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TRIPLET-STATE EPR STUDY OF THE EFFECT OF DEUTERATION ON THE PHASE TRANSITION IN ANTHRACENE-TCNB CRYSTALS

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A triplet-state EPR investigation of the effect of anthracene deuteration on the phase transition in anthracene-TCNB crystals has shown that: (1) The transition temperature is lowered by 28 K, (2) the two phases coexist over a 10 K temperature range, and (3) two distinct sets (excitons and X-traps) of symmetry-related triplet states are populated in the low temperature phase.

INTRODUCTION

A few years ago we showed[1] that, in the low temperature phase[2] of the 1:1 complex between anthracene and 1,2,4,5-tetracyanobenzene (TCNB), the anthracene molecules take two symmetry-related orientations in which the long molecular axes make an angle ∿16° -- a result which has now been confirmed by X-ray diffraction.[3] In the high temperature phase the anthracene long axes have a single orientation, between the two low temperature orientations. The phase transition is relatively sharp (within 1 K) and takes place at ∿202 K with coexistence of the two phases. These results were obtained by electron paramagnetic resonance (EPR) under continuous excitation into the charge-transfer absorption band of the complex. Above 30 K the spectrum is due to mobile triplet excitons which reflect the bulk properties of the crystal, rather than those of defect sites (X-traps) which immobilize the excitation at lower temperature. We discuss here the results of a similar survey of the phase transition in crystals of the complex between anthracene-d_{10} and TCNB.

The relevant earlier work[1] on anthracene-TCNB crystals may be summarized as follows. The low temperature structure accommodates two magnetically distinct triplet excitons which move within one or the other of two symmetry-related sublattices, each consisting of identically oriented anthracene molecules designated A and B. The triplet exciton EPR lines have very narrow intrinsic widths ($\lesssim$ 0.5 gauss) but, in the low temperature phase, are broadened to $\lesssim$ 2 gauss by A-B hopping. That this is the source of broadening is ascertained by orienting the magnetic field so that lines A and B overlap: A-B hopping ceases to contribute to the linewidth, which is reduced to $\lesssim$ 0.5 gauss. Because A-B hopping is thermally activated the linewidths increase with temperature and, if lines A and B are close enough at low temperature, they merge into a single line before the phase transition takes place.

EXPERIMENTAL

Anthracene-d_{10} (Merck, Sharp & Dohme, 98.1% isotopic purity), extensively purified (sublimed, zone-refined, and directionally frozen) by Dr. G.J. Sloan, was kindly supplied to us by Professor C. A. Hutchison Jr. Tetracyanobenzene (Frinton and K & K) was purified by chromatography on alumina followed by recrystallization from ethanol and vacuum sublimation. Crystals of the complex were grown by slow evaporation of spectrophotometric grade acetone (Aldrich) solutions containing equimolar amounts of anthracene-d_{10} and TCNB.

The EPR experiments were performed on a Varian E-12 spectrometer equipped with a temperature-regulated gas flow cryostat. The temperature was measured with a thermocouple placed in the immediate vicinity of the sample, and was calibrated against the sublimation point of CO_2 and the boiling point of oxygen. Excitation was made with a 1 kW mercury-xenon arc lamp (Hanovia) filtered to provide light only at wavelengths longer than 400 nm.

RESULTS AND DISCUSSION

The room temperature EPR spectrum of anthracene-d_{10}-TCNB (d_{10}) crystals is very similar to that previously obtained[1,2] for anthracene-TCNB (h_{10}). However, cooling d_{10} crystals leads to quite different results, a first indication of which can be seen in Fig. 1. This Figure shows the high field half of the EPR spectrum when the magnetic field, $\vec{H}$, is parallel to the b axis of the room temperature structure. The observation of a single sharp line at 192 K indicates that the high temperature structure is still maintained 10 K below the transition temperature, T_c, reported by us[1] for h_{10}. We

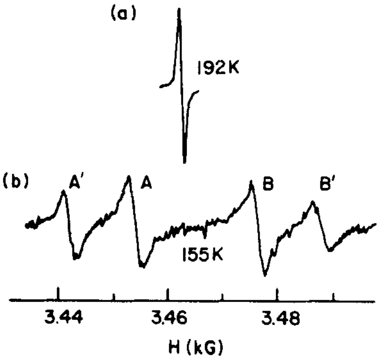

FIGURE 1 High field half of the EPR spectrum of a d_{10} crystal when $\vec{H} \| b$. (a) At 192 K in the high temperature phase. (b) At 155 K in the low temperature phase. The magnetic field modulation amplitude is 0.8 gauss.

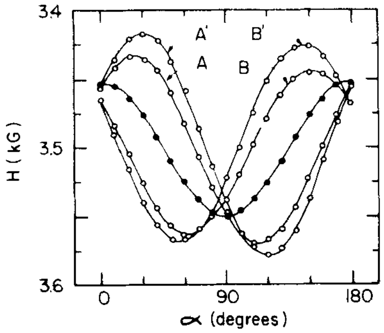

FIGURE 2 Angular dependence of the high field half of the EPR spectrum of a d_{10} crystal when $\vec{H}$ is rotated in the $a'b$ plane. The full circles correspond to 300 K and the open circles to 100 K. The angle α is measured from the b axis.

return later to the determination of T_c in d_{10} crystals, but let us now direct our attention to their EPR spectrum in the low temperature phase. This is shown for $\vec{H}\parallel b$ at 155 K in Fig. 1(b) which reveals two pairs of relatively broad lines ($\Delta H \sim 2$ gauss for A and B, and $\Delta H' \sim 5$ gauss for A' and B'). Lines A and B correspond closely to those found in h_{10} crystals for $\vec{H}\parallel b$. The anisotropy of the spectrum when $\vec{H}$ is rotated in the $a'b$ plane is shown in Fig. 2 at 300 K (full circles) and at 100 K (open circles). Again the A and B patterns are similar to those observed[1] for h_{10} crystals.

In an attempt to understand the origin of the difference between ΔH and $\Delta H'$ we oriented $\vec{H}$ so as to bring lines A and B into coincidence: As with h_{10} a linewidth reduction to 0.5 gauss was observed, which shows that ΔH is determined by A-B hopping.[1] On the contrary, selecting the orientation of $\vec{H}$ so as to superimpose only lines A' and B' led to no observable linewidth reduction, which eliminates A'-B' hopping as the source of the larger $\Delta H'$. In addition to this, raising the temperature causes sufficiently close A and B lines to merge, while equally separated A' and B' lines show no signs of shifting towards each other. We conclude therefore that the intrinsic width of lines A' and B' is one order of magnitude larger than that of lines A and B. Finally, while the total area under lines A and B is roughly independent of temperature (as with h_{10}), lines A' and B' become progressively weaker as the phase transition is approached. All this shows clearly that lines A and B arise from triplet states quite different from those responsible for lines A' and B'. Experiments at 10 K with $\vec{H}$ rotating in the $a'b$ plane give patterns very similar to those in Fig. 2, but now arising from lines which are all ~ 5 gauss wide, as expected for trapped triplet states. With these results in mind we view the spectrum of Fig. 1(b) as arising both from triplet excitons as in h_{10} crystals (lines A and B), and from immobilized triplets (lines A' and B').

Fairly convincing circumstantial evidence indicates that the extra lines come from anthracene-d_{10} X-traps and not from impurities. First the zero-field splitting parameters of the two pairs of lines are very similar. Secondly, in recent EPR experiments[4] on h_{10} crystals we have managed to resolve a four-line pattern similar to that of Fig. 2, although this was possible only for some of the $\vec{H}$ orientations because of the larger linewidths. Finally, preliminary optically detected magnetic resonance (ODMR) experiments[5] in both h_{10} and d_{10} crystals at 4.2 K have shown in each case the existence of two different types of major traps, both with a phosphorescence spectrum characteristic of the anthracene-TCNB complex. It is hoped that further ODMR work in progress will explain why only one trap remains populated at high temperature in d_{10} crystals, while no detectable population is found above 30 K for either trap in h_{10} crystals.

Let us now return to the question of the determination of T_c. In d_{10} crystals the transition takes place over at least 10 K, which is the temperature range in which both phases are observed to coexist. Part of the spectral changes observed when the crystal is warmed up towards the phase transition are shown in Fig. 3 for an orientation of $\vec{H}$ such that lines A and B are well separated from lines A' and B'. (Only lines A and B are shown in Fig. 3). Comparing the spectra in this Figure we see that the sharp high temperature line is visible first at 169 K and grows in intensity as the temperature increases.

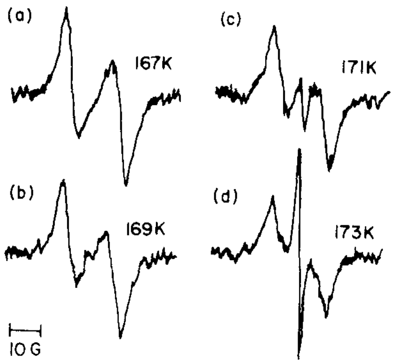

FIGURE 3 Temperature dependence of the high field lines A and B in a d_{10} crystal when the phase transition is approached from below. (Lines A' and B' appear at lower fields and are not shown.) The orientation of $\vec{H}$ is near the long anthracene molecular axes.

This trend continues beyond the temperature range shown, with the broad lines of the low temperature structure still detectable at 179 K. The behavior is the same upon cooling, with no apparent hysteresis. We chose $T_c \sim 174$ K as this is the temperature at which the intensity of the sharp center line is half of its high temperature limiting value. This behavior may be contrasted to the transition in h_{10} crystals, which takes place within 1 K at T_c ∿202 K. There appears to be, therefore, a remarkably large decrease in T_c, ΔT_c∿28 K, upon deuteration of the anthracene partner in the complex. The unsually large magnitude of this effect was confirmed by an experiment in which h_{10} and d_{10} crystals mounted side by side (but orientated differently so that their signals could be easily separated) were taken through their phase transitions.

When viewed against the background of earlier work the results described in the preceding paragraph are surprising. By itself, lowering (rather than raising) of T_c upon deutertion is not without precedent: Bernstein *et al.*[6] observed a decrease ΔT_c = 7 K upon deuteration of naphthalene in naphthalene-TCNB crystals. However, Dalal *et al.*[7] have reported recently T_c = 212 ±2 K for anthracene-TCNB and T_c = 199 ±2 K for anthracene-d_{10}-TCNB. Not only do their results give ΔT_c less than half of the value reported here, but their T_c values are much higher than ours. Because we took special care in checking the temperature calibration near 200 K we feel that our absolute temperatures are accurate to better than ±1 K. Furthermore, the experiment with h_{10} and d_{10} crystals mounted together reinforces our confidence in the large ΔT_c value we measured. The reason for the discrepancy between the present results and those of Ref. 7 is not known. For this reason we are reluctant to even begin speculating on the mechanisms which might be responsible for the surprisingly large ΔT_c we found. It may be useful to point out in concluding that quite spectacular deuterium isotope effects have been reported[8] for one of the *p*-dichlorobenzene phase transitions.

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