

# MOLECULAR CRYSTALS UNDER PRESSURE

## APPLICATION BRIEF

This application demonstrates the use of density functional theory with Tkatchenko-Scheffler dispersion correction to explore several crystalline oligoacenes (naphthalene, anthracene, tetracene and pentacene) under pressures up to 25 GPa in an effort to uncover unique electronic/optical properties.

### INTRODUCTION

Pressure has been used to reduce the resistivity of these semiconductors, suggesting that oligoacenes could be the first single component organic molecular crystals (OMC) to show “metallic” behavior<sup>2</sup>. The idea that oligoacenes (particularly pentacene) under pressure are conductors is perpetuated in recent articles<sup>3</sup> and reviews<sup>4,5</sup>. However, a high pressure optical study of pentacene up to ~32 GPa<sup>6</sup> showed no metallization due to condensation reactions, though a steady narrowing of the HOMO-LUMO band gap was observed until the molecular identity of the acene components was compromised.

The pressure dependent narrowing of the band gap in the oligoacenes and other monomolecular OMCs<sup>7</sup> presents the possibility that a semiconducting single component organic system could exhibit conductance under pressure, but predicting which structures to investigate experimentally is a daunting challenge as the pool of potential materials is enormous. Therefore, it would be valuable to

have a computational method that can be used in a high-throughput scenario to accurately predict the pressure-induced structural changes of OMCs as well as the corresponding electronic and optical properties. In an effort to establish a consistent methodology for the optimization of OMCs under varying thermodynamic conditions, the Tkatchenko-Scheffler dispersion-corrected density functional theory (PBE+vdW) method had been employed to observe the pressure induced changes in the structural and electronic properties of naphthalene (2A), anthracene (3A), tetracene (4A), and pentacene (5A).

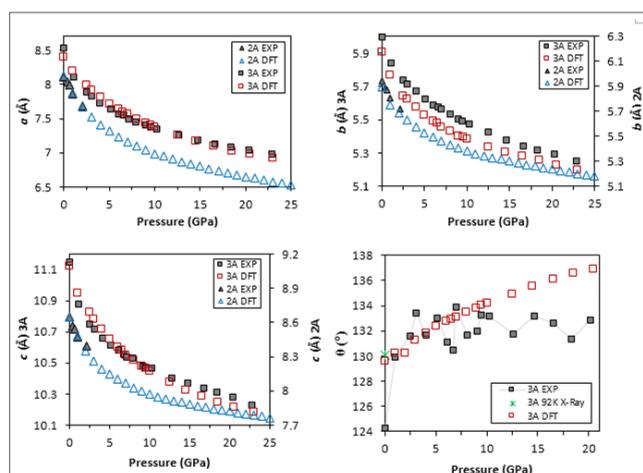
### METHODOLOGY

Density functional theory<sup>8</sup> implemented in the program CASTEP<sup>9</sup> was used in this investigation. Starting structures of each acene were obtained from the lowest temperature data sets available in the Cambridge Structural Database (CSD). The low temperature polymorphs were chosen for tetracene and pentacene. Pressure was increased in 0.5 GPa steps. The structure at each pressure was geometry optimized using the BFGS minimizer within CASTEP which uses a starting Hessian that is recursively updated during optimization<sup>10</sup>.

Norm-conserving potentials were utilized. The planewave basis set cutoff was 750 eV. The k-point grid was kept to maintain a spacing of ca. 0.07 Å<sup>-1</sup>. The GGA functional of Perdew, Burke and Ernzerhof (PBE)<sup>11</sup> was employed. An essentially nonempirical method, introduced by Tkatchenko and Scheffler (TS)<sup>12</sup>, was used to add the pervasive van der Waals (vdW) interactions common in molecular crystals which are missing in the PBE functional.

### RESULTS

The ability of PBE+vdW to model the pressure-induced structural changes of oligoacene crystals as observed via x-ray diffraction is demonstrated in Figures 1-3. The structural response of 2A and 3A up to 25 GPa is shown in Figure 1, and excellent agreement with experiment is obtained for the unit cell parameters. PBE+vdW reveals discontinuities in the unit cell parameters and  $\theta$  between 6-7 GPa (this is indicative of a phase transition as will be explained later). Similar discontinuities are also observable in the experimental parameters of Figure 2 (though not noted in the original manuscript<sup>13</sup>). There is no change in the symmetry or motif<sup>14</sup> of the crystal associated with the calculated discontinuities (also observed in comparison with the experimental structures of the two phases<sup>15</sup>). The structural rearrangement increases the packing efficiency by increasing  $\theta$ . Between 0-6 GPa, the structure compresses anisotropically (despite the isostatic



**Figure 1.** Unit cell parameters and interplanar angles of 2A [44] and 3A [19] as a function of pressure from powder x-ray and PBE+vdW. In (d), ‘EXP’  $\theta$  values are from [20], 92 K  $\theta$  value at 0 GPa is from ANTEN09. b and c of 2A are on the secondary axis for clarity.

pressure conditions). The compression ratio with increasing pressure is 6.8%, 11.0%, and 4.6% along *a*-, *b*-, and *c*-cell dimensions respectively. The phase transition can then be characterized by a sudden increase in the *c*-dimension and

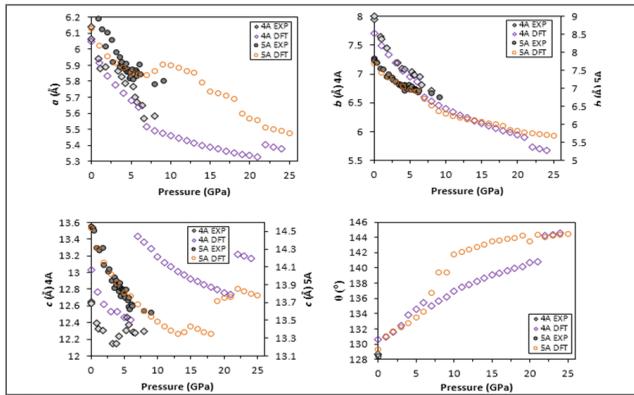


Figure 2. Unit cell parameters and  $\beta$  of 4A and 5A as a function of pressure from x-ray [20] and PBE+vdW. The low temperature values are from TETCEN01 and PENCEN04 (polymorph H).

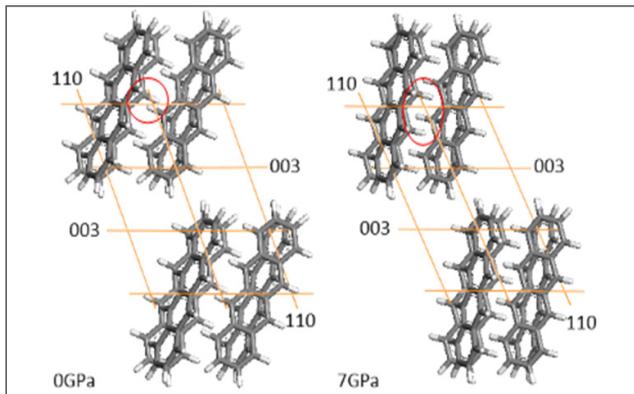


Figure 3. Molecular arrangement of 4A before and after the phase transition at 0 GPa and 7 GPa. Red circles emphasize the shift between interlocking hydrogens.

a 22% density increase from 1.685 g/ml to 1.722 g/ml; while atomistically, the phase transition corresponds to a change/shift in stacking patterns in the molecular crystal. As illustrated in Figure 3, the stacking shift is along the molecular axis, where the interlocking hydrogens shift along the long molecular axis by about one quarter of the repeating distance.

The phase transition can also be characterized by a relatively subtle but important structure change in the position of the 110 reflection in the powder X-ray diffraction (PXRD) pattern (see Figure 4). At ambient pressure, the  $2\theta$  position of 110 is of lesser magnitude than those of the near-degenerate  $1\bar{1}0/112$  reflections. The relative position remains unchanged up to 6 GPa, but at the phase transition the position of the 110 reflection moves significantly higher (by  $1.82^\circ 2\theta$ ). This corresponds to a sudden decrease in d-spacing from 4.23 Å at 6 GPa to 3.85 Å at 7 GPa. The phase transition can therefore be characterized by a simultaneous increase in the

*c*-dimension and a decrease in the 110 d-spacing (also refer to Figure 3). These structural changes appear frozen-in after the structure is quenched to ambient pressure (see Figure 4).

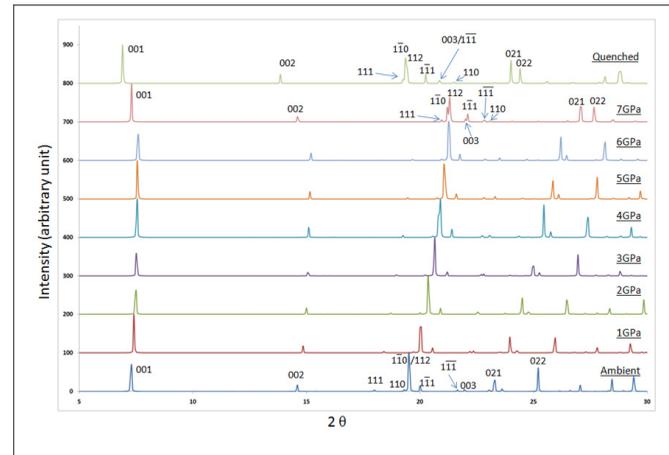


Figure 4. Simulated powder X-ray diffraction patterns of 4A under increasing isostatic pressure.

## DISCUSSION

Oligoacenes have been extensively studied under a variety of thermodynamic conditions where interesting optical/conductive properties are expected to emerge. High pressure conditions are of specific interest as one may tune the optical properties of these materials, directly altering the conductivity/resistivity due to increased overlap of adjacent molecules within the unit cell<sup>16</sup>. Of particular interest is 'Polymorph I'<sup>15</sup> (TETCEN01) of 4A that undergoes a phase transition above 6 GPa<sup>15</sup> to a phase possessing similar Raman lattice phonon lines to "polymorph II"<sup>15,17</sup>. This system had been well-characterized by high pressure x-ray experiments<sup>13</sup> which made it a useful benchmark for computational studies. It is worthwhile to point out that, while previous classical QHLD calculations<sup>13</sup> reasonably modeled the unit cell parameters of 4A as a function of pressure, no notable structural rearrangements indicative of a phase transition were reported from these simulations (possibly the result of the rigid molecule assumption).

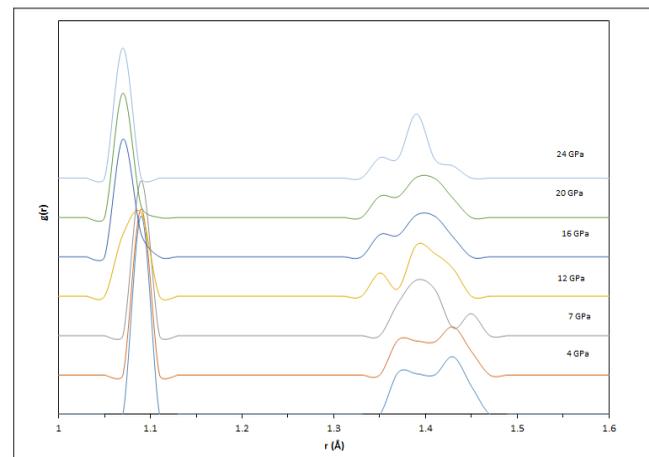


Figure 5. Radial distribution function of 4A as a function of pressure.

Another important point to emphasize with regard to the phase transition is the change in the intra-molecular structure. **Figure 5** shows the C-H and C-C bond distance distribution through radial distribution function (RDF) analysis, and its evolution as a function of applied pressure. It is evident that immediately after the phase transition at 7 GPa, the C-C bond distance distribution changes significantly; i.e., there is a more pronounced split for the two groups of C-C bond distances, one centered at 1.37, and the other at 1.43 Å, respectively. Moreover, the shorter C-C bond distances (centered at 1.37 Å) become prominent, which is reversed before the transition.

## CONCLUSIONS

The use of Tkatchenko-Scheffler dispersion corrected DFT (PBE+vdW method) in investigating oligoacenes under pressures can produce excellent agreement between calculated and experiment crystal structures, both at ambient- and high-pressure regimes. The ability of PBE+vdW to dynamically adapt to changes in the chemical environment was demonstrated by the reproduction of the pressure-induced phase transitions of tetracene. The good correlation achieved in this investigation demonstrates the versatility of PBE+vdW in the calculation of organic molecular crystal properties, and future high-throughput investigations of OMCs using PBE+vdW may uncover several useful low band gap materials.

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