High pressure infrared study of 1,3,5,7-cyclooctatetraene (COT)

Michael Pravica1*, Edward Romano1, Sergey N. Tkachev1 and Zhenxian Liu2

1 Department of Physics and Astronomy, and High Pressure Science and Engineering Center (HiPSEC), University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas, Nevada 89154-4002

2 Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015-1305

*Corresponding author e-mail: pravica@physics.unlv.edu

Abstract. We have performed a high pressure synchrotron mid-infrared study 1,3,5,7-cyclooctatetraene up to ~22 GPa and at ambient temperature in a diamond anvil cell. We have confirmed our prior observations of phase transitions via Raman spectroscopy and x-ray diffraction near 3-4 GPa, and 7-10 GPa. We have also observed chemical reaction culminating in irreversible dimerization/polymerization of the material above 15 GPa.

1. Introduction
The aromaticity, nonaromaticity, and anti-aromaticity of cyclic hydrocarbons represents a fundamental and widely studied field in chemistry and physics with wide ranging importance to industrial, geological, astrophysical and biological chemistry.1 Better understanding of the behavior of cyclic hydrocarbons under extreme conditions of pressure and temperature (P, T) can yield insight into the mechanisms of their formation/synthesis and P,T regions of stability deep within planets (such as our own) and moons (such as Titan2-4). High pressure investigations can also open up novel routes of chemical synthesis (e.g the Haber process)1 as intermolecular and even intramolecular interactions increase with pressure breaking and/or forming new chemical bonds. In particular, we have been interested in ascertaining the effect of pressure on the aromatic character of conjugated cyclic hydrocarbons via conformational and/or electronic transfer. We have focused on 1,3,5,7 cyclooctatetraene (C8H8) as a candidate for study.5 The molecule is nonaromatic under normal conditions with a tub shape6 conformation (see Fig. 1) and a cyclic sequence of alternating double and single bonds. COT does not obey Hückel’s 4n+2 rule1 and as such is not considered to be either aromatic or anti-aromatic.6 Due to the combination of sp2 and sp3 hybridization, COT is not planar (unlike benzene, C6H6) but exhibits a geometrically-stressed tub shape.7 As a result, the molecule is highly reactive as it is less thermodynamically stable than comparable aromatic molecules.8

It has been suggested that COT transforms into polymorphs of itself (ring inversion9) by temporarily adopting either the planar D4h symmetry (conjugated) or the planar D8h symmetry (ring structure) as an intermediate state between tub-shaped/puckered conformations12 which are of D2d symmetry.8,10 COT will aromatize and flatten when reacted with potassium11 or uranium12 to form COT+.13 or COT2-.14,15

Due to the apparent ease with which the planarization of the molecule can occur, we sought to determine if pressure would have a similar role by increasing intermolecular interactions via decreasing intermolecular distance: either by mechanically deforming the molecule to physically planarize it (resulting in a quantum mechanically degenerate electronic state) or to induce electron
transfer to and from other neighboring molecules. With increased intermolecular density, there is also a likelihood that dimerization/polymerization of molecules may occur for which we have evidence when pressurizing the sample above 15 GPa.5

In the present study, we expand the scope of our high pressure studies on COT to include infrared spectroscopy (IR) as a complement to our recent Raman studies,5 and to further confirm our recent observation of at least two phase transitions with pressure within the 20 GPa range. Prior IR studies of COT were performed at ambient temperature and pressure.16-18 To the best of our knowledge, this is the first reported IR measurement of COT at elevated pressure.

Figure 1: COT molecule (left) top view and (right) side view. The figure is taken from Ref. 5.

2. Experimental techniques
To pressurize the sample, we utilized a diamond anvil cell, or DAC (Mao-Bell type), with 300 micron diameter Type IIa diamond culets. Sample confining gaskets made of rhenium metal were constructed by pressing 0.254 mm thick rhenium metal between the diamonds to roughly 20 microns thickness. A ~100 μm diameter hole was then drilled using the gasket preindentation as a centering guide via electric discharge machining. A thermally-annealed ruby sphere (~5-10 microns in diameter) was placed in the sample chamber (prior to sample loading) and constituted the pressure sensor. A liquid sample of COT (obtained from Alfa Aesar® with 98% purity and with 0.1% hydroquinone as a stabilizing/anti-polymerization agent) was introduced into the unsealed sample hole via a syringe. The DAC was then quickly assembled and the diamonds manually translated to seal and then pressurize the sample. No pressurizing medium was used in our experiments. As typical sample volumes in diamond anvil cell tend to be in the nanoliter range, we performed our measurements using synchrotron IR radiation to maximize signal to noise and accelerate data acquisition.

Our experiment was performed at the U2A beam station which is part of the Vacuum Ultraviolet (VUV) ring of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Infrared spectra were taken in the middle range of energy (500-5000 cm⁻¹). The synchrotron beam produced by the VUV ring passes through a wedged diamond window, is collimated, and then is guided into a Bruker IFS 66s/V® Fourier transform infrared spectrometer (FTIR) via an evacuated tube. There are three distinct microscope systems in the FTIR spectrometer that enable measurements in the mid-IR and far-IR spectral regions. For mid-IR region (which is a focus of this paper), the beam is focused onto the sample using a nitrogen-purged IR microscope (Bruker IR Scope II®), and spectra are collected either in transmission or reflection modes. All of the microscopes can typically focus the IR beam to a 30 μm spot which is then spatially filtered to a 20 μm x 20 μm square. The resolution for all of our measurements was roughly 4 cm⁻¹ and all data was collected at room temperature. More details about the experimental setup can be found in Ref. 19.

3. Results
We present our results in Figure 2. The acquisition time for each scan was ~10 minutes. One background spectrum was obtained with an empty DAC in place (but no gasket) and was used for
background subtraction for all of the acquired data. Closer examination of the low pressure spectrum at 1.59 GPa shows many of the features seen in Refs. 16-18 including C-H stretch frequencies near 3013 cm\(^{-1}\) of the A1, B1, B2, and E species\(^{18}\), two C=C stretching lines near 1608 cm\(^{-1}\) and 1640 cm\(^{-1}\) of B2 and E symmetry\(^{18}\), among many other lines.

At higher pressures, a number of spectral alterations are evident suggesting phase transitions. In the 2.55 GPa spectrum, a tiny peak emerges just the right of the strong C-H in-plane bend and C-C stretch lines around 1204/1221 cm\(^{-1}\) that slowly but steadily grows with pressure. Above 3.43 GPa, the line near 3013 cm\(^{-1}\) appears to split. The strong line around 800 cm\(^{-1}\) also splits above 3.43 GPa. We believe that these spectral modifications occur near the completion of the liquid→solid phase transition around 3-4 GPa.\(^{5}\)

At higher pressures above 7.38 GPa, a small spectral line near 1651 cm\(^{-1}\) disappears and a line near 1439 cm\(^{-1}\) appears to split. In fact, examining the entire progression of the two lines near this frequency, it is immediately obvious that the two lines eventually become five lines above about 10 GPa. At even higher pressures near 10 GPa, the third of the trio of lines just below 1000 cm\(^{-1}\) begins to vanish beginning around 8 GPa and then the second of the original trio splits around 15.9 GPa.

![Figure 2: Stacked plot of mid-IR spectra of COT with pressure.](image)

We show the frequency progression of selected spectral lines in Figure 3. In all cases, discontinuities are evident around 4 GPa, 8-10 GPa, and then above 15 GPa. The errors attributed to fitting spectral peaks are all less than or equivalent to the size of the points chosen to display the peak frequencies. Both figures reinforce our claim of two phase transitions with pressure followed by irreversible reaction/polymerization of the sample. When the sample was depressurized, it had
irreversibly reacted to a tough wax-like substance which is likely some sort of amorphous hydrogenated carbon as observed in our prior experiments.\footnote{5}

Figure 3: (Left and right) Stacked plots of mid-IR spectra of COT with pressure.

4. Discussion
As this is the first IR study of COT with pressure, we will leave more quantitative analysis of the modal behavior that we have observed to a future paper. However, we can say qualitatively that it appears that at least two phase transitions, observed earlier in our Raman studies,\footnote{5} were confirmed in the liquid→solid phase transition somewhere between 3-4 GPa and another phase transition in the 7-10 GPa regime. In our earlier studies of cyclohexane, we also found similar behavior of sluggish, hysteretic phase transitions.\footnote{20} Finally, above 15 GPa, irreversible changes occur to the sample indicating chemical reaction and dimerization/polymerization. Examination of our data in Figure 2 displays relatively clean data that is not contaminated with fluorescent signal unlike our obscured Raman data\footnote{5} at high pressures and demonstrates the usefulness of IR spectra when Raman spectra are unobtainable due to fluorescence signal.

5. Conclusion
In summary, we have conducted the first high pressure infrared spectroscopic study of solid 1,3,5,7-cyclooctatetraene up to 22 GPa. We confirmed that solid COT undergoes at least two phase transformations with pressure, followed by the formation of denser cross-linked species. Further studies will be conducted to ascertain the behavior of the molecule with pressure in the far-IR regime.

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