Phase Transition between Cubic and Monoclinic Polymorphs of Tetracyanoethylene Crystal: The Role of Temperature and Kinetics

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Abstract: Prediction of the relative stabilities and phase transition behavior of molecular crystalline polymorphs is highly coveted as distinct phases can possess different physical and chemical properties while having similar energies. Crystalline tetracyanoethylene (TCNE, C₆N₄) is known to exhibit rich solid state phase behavior under different thermodynamic conditions, as demonstrated by a wealth of experimental studies on this system. Despite this fact, the role of temperature and kinetics on the phase diagram of TCNE remains poorly understood. Here, first-principles calculations and high-resolution Fourier-transformed infrared (HR-FTIR) spectroscopy experiments are used to study the relative stabilities of the cubic and monoclinic phases of TCNE as a function of temperature. Specifically, density-functional theory with the van der Waals interactions method of Tkatchenko and Scheffler (DFT+vdW) is employed. The accuracy of this approach is demonstrated by the excellent agreement between the calculated and experimental structures. We find that the cubic phase is the most stable polymorph at 0 K, but becomes less favorable than the monoclinic phase at 160 K. This temperature-induced phase transition is explained on the basis of varying close contacts and vibrational entropies as a function of temperature. These findings are supported by a temperature-dependent HR-FTIR linewidth study of the CΞN vibrons.

KEYWORDS: Molecular Crystal, Tetracyanoethylene, TCNE, Density-functional theory with van der Waals interactions, Hirshfeld surface, High resolution FTIR (HR-FTIR).

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1. Introduction:

Molecular crystals usually have several polymorphic forms which often possess different physical and chemical properties, but are typically very close in energy. The small energetic gaps between different structural motifs makes the prediction of polymorphic transitions very challenging, and sets the precedent for continuous improvement of atomistic modeling methods which can eventually be used for crystal engineering [1-4].

Crystalline tetracyanoethylene (TCNE, C₆N₄) possesses rich solid state behavior, exhibiting many polymorphs. Being the strongest π-acid [5], it also acts as a unique electron acceptor in many key charge-transfer complexes. As a result of TCNE’s singular properties, it has been extensively investigated from both basic and applications stand points; e.g. it has been used as a fundamental system for solid state phase transition [6-8] and ionization energy investigations [9]. TCNE has also served as a vital component in both organic superconductors (Bechgaard salts) [10] and molecule-based magnets [11]. Here we concentrate on understanding the fundamental properties that dictate the phase behavior of crystalline TCNE, with an outlook to study the more complex materials mentioned above.

To date, five different polymorphic forms of TCNE have been reported [12-22]. These different crystal symmetries are accessible via variations in the temperature, pressure, and crystallization conditions. The most commonly investigated TCNE structures, monoclinic and cubic, accompanied by their Hirshfeld surfaces (discussed in detail in Section 3.3) are presented in Figure 1. Growth of the cubic phase has only been reported from slow evaporation of ethyl acetate below room temperature [12-15]. In contrast, the monoclinic phase can be grown in a variety of ways: it can be grown from a) ethyl acetate at room temperature [16, 17] b) sublimation (vapor deposition) [18, 19] c) ethyl acetate/carbon tetrachloride solution at room temperature [14, 20] or d) *via* rapid crystallization in ethyl acetate at low temperatures suitable for cubic growth [17]. A third phase of hexagonal/trigonal symmetry has been grown from a methylene chloride/ethyl acetate solution at room temperature [20]. As evident from the wide variety of phases grown by slight variations in the crystallization conditions, the thermodynamics and kinetics involved in TCNE solidification is complex.
Figure 1. Cubic and monoclinic polymorphs of TCNE. The central molecules are surrounded by the 12 nearest neighbors. The cubic structure is viewed down the \( b \) unit cell axis and the monoclinic structure is viewed down the \( a \) unit cell axis. Also shown are the Hirshfeld \( D_{\text{norm}} \) surfaces (see Section 3.3 for explanation). Red atoms correspond to shorter than van der Waals-distance close contacts. \( D_{\text{norm}} \) surfaces were standardized to a color scale with minimum = -0.038 and maximum = 2.

Once crystallized, TCNE exhibits pressure- and temperature-induced polymorphic phase transitions. The first order temperature-induced phase transition from the cubic into the monoclinic phase occurs at temperatures above 318 K and is determined to be irreversible to 4 K [17-19, 23]. While the majority of the temperature dependent data involves the cubic to monoclinic transition, a second temperature induced transition has been noted; \( i.e., \) upon rapid cooling with liquid nitrogen, the monoclinic phase will change into an unidentified phase (not cubic) [21]. A second set of pressure-induced phase transitions has also been investigated [6-8, 21, 22, 24-26], where the monoclinic phase converts to an unidentified intermediate phase (thought to be triclinic) when pressurized between 2.0-6.3 GPa. Upon release of pressure, the intermediate phase is followed by conversion to either a) the cubic phase (provided sufficient time under high pressure) or b) the original monoclinic phase.

Finally, high pressure polymerization reactions of TCNE at room temperature have been observed when starting from either the monoclinic or cubic phases [6-8, 21, 22, 24-26]. The most
recent investigations indicate that when using no pressure medium, the monoclinic phase completely polymerizes above 6.4 GPa while the cubic phase is stable up to 14 GPa [22]. Interestingly, the polymerized material is a form of amorphous carbon with 52% less nitrogen than crystalline TCNE, and the C:N ratio obtained from neutron/x-ray diffractions was 7:1 for the polymerized product compared to 3:2 for the original material [7].

Attempts have been made to explain the temperature and pressure dependence of the monoclinic and cubic phases using quasi-harmonic dynamical calculations with simple empirical force fields. It was determined from those calculations that the monoclinic phase was the more stable of the two phases at elevated temperatures. The reasoning was that the monoclinic polymorph has a higher degree of vibrational entropy compared to the cubic phase, resulting in a lower free energy [27]. The phase diagram developed from this investigation also demonstrated that the cubic phase is never energetically favorable at ambient pressure. This may be unlikely due to the fact that the cubic phase is obtained via controlled growth at low temperature. Though many qualitative trends of TCNE were replicated, several problems exist with the methodology of these calculations, as pointed out by the author [27] and others [28]. Further attempts were made to improve upon these calculations by including the electrostatic interactions within the crystal, but only the monoclinic phase was investigated, so a reliable comparison between the two polymorphs was never performed [28].

In order to elucidate the energetic variations leading to the temperature dependent phase transition of TCNE, the DFT+vdW method is used in this study to explore the free energies of the cubic and monoclinic polymorphs as a function of temperature. We find that the DFT+vdW approach leads to excellent agreement of the unit cell volumes compared to experiment. The temperature-induced phase transition between cubic and monoclinic polymorphs of TCNE is attributed to the difference in the intermolecular close contacts between these two polymorphs. Finally, a temperature dependent HR-FTIR investigation of the vibrational lifetimes of the CΞN vibrons confirms the theoretical findings.

2. Methodology

2.1 Computational Details: Density functional theory [29] method implemented in the program CASTEP [30] was used in the investigation. Norm-conserving potentials were
employed for C and N, where valence electrons included 2s\(^2\) 2p\(^2\) and 2s\(^2\) 2p\(^3\), respectively. The planewave basis set cutoff was 770 eV. The use of a relatively high plane wave basis set cutoff is to ensure that the total energy and unit cell volume converge, as demonstrated in a similar study of crystalline indole [31]. The k-point grid was kept to maintain a spacing of ca. 0.07 Å\(^{-1}\). The GGA functional of Perdew, Burke, and Ernzerhof (PBE) [32] was used. The convergence criteria for total energy, maximum force, maximum stress, maximum displacement, and SCF iterations were 5E\(^{-6}\) eV/atom, 0.01 eV/Å, 0.02GPa, 5E\(^{-4}\) Å and 5E\(^{-7}\) eV/atom, respectively. The phonon density of states was calculated with CASTEP’s implementation of density functional perturbation theory (DFPT) [33]. K-spacing of 0.0286 Å\(^{-1}\) was employed in sampling the vibrational density of states with sufficient resolution.

The DFT+vdW method [34] was used to account for the ubiquitous van der Waals (vdW) interactions, known to be important for molecular crystals [35-37]. In the DFT+vdW approach, both the vdW \(C_6\) coefficients and the vdW radii are determined dynamically, based on the Hirshfeld partitioning of the self-consistent electron density of a given structure. This is of particular importance for molecular crystals, where non-conventional bonding patterns are often present.

The Hirshfeld surfaces and finger print plots were produced in the program Crystal Explorer [38], where the vdW radii are derived from Bondi [39]. Initial structures for each calculation were taken from the corresponding x-ray investigations of each polymorph [12, 20].

We note that recent studies [40, 41] suggest that a many-body approach may be necessary for an accurate determination of the intermolecular binding energies. The present pairwise method for vdW interactions has been shown to reliably model the structures and energetics of other molecular crystals (indole, naphthalene, anthracene, tetracene, and pentacene) up to 25 GPa [31, 42].

2.2 HR-FTIR: TCNE was purchased from Sigma-Aldrich (T8809 - 98%). The monoclinic phase was obtained via sublimation according to references 18 and 19. The cubic phase was obtained from ethyl acetate solution as described elsewhere [12-15]. Spectra were obtained using a Bruker HR-120 FTIR at a resolution of 0.1 cm\(^{-1}\). The polycrystalline samples were mounted onto a closed cycle He cryostat and coupled into the sample compartment of the
FTIR with cassegrain optics as previously described [43]. Only intense isolated bands with high Lorentzian character (> 85%) were analyzed. Bruker’s OPUS software was used to fit a sum of Lorentzian bands [44] to the IR lineshapes as described elsewhere [45, 46].

3. Results and Discussion:

3.1 Structure. The ability of the PBE+vdW method to accurately model the two crystalline phases of TCNE is demonstrated in Figure 2 and Table 1. In Table 1, the unit cell parameters, density and molar volumes are presented, showing overall agreement to experiment of 1% for the monoclinic phase and 3% for the cubic phase. X-ray studies [12, 20] show that the monoclinic phase has a molar volume that is ~5% larger than that of the cubic phase. The calculated (PBE+vdW) molar volume of the monoclinic phase is ~4% greater than that of the cubic phase, improving upon the previous simulation study [27] which gave just a 1% difference.

Figure 2. TCNE molecular geometry in monoclinic and cubic crystalline phases as derived from X-ray spectroscopy, Neutron diffraction, and the PBE+vdW method. The measurements come from the following references: Monoclinic X-ray at 295 K [20], monoclinic neutron at 5K [18], cubic x-ray and double atom refinement at 295 K [12].
Figure 2 examines the details of the computed molecular structures as compared to x-ray diffraction (XRD) and neutron structure determinations. In both the monoclinic and cubic phases, the computed values for the CΞN distances are ~1.16 Å, whereas the corresponding values from XRD are ~1.13 Å for both phases, resulting in a 2.6% difference. On the other hand, available neutron diffraction data at 295 K and 5 K for the monoclinic phase gave CΞN distances of 1.156 Å [47] and 1.150 Å [18] respectively, agreeing well with the DFT results (to within 1%). The observed shortening of the CΞN bonds in the XRD structures of TCNE and other structures has previously been addressed using high-angle data [48] and double-atom refinement [12]. It is important to note that, the bond lengths obtained from the calculations and neutron data correspond to the distances between atomic nuclei, whereas those from XRD experiments correspond to the centers of the electron densities for each atom. These two sets of data may not coincide in cases where polar or high order bonds are involved [12, 49]. One way to correct for this in XRD experiments is with a double atom approach, where the electron densities for the core and shell electrons are refined separately. When applied to the cubic polymorph, the structure obtained from the double atom refinement corresponds well with DFT, yielding a “corrected” CΞN length of 1.166 Å [12].

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Table 1. Crystallographic and energetic parameters of the cubic and monoclinic phases of TCNE. All energetic terms are reported per molecular unit (C₆N₄). ΔH_lattice (ΔH_sub) is obtained from the difference of total energy of the crystal and the isolated molecule, including the respective zero-point energies.

The same case can be made for the C=C and C-C bond variation between x-ray and DFT. The C=C bond’s electron density is contracted towards the center of the bond, resulting in a “shorter” bond length when determined via XRD (1.32 Å [20]). With that being said, both neutron diffraction [18, 47] and DFT show the C=C bond to be 1.38 Å, and the double atom...
refinement for the cubic phase [12] shows it to be 1.36 Å. The C-C bond is “elongated” when observed via XRD, due to the withdraw of electron density into the neighboring high order/polar bonds. In contrast, the C-C bond lengths obtained from neutron, DFT, and double atom refinement are all consistently shorter (see Figure 2). The excellent agreement achieved between the calculations, neutron diffraction, and double atom refinement molecular geometries, as well as the XRD and calculated unit cell parameters, displays the usefulness of the present PBE+vdW methodology.

3.2 Energetics:

As mentioned, previous rigid body calculations of TCNE with a simple empirical force field attempted to demonstrate the relative stabilities of the two crystalline phases with respect to pressure and temperature, resulting in a calculated phase diagram [27]. It was concluded that the static potentials of both the monoclinic and cubic phases were very close across the entire temperature and pressure range, but that the monoclinic phase exhibited increased energetic stability at elevated temperatures; this was attributed to increased vibrational entropy when compared to its cubic cousin. While the qualitative phase stabilities trends were followed at elevated pressures, the monoclinic phase was calculated to always be energetically favorable at pressures below ~0.5 GPa regardless of temperature. This would mean that the cubic phase is always metastable at ambient pressure.

While the present study confirms that the stability of the two phases are similar, it is shown in Table 1 and Figure 3a that the cubic phase is energetically more favorable at 0 K than the monoclinic phase by 0.04 eV (contrary to the previous study [27]). This difference in crystal packing energies is in agreement with the experimental observation that slow crystallization of TCNE from solution at low temperatures results in the cubic phase. Yet, the difference in energy of the two phases is so small that fast crystallization at temperatures suitable for cubic phase growth can result in the monoclinic polymorph [17].
We used harmonic phonon calculations \cite{33} of the two polymorphs to determine the phonon density of states (DOS), providing insight into the temperature dependence of the enthalpy, entropy, and therefore free energy (see Figure 3). The results of these calculations show that the cubic phase is energetically favorable at temperatures below 160 K, and that the monoclinic phase becomes the preferred polymorph at higher temperatures (see Figure 3a). It should be pointed out that, while the cubic to monoclinic transition temperature is found at 160 K in Figure 3a, no temperature induced transition is observed experimentally until 318 K. This fact can be attributed to the large phase transition barrier (230±20 kJ/mol [~2.38 eV]) which hinders molecular reorientation at low temperatures \cite{17}, causing metastability of the cubic phase between 160 and 318 K. The large transition barrier also explains the fact that the cubic phase retains its symmetry at room temperature, even after several months \cite{23}. On the other hand, the transition barrier, in addition to the very small difference in energetics, explains why
the inverse phase transition (from monoclinic to cubic) is not observed when the sample temperature drops below 318K.

The temperature dependence of the entropy and enthalpy are presented in Figures 3b and 3c respectively. It is demonstrated that the monoclinic phase has a greater entropy temperature dependence than the cubic phase (see Figure 3b). On the other hand, while the temperature dependence of the enthalpy of the monoclinic phase is greater than that of the cubic phase below 50 K, it becomes equivalent at higher temperatures (see Figure 3c). Both of these trends contribute to the lower free energy of the monoclinic phase at elevated temperatures.

The phonon DOS of the two polymorphs below 10 THz is compared in Figure 4. It’s known that low-frequency phonons, particularly those below 6 THz, assert heavier weight in changing the vibrational entropy component of the free energy than those of higher energy [27]. Therefore, any shift in the density of states below 6 THz will have a larger impact on the free energy than shifts above 6 THz. As evident in Figure 4, the monoclinic phase has a higher phonon DOS in the low frequency regions, particularly below 2 THz, compared to that of the cubic phase. The substantially greater density of vibrational states below 2 THz in the monoclinic phase favors this phase’s stability at elevated temperatures due to increased vibrational entropy.

![Phonon density of states for the cubic and monoclinic phases of TCNE, computed with PBE+vdW.](image)

Figure 4. Phonon density of states for the cubic and monoclinic phases of TCNE, computed with PBE+vdW.

3.3 **Increased intermolecular coupling leads to higher entropy for the monoclinic polymorph**
While the energies of the two polymorphs are very close, their individual crystal structures are quite different, as shown in Figure 1. In order to further rationalize the increased entropy of the monoclinic structure with respect to the cubic polymorph, we calculated the Hirshfeld surfaces of both phases. Hirshfeld surfaces sample the electron density surrounding the molecules and correlate intermolecular close contacts occurring at the surface to specific atom types. This provides the ability to demonstrate specific atom-atom intermolecular interactions, as well as providing a quantitative value to the amount of a given contact type with respect to all others in a 2D fingerprint plot [50-52].

The D$_{\text{norm}}$ Hirshfeld surfaces generated from the crystalline x-ray structures of both polymorphs surrounded by the 12 nearest neighbors are shown in Figure 1. There are essentially only C···N and N···N contacts existing within the two polymorphs (see Figures a and b in supplementary data for the decomposed D$_{\text{norm}}$ surfaces, fingerprint plots, and close contact histograms). Here, color is the index, where the bright red spots on the D$_{\text{norm}}$ surfaces represent the C···N contacts of neighboring molecules that are shorter than the vdW radius of the two interacting atoms, while the white areas on the surfaces represent contacts occurring at vdW separations and the blue represents contacts occurring beyond the vdW radii [39].

Bright blue tips visible at either end of the cubic structure’s D$_{\text{norm}}$ surface in Figure 1 are indicative of voids present in the structure and are not observed for the monoclinic phase (also see D$_{c}$ surface in Figure a of supplementary data). When the temperature is lowered or pressure is increased, these voids aid in denser packing [21, 22]. The D$_{\text{norm}}$ surfaces in Figure 1 also demonstrate that the monoclinic phase possess 20 C···N contacts which occur at distances shorter than vdW separations (bright red circles). Conversely, the cubic polymorph contains only 16 centers of C···N contacts which occur at shorter than vdW separations. As a result of the higher number of shorter than vdW-distance C···N contacts in the monoclinic phase, and its lack of crystalline voids, it would be reasonable to expect increased intermolecular coupling between the CΞN vibrational modes under ambient conditions when compared to the cubic phase.

In order to verify this hypothesis, we carried out temperature-dependent measurements of the IR linewidths for both the cubic and monoclinic polymorphs. In general, it’s known that variations in the close contact interactions (both length and number) can affect the strength of intermolecular mode couplings and lead to shifts in the phonon density of states, each of which
can affect the vibrational dynamics that determine the vibrational linewidth. It has been demonstrated via high pressure IR experiments on TCNE that since the cyano groups are oriented outward from the central C=C bond, that the CΞN stretching frequencies are particularly sensitive to molecular approach and rearrangement [21]. In addition to the preceding statements, since all shorter than vdW interactions were determined to be between nitrogen and carbon atoms, particular attention was paid to the characteristic temperature dependencies of the CΞN vibrational linewidths.

Since the monoclinic phase has a greater number of shorter than van der Waals C⋯N contacts under ambient conditions, faster depopulation/dephasing of the CΞN modes should occur under such conditions; i.e., conceivably more ways exist to strongly couple modes involving nitrogen to neighboring molecules in the monoclinic phase under ambient conditions, so the full width at half max (FWHM) of these bands should be broader above the free energy transition temperature. On the other hand, as the temperature is lowered and the cubic phase packs more efficiently, the intermolecular mode couplings and bandwidths of the cubic phase should approach that of the monoclinic phase.

The temperature dependent linewidths (FWHM) for the IR active CΞN stretching vibrons are presented in Figure 5. The monoclinic and cubic structures show distinctly different linewidth temperature dependencies, with the monoclinic phase possessing broader bands at temperatures > ~160 K (remarkably similar to the free energy crossing, see Figure 3a). This difference in linewidth temperature dependence is associated with the higher number of shorter than vdW C⋯N contacts in the monoclinic phase at high temperature compared to the higher packing ability of the cubic phase at low temperature. Therefore, the noted variations in the number and distances of intermolecular close contacts observed in the Hirshfeld surface analysis are shown to have a dramatic effect on the manner/rate of energetic depopulation.
Figure 5. Temperature dependent linewidths (FWHM) of the CΞN stretching modes obtained from HR-FTIR measurements for the cubic and monoclinic polymorphs. The differing number of modes between the two phases results from the two CΞN stretching modes of the free molecule (B_{1u} and B_{2u}) splitting into four modes (2A_u/2B_u) in the monoclinic phase while translating into two F_u modes in the cubic phase [21]. The fourth CΞN stretching band of the monoclinic phase is a shoulder and is not included in the analysis (see figure c in supplementary data).


Density-functional theory with van der Waals interactions (DFT+vdW) method is capable of yielding excellent agreement with experiment for the two established polymorphs of TCNE. It was found that, for the cubic and monoclinic polymorphs of TCNE, the enthalpies of formation at 0 K differ by only 0.04 eV. The cubic phase is determined to be slightly more stable at 0 K, but becomes less favorable in free energy at 160 K. The Hirshfeld surface analysis of the two crystalline polymorphs demonstrates varying qualitative interactions between the neighboring molecules of the two phases, but reveals only slight quantitative variation between the fractions of intermolecular close contact interactions. A higher number of shorter than vdW-distance close contacts was observed within the monoclinic phase as compared to that of the cubic phase, underlining the increased vibrational entropy at elevated temperatures within the monoclinic phase, and serving as the primary driving force for the temperature induced phase transition.
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References:


[40] Podeszwa, R.; Rice, B. M.; Szalewicz; *K. Phys. Rev. Lett.* **2008** *101* 115503.
[42] Schatschneider, B.; Liang, J. J.; Tkatchenko, A. “Simulated high-pressure dynamics of polyacenes: DFT+vdW study” (To be Published 2012).
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 C···N, N···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.
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% (± 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 CΞN 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 b.** Relative contribution to the Hirshfeld surface area from various close contacts for the monoclinic and cubic phases of TCNE.
Figure c. IR spectra of the cubic and monoclinic phases of TCNE CΞN stretching vibration region measured at 100 K and 0.1 cm$^{-1}$ resolution. The two F$_u$ bands of interest for the cubic phase come at 2262 cm$^{-1}$ and 2222 cm$^{-1}$ whereas the monoclinic phase has two A$_u$ and two B$_u$ CΞN stretching modes occurring at 2267 cm$^{-1}$ (shoulder), 2265 cm$^{-1}$, 2231 cm$^{-1}$, and 2215 cm$^{-1}$. Discrepancies in the number of predicted bands in this region are attributed to combinatorial peaks [21].