms and data sets, despite statistically good fits to the data. Variability in calculated $K_{0,298}$ and $K'_{0,298}$ were previously found for HMX [18, 19], and in this study, TNT also shows deviations. The majority of data sets have errors of < 1 GPa for $K_{0,298}$ and $K'_{0,298}$ and yet the bulk moduli values obtained for non-hydrostatic data range between 7.1 and 10.8 GPa depending on the data set and the fitting form used (table 1). The variability between the results of different equations of state used was as small as 0.2 GPa [4] and as large as 3.8 GPa (hydrostatic run). As pointed out in [18], low pressure data (< 1 GPa) is paramount to having acceptable fits to isothermal data for constraining $K_{0,298}$. Two experiments, Experiment 2 and Stevens [4], had multiple P-V states below 1 GPa; these differ significantly in volume at low pressure resulting in $K_{0,298}$ values of 9.8 and 7.3 GPa, respectively when the Murnaghan EOS is used. The values are within error of one another when the Vinet EOS is used. As shown in figure 1(a), the hydrostatic data set is stiffer than non-hydrostatic compression curves differing from literature reports of HMX which show large differences between hydrostatic and non-hydrostatic data sets [19, 20].

Anisotropic compression of the three unit cell axes was observed over the pressure range studied, as shown in figure 1(b). This trend is shown even though all data sets show scatter in refined lattice parameters associated with non-hydrostatic forces causing lattice distortion, as illustrated in figure 1(b). For example, Experiment 1 showed a volume collapse of 25% between 0.2 and 10.1 GPa, corresponding to 7.2% decrease in $a$-axis, 7.3% decrease in $b$-axis, 12.3% decrease in $c$-axis and an increase of angle $\beta$ of 1°. The nearly identical decrease in $a$- and $b$-axes is identical to low temperature studies performed on monoclinic TNT [5, 21]; the $c$-axis is observed to be the most sensitive to compression. The difference in volume between all data sets was 50 Å³ and 44 Å³ at 0.2 and 10.1 +/- 0.1 GPa, respectively. Considering the large volume of the unit cell, this amounts to a 3% variation in volume at both pressures.

**Figure 1.(a)** Room temperature P-V/V₀ (V₀ = 1828.8 Å³) isothermal data for TNT. Murnaghan fits to Experiment 1 and Experiment 2 shown. Error bars are indicated on Experiments 1-3 data.

**Figure 1.(b)** Lattice parameters as a function of pressure for each non-hydrostatic data set up to 10 GPa of TNT. Angle $\beta$ omitted.
In agreement with [4], a low pressure phase transition can be ruled out, as in figure 1(a) and figure 2; diffraction patterns below and above 2 GPa of all experiments were fit to a monoclinic space group and no apparent cusp is observed in the $P-V/V_0$ curve. Small pressure steps were performed in Experiment 2 and the integrated patterns are overlaid as intensity versus 2θ ($\lambda = 0.61992$ Å) in figure 2; only a portion of the entire pattern is shown illustrating low angle peaks representing the $20\bar{2}$, $20\bar{3}$, $110/11\bar{1}$, $11\bar{2}$, $20\bar{4}$, $21\bar{1}$, 113 and $21\bar{1}/21\bar{3}$ reflections of monoclinic (space group $P2_1/a$) TNT.

![Figure 2](image_url)

**Figure 2.** Selected spectra at various pressures illustrating the lack of any structural changes in 2-theta as a function of pressure around 2 GPa.

Previously reported Raman spectra from ambient pressure to 3 GPa [1] indicated a possible phase transition marked by a discontinuity in frequency versus pressure ($d\nu/dP$) and low frequency (< 250 cm$^{-1}$) mode splitting at 2 GPa. As shown in figures 3(a)/(b), the low frequency region of the Raman spectrum is complex, and many broad bands are observed to mask multiple modes making interpretation challenging. Two librational lattice modes, $\nu_5$ and $\nu_7$, and $\nu_8$ (CH$_3$ and C-CH$_3$ deformation) split in addition to three modes gaining intensity, $\nu_{3a/b}$ (lattice), $\nu_4$ (lattice), and $\nu_9$ (C-N in-plane deformation), between 0.4 and 2.1 GPa (figure 3(a)). An apparent discontinuity in $d\nu/dP$ for nearly all modes (60-3100 cm$^{-1}$, >300 cm$^{-1}$ not shown) was observed between 2.1 and 2.8 GPa highlighted in figure 3(b) by the grey shaded box. Near ambient pressure, four bands, attributed to lattice modes $\nu_{5b}$, $\nu_6$, $\nu_{7b}$ and $\nu_8$ (CH$_3$ and C-CH$_3$ deformation) were observed between 60-250 cm$^{-1}$; at 2.1 GPa, a total of 11 modes associated with $\nu_3 - \nu_9$ were observed. The broad nature of the original 4 bands likely masked individual modes that later were observed to split with increasing compression due to different $d\nu/dP$. $\nu_3$ and $\nu_{7b}$ shift to frequencies > 60 cm$^{-1}$ at 2.1 GPa (figure 3(a), e).

Generally, TNT is more compressible below 2 GPa with $d\nu/dP > 10$ cm$^{-1}$/GPa observed at pressures below 2.8 GPa for all modes less than 250 cm$^{-1}$; $\nu_8$ was most sensitive to compression with $d\nu/dP = 21$ cm$^{-1}$/GPa (table 2). Above 2.8 GPa, $d\nu/dP = 2-11$ cm$^{-1}$/GPa for low frequency (< 250 cm$^{-1}$) Raman modes. Mode splitting and discontinuity in shift rate indicates these intramolecular low frequency vibrations (< 250 cm$^{-1}$) are highly sensitive to a structural rearrangement near 2 GPa that lacks a change in space group.
Figure 3. (a) Representative Raman spectra from 60-300 cm\(^{-1}\). As a function of compression, new modes appeared at: a – 116 cm\(^{-1}\); b – 103 cm\(^{-1}\); c – 196 cm\(^{-1}\); d – 215 cm\(^{-1}\); e – 81 and 92 cm\(^{-1}\); f – 183 cm\(^{-1}\). Lines are drawn to guide the eye, and are based on centroid of Gaussian fits to modes.

Figure 3. (b) Low frequency (70-300 cm\(^{-1}\)) Raman \(d\nu/dP\) plots to ~ 10 GPa at 298 K. Lines are drawn to guide the eye. Grey outline highlights non-linear shifts of frequency with pressure.

Table 2. Theoretical and near ambient pressure Raman vibrational mode assignments and \(d\nu/dP\) of TNT. Band splitting at: a - 0.4 GPa, b - 0.8 GPa, c - 1.2 GPa, d - 2.1 GPa and e - 4.2 GPa.

| Mode | Assignment: | Theoretical Values [22] | Raman [1] | Raman (This Study) | \(< 2\) GPa \(d\nu/dP\) (cm\(^{-1}\)/GPa) | \(> 2\) GPa \(d\nu/dP\) (cm\(^{-1}\)/GPa) |
|------|-------------|-------------------------|-----------|---------------------|--------------------------------|--------------------------------|
| 1    | Lattice (trans.) | Conf. A Freq. (cm\(^{-1}\)) | 43        | 25  | 79\(^c\) | --        | 1.7 ± 0.3 |
| 2    | Lattice (lib.) | Conf. B Freq. (cm\(^{-1}\)) | 46        | 34, 36 | 81\(^d\) | --        | 4.7 ± 0.2 |
| 3    | Lattice (lib.) |                  | 52        | 54  | 92\(^d\) | --        | 4.8 ± 0.3 |
| 4    | Lattice (lib.) |                  | 91        | 86  | 103\(^b\) | 17.3 ± 3.8 | 6.9 ± 0.5 |
| 5    | Lattice (lib.) |                  | 116\(^a\) | 119 ± 3.4 | 116 | 11.9 ± 3.4 | 6.2 ± 0.4 |
| 6    | Lattice (lib.) |                  | 120 | 17.9 ± 1.9 | 120 | 17.9 ± 1.9 | 9.3 ± 0.2 |
| 7    | Lattice (lib.) |                  | 144 | 11.9 ± 0.7 | 144 | 11.9 ± 0.7 | 9.7 ± 0.4 |
| 8    | \(\delta_{oo}(\text{CH}_3) + \delta_{ip}(\text{C-CH}_3)\) |                  | 183\(^d\) | -- | 183\(^d\) | -- | 7.4 ± 0.4 |
| 9    | \(\delta_{ip}(\text{CN})\) |                  | 161 | 16.7 ± 2.2 | 161 | 16.7 ± 2.2 | 7.1 ± 0.4 |

4. Conclusion
Refinement of the room temperature isotherm of TNT to 10 GPa resulted in a best estimate of initial compressibility and illustration of the shortcomings of semi-empirical equations of state fitted to \(P-V\) data. Unequivocally, the monoclinic phase (space group \(P 2_1/a\)) is stable up to 10 GPa; no appearance of a cusp in the \(P-V/V_0\) curve of TNT or phase transition during LeBail refinement of XRD patterns.
was observed. TNT, like most molecular solids, is observed to have rapid shifting lattice modes (< 250 cm\(^{-1}\)) up to 2 GPa with multiple modes splitting. The qualitatively confirmed discontinuity in \(\frac{d\nu}{dP}\) was attributed to the significant (~ 13%) unit cell volume collapse between 0 and 2 GPa associated with reduction of free space between molecules in the unit cell representing a structural rearrangement.

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