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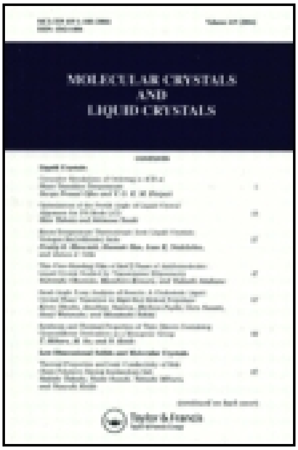

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Orientational Disorder in π–π Molecular Compounds by Cryogenic Thermophysical Measurements†

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We have studied the heat capacities of three naphthalene charge-transfer complexes (with tetracyanobenzene, with tetracyanoethylene, and with pyromellitic dianhydride) to supplement the little data available and resolve questions about the orientational disorder in these molecules. The first has a broad maximum in the heat capacity near 70 K, the second a bifurcated peak near 160 K and a broad transition culminating in a rounded hump near 222 K. The third has a curve on which no anomalies are evident. The interpretation of these data and their correlation with results for other compounds is considered.

INTRODUCTION

Although solid state π–π molecular compounds formed from the interaction of aromatic hydrocarbons and various electron acceptors have been the subject of many structural, spectroscopic and theoretical studies, only a single thermophysical study has been reported.[1] Consequently, we have studied the thermal behavior of three naphthalene compounds: naphthalene-tetracyanoethylene (or N-TCNE), naphthalene-tetracyanobenzene (or N-TCNB), and naphthalene-pyromellitic dianhydride (or N-PMDA). Two compounds in which pyrene is the donor moiety have been studied in the Oxford laboratory of Dr. Lionel Staveley.[1,2]

For convenience the structures of these three compounds and the two studied by Staveley *et al.*[1,2] are shown in Figure 1, together with the code names which will be used throughout this paper.

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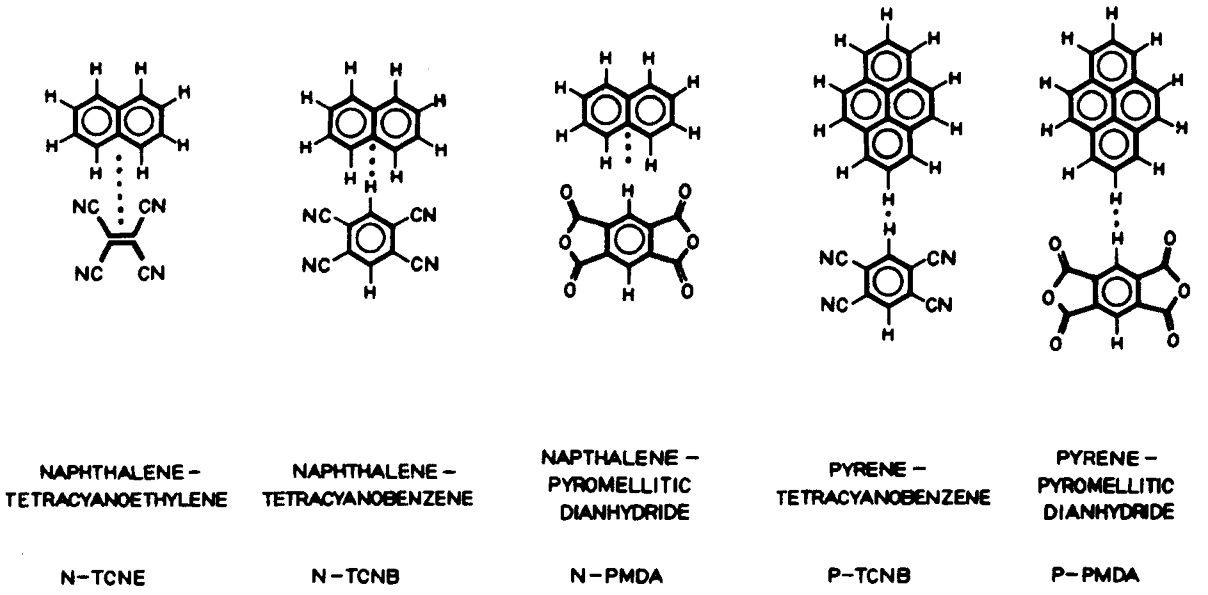

FIGURE 1 Structures, names and codes for the five compounds featured in this paper.

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The ambient temperature structures of more than 40 comparable crystalline donor-acceptor compounds have been reported. They have a characteristic arrangement in mixed stacks with an alternating donor-acceptor sequence along the stack axis. The stack axis is parallel to the *c*-axis of the unit cell and the planes of the donor and acceptor molecules are nearly parallel (but inclined somewhat to the *c*-axis). Authors of the original structural determinations claimed the donor molecules had an anomalously large degree of thermal motion. More recently, the apparent motion in many of these studies has been reinterpreted as indicating the presence of a static disorder in which the donor molecules can occupy two equilibrium positions.[3]

Dr. Colin Fyfe of the University of Guelph, Canada, has studied many of these same compounds by measuring the second moments of their wide-line n.m.r. spectra[4,5] and their spin-lattice relaxation times[6] as a function of temperature and his results show that there is indeed a high degree of motion present in these substances. They also suggest that the disorder indicated by the diffraction studies is of a dynamic rather than a static nature. Two distinct kinds of motion are observed for the naphthalene compounds and it is believed that these begin to take place at different temperatures. The naphthalene molecules are considered to occupy two orientations related by an in-plane rotation about the *c*-axis. At low temperatures, it appears that the molecules are able to jump over an acute angle from one orientation to the other. As the temperature is increased, the molecules begin to jump over the supplementary angle as well, which results in a complete in-plane reorientation of the naphthalene molecules. As the angle between the two orientations becomes smaller, it becomes more difficult for the n.m.r. technique to distinguish between the occurrence of a small angle jumping motion between two sites and a motion in which the molecule sits at one orientation and undergoes a large in-plane vibration. For N-TCNB it appears certain that the molecules occupy two sites separated by about 36° and that the molecules jump from one orientation to the other by jumping over the small angle at 77 K. In N-TCNE, where the motion must be over about a 17° angle to account for the observed second moment a large amplitude libration is also a possible explanation.

Heat capacities have long been used to study order-disorder transitions in solids[7] and therefore, it seemed likely that such measurements would prove valuable in confirming the presence of disorder in the compound, ascertaining the nature of the molecular motion observed in charge-transfer complexes. and determining the temperature at which motion begins. If the molecular motion arises from small angle jumping over two distinguishable orientations, then disorder is introduced into the crystal. The onset of a disordering process in usually observed in the heat capacity curve as a transition whose entropy can be on the order of $R \ln N$ where N is the number of non-equivalent

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sites which can be occupied. If, on the other hand, the naphthalene molecules occupy a single orientation and the observed motion arises from a large amplitude vibration, no disorder is present and the heat capacity will show no anomaly.

EXPERIMENTAL

Samples for this work were prepared and characterized by Dr. Colin Fyfe and his co-workers at the University of Guelph. Considerable care was taken to insure the highest purity possible despite difficulties in the synthesis of these materials. The heat-capacity measurements were made using intermittent-heating, adiabatic calorimetric techniques from 5 to 300 K. The calorimetric apparatus has been previously described.[8] Calibrations have been referred to standards at the National Bureau of Standards. The calorimetric methods were such that equilibrium was achieved before the next energy input was made. Extreme care was taken upon cooling to ensure that complete conversion to lower-temperature phases was achieved.

RESULTS

N-TCNE

Heat capacity measurements made by adiabatic (equilibrium) calorimetry from 5 to 300 K for N-TCNE show a bifurcated peak near 160 K and an extended transition culminating in a rounded hump at 222 K as shown in Figure 2. The bifurcated peak region is shown in greater detail in Figure 3. The total enthalpy under both transitions was quite reproducible as determined by a number of enthalpy determinations which spanned each of the two transitions. In order to determine the transitional thermophysics, it is necessary to determine a lattice heat capacity which contains all the contributions to the total heat capacity not related to the transition. Even in the best of situations, the choice of a lattice heat capacity is somewhat arbitrary. In this compound where the two transition regions overlap and the regions of excess heat capacity extend over 100 K, it becomes extremely difficult to choose a good lattice. Inspection of the Debye thetas calculated from data below 150 K and above 230 K showed that a smooth interpolation could be made connecting the heat capacities of the non-transition regions.

The entropy contributions were arbitrarily resolved into two segments covering both transition regions. The first includes the region from 150 to 172.5 K and contains all of the transitional entropy from the bifurcated peak. The second segment goes from 172.5 to 240 K and involves most of the entropy from the transition which culminates at 222 K. The entropies from these two regions were approximately equal at 1.22 and 1.20 cal K^{-1} mol^{-1}.

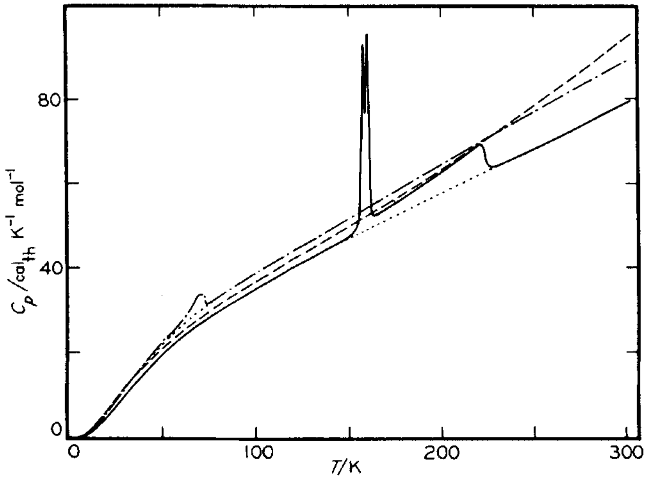

FIGURE 2 Heat capacities of: N-TCNE, N-TCNB, N-PMDA. (For clarity the experimental points have been omitted. For all the curves a dotted line (. . . . .) indicates the assumed lattice heat capacities.)

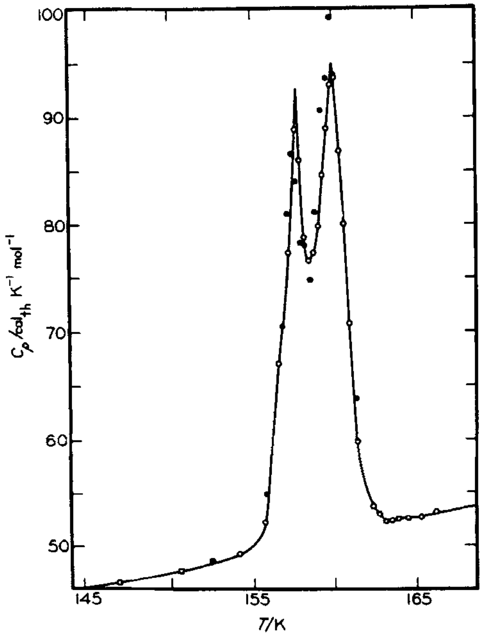

FIGURE 3 Details of the bifurcated peak in N-TCNE showing experimental points.

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Both are close to $R \ln 2$ which is the value that might be expected for an order–disorder transition involving two distinct sites in the high-temperature phase.

The conclusions reached from various adjuvant studies of this compound are the following: x-ray diffraction measurements[9] indicate that the naphthalene molecules are disordered at 300 K and that a monoclinic to triclinic transformation takes place at 150 K.[3] The second moment, $(\Delta H)^2$, studies suggest that two separate motional processes are taking place but cannot differentiate whether the low energy process involves jumping over the small angle.[5] They do indicate that the motion is still going on below 77 K and yet this is a region in which no anomaly appears in the heat capacity. The pulsed measurements[6] are able to give an approximate value for the activation energy of the high-energy jumping process (that is, the large angle jumping motion which is thought to begin above 250 K) but are unable to determine one for the low energy process. A ^{14}N nuclear quadrupole resonance study[10] also suggests that some type of transition takes place between 300 and 77 K because non-equivalent nitrogen atoms are observed at this low temperature while one would expect equivalent atoms from the 300 K x-ray structure.

The heat capacity study is interpreted in that the bifurcated peak almost certainly arises from the monoclinic to triclinic conversion observed by the crystallographers, but we cannot explain why this peak is split in two. The lack of a transition in the region from 50 to 60 K leads us to suspect that the motion observed by n.m.r. techniques below 77 K arises from librational rather than small angle jumping motion. The phase change may alter the lattice slightly so as to allow complete reorientation to take place at temperatures above 150 K and, consequently, for disorder to be introduced into the crystal. It also seems likely that the extended transition observed above 172.5 K may be due to the gradual onset of molecular reorientation so the crystal does not become disordered immediately but the degree of disorder becomes greater as the temperature is increased. We admit the possibility of disorder below the transition and existence of residual entropy at 0 K, but additional information necessary to determine zero-point entropy is not presently available.

N-TCNB

The results are quite different for the N-TCNB compound[11] as shown in Figure 2. Only one anomaly located near 70 K, shown in detail in Figure 4, was found. The heat capacity curve is a broad maximum similar to the higher-temperature transition in N-TCNE in that the transition begins very gradually, extends over a 50 K region and then stops abruptly. Assignment of the

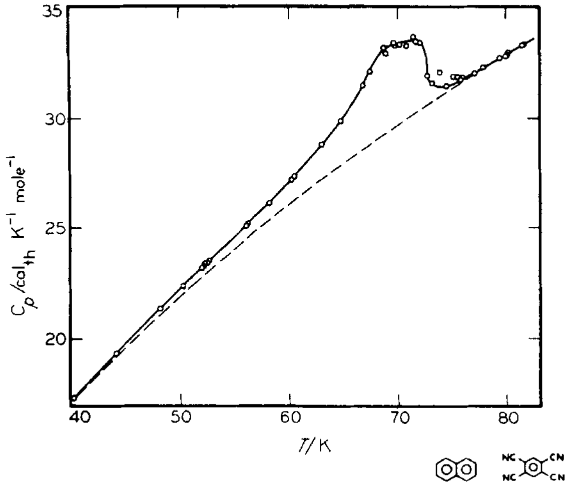

FIGURE 4 Details of the gradual peak in N-TCNB showing experimental points.

lattice heat capacity is again somewhat arbitrary, this time the situation is complicated by the location of the anomaly in a region in which the total heat capacity is changing very rapidly with temperature. The entropy of transition is evaluated as 0.71 cal K^{-1} mol^{-1}.

Results accumulated from other studies,[12] clearly favor the presence of disorder in the N-TCNB crystals down to very low temperatures. Two distinct motional processes are observed in both the second moment and spin-lattice relaxation time measurements, (T_1 and $T_{1\rho}$).[6] From the latter technique, values for the activation energy barriers for both types of motion have been determined. Raman spectroscopy has also been used to study this compound and these results suggest that an order–disorder transition takes place near 63 K.[13] Our heat-capacity measurements can be interpreted similarly, with the gradual rise in C_p from 30 to 80 K attributed to the gradual onset of small angle jumping and hence an increase in the disorder of the system. At higher temperatures, the large angle jumping motion becomes important but this does not introduce additional disorder into the system and there is not a second transition in the heat capacity.

N-PMDA

Measurements on naphthalene-pyromellitic dianhydride (N-PMDA) are also shown in Figure 2. No anomaly has been observed over the region from 5 to 300 K except for a small peak at 287 K which is believed to be due to a

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small amount of acetic acid. This suggests that the molecular motion observed by the n.m.r. techniques arises from librations and not from reorientations of the naphthalene molecules. This result agrees with a Raman spectroscopic study on this compound.[13]

PYRENE COMPOUNDS

We mention briefly the results of the studies conducted by Dr. Staveley's group on two pyrene compounds. Pyrene-tetracyanobenzene (P-TCNB),[1] showed a single anomaly in the region from 220 to 245 K. The transition was very ill-behaved and could not be made to reproduce, even following identical cooling procedures. The authors chose to draw the heat-capacity curve through the set of measurements giving the most prominent peak and reported the entropy of transition at 2.2 cal K^{-1} mol^{-1}.

The results of the last study,[2] that of the pyrene (P-PMDA) compound, are entirely different from any of the previous measurements. A small peak at 155 K was reproducible. In the region above 270 K a transition appeared two or four times through the region. No values for the entropies of transition have been reported but an interpretation has been made that a disordering process begins to take place at very low temperatures and proceeds in several steps until both components are disordered at 300 K. These results cannot be completely reconciled with the x-ray diffraction studies[14] which indicate that a gradual disordering process does take place but only between 170 and 230 K or with the n.m.r. results which suggest that there is a rigid lattice with no anomalous motion present at 77 K (on an n.m.r. time scale).[4] The large angle jumping is believed to take place above 250 K with no evidence for the independent existence of small angle jumping. We believe that it would be worthwhile to repeat the heat capacity study of this compound using a purer sample in hopes of resolving the differences between the conclusions from the various studies.

CONCLUSIONS

The addition of thermodynamic data to those of other methods has thus helped to elucidate the motional behavior of several molecular crystals. In N-TCNE, heat-capacity measurements have pinpointed the occurrence of a structural transition at 160 K and they suggest that the molecular motion observed below this temperature is due to large amplitude libration of the naphthalene molecules. In P-TCNB, an order–disorder transition was found at 232 K which indicates that the molecular motion taking place at room temperature must begin at this lower temperature. The heat-capacity measurements on N-TCNB provided additional evidence for the presence of orientational disorder and suggest that the small angle jumping begins below 50 K. The results of the heat capacity study of N-PMDA have enabled us to conclude that librational but not reorientational motion of the naphthalene molecules occurs in this compound. The only compound in which the heat-capacity measurements were inconclusive was P-PMDA but additional studies may yet resolve the conflicting data.

We anticipate that heat-capacity measurements will continue to be valuable in understanding motion in molecular crystals and we propose to extend our study to several other charge-transfer compounds.

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