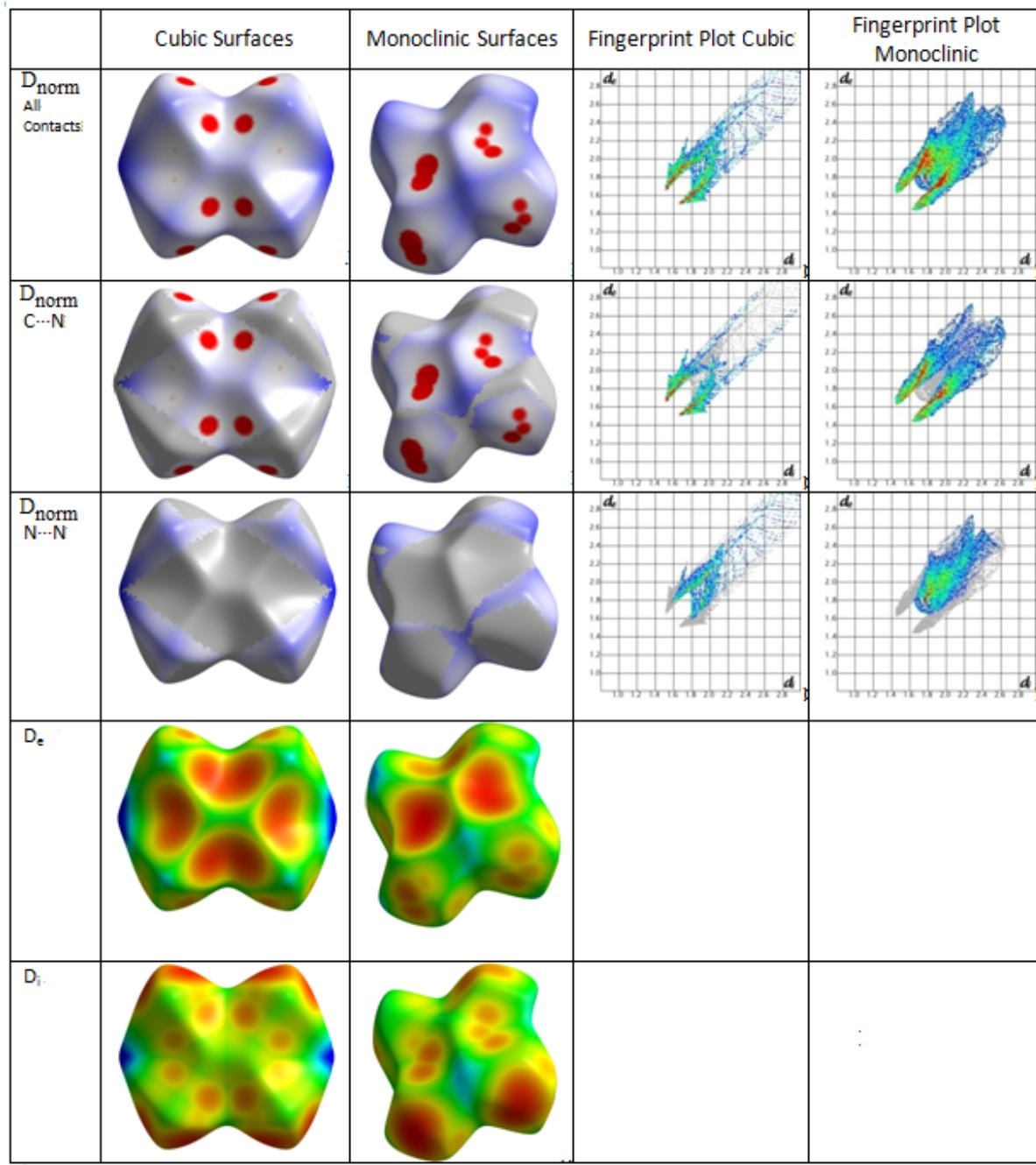
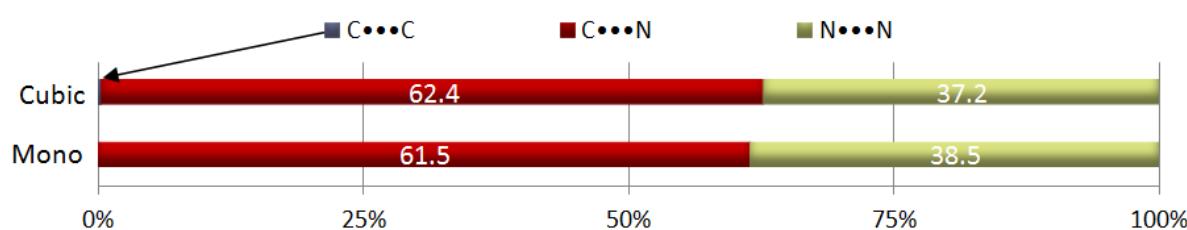


## Supplementary Information:

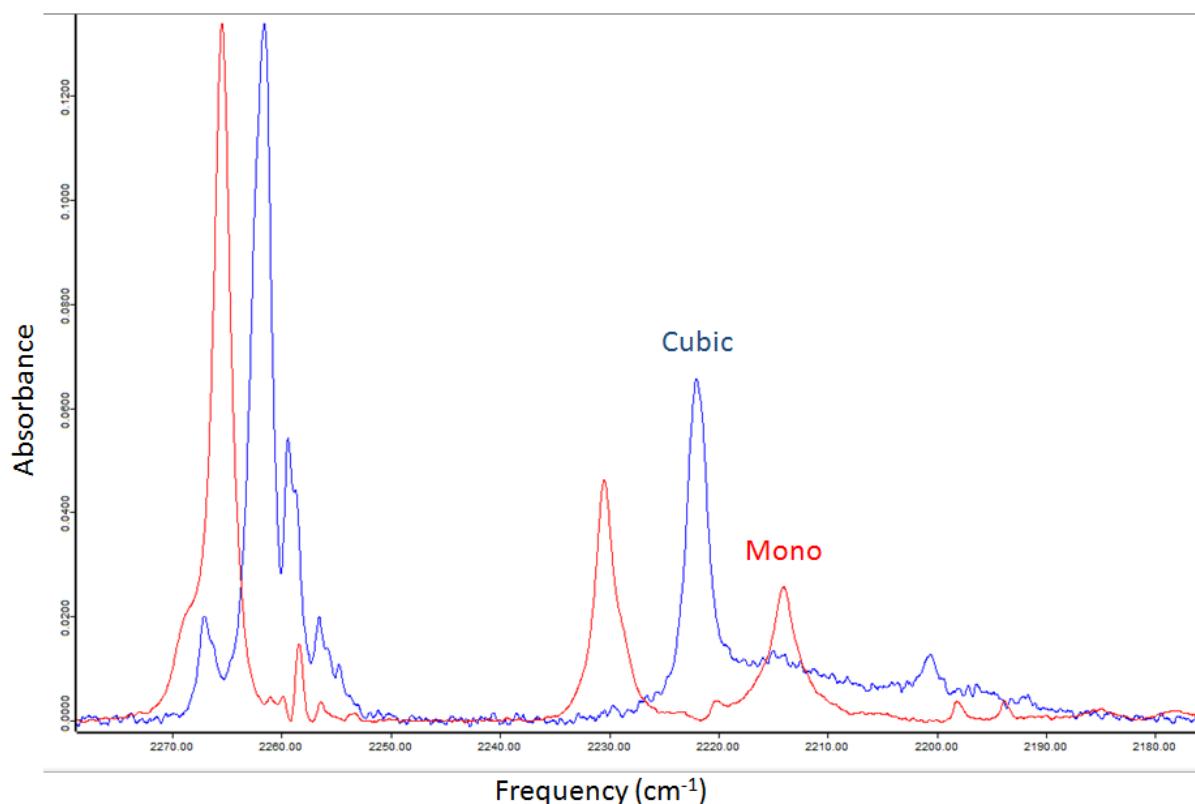


**Figure a.** Hirshfeld surfaces mapped with  $D_{\text{norm}}$ ,  $D_e$ , and  $D_i$ . Decomposed surfaces for  $D_{\text{norm}}$  and associated fingerprint plots are provided for  $\text{C}\cdots\text{N}$ ,  $\text{N}\cdots\text{N}$ , and all interactions. All  $D_{\text{norm}}$  surfaces were standardized to a color scale of Min. = -0.038 and Max = 2.  $D_e$  and  $D_i$  surfaces were standardized at Min = 1.45 and Max = 3.0.



**Figure b.** Relative contribution to the Hirshfeld surface area from various close contacts for the monoclinic and cubic phases of TCNE.

While the Hirshfeld surfaces and fingerprint plots of each phase are visibly different, their individual fingerprint plot breakdowns appear quite similar. In light of the seeming similarities, there are notable close contact discrepancies existing between the structures, namely; the cubic phase has a 0.4% ( $\pm 0.2\%$  [53]) contribution from C···C contacts while the monoclinic phase has none. It is also interesting to note that the cubic phase has 0.9% greater fraction of C···N contacts than the monoclinic phase. The fact that increased coupling between the C≡N vibrons is observed within the monoclinic phase under ambient temperatures points to the fact that not only are the number of contacts between atoms important for energetic coupling, but so are the distances at which these contacts come. This perpetuates the idea that only slight differences in intermolecular contacts are necessary for the variations observed in the phonon DOS and consequently the entropies of each polymorph.



**Figure c.** IR spectra of the cubic and monoclinic phases of TCNE C≡N stretching vibration region measured at 100 K and 0.1cm<sup>-1</sup> resolution. The two F<sub>u</sub> bands of interest for the cubic phase come at 2262 cm<sup>-1</sup> and 2222 cm<sup>-1</sup> whereas the monoclinic phase has two A<sub>u</sub> and two B<sub>u</sub> C≡N stretching modes occurring at 2267cm<sup>-1</sup> (shoulder), 2265cm<sup>-1</sup>, 2231cm<sup>-1</sup>, and 2215cm<sup>-1</sup>. Discrepancies in the number of predicted bands in this region are attributed to combinatorial peaks [21].