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Optical Study of the Phase Transition in Phenanthrene Single Crystals

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A definite change in birefringence has been shown to accompany the solid-solid phase transition in solution-grown single crystals of phenanthrene. The birefringence versus temperature data indicate an onset of the transition at around 45°C and a maximum rate of change at around 70°C, in agreement with other studies. The presence of a birefringence change somewhat relaxes the constraints on possible models for this transition.

Evidence concerning a solid-solid phase transition in phenanthrene, in the vicinity of 70°C, has been accumulating for some time. Various physical methods have been employed to study this phenomenon, including measurements of heat capacity,[1,3,4] thermal expansion,[1,3,5,9] thermal conductivity,[1] electrical conductivity,[2,5,7] dielectric constant,[5,8,9] shifts in infrared absorption maxima,[10] inelastic neutron scattering,[8] and crystal unit cell dimensions.[5,6] The physical nature of this transition has remained unclear.[8,9]

It has been reported that there is no change in birefringence in phenanthrene in the temperature range in question and thus no optical evidence for a phase change.[8] Since one would expect the birefringence to be quite sensitive to changes in molecular orientation, we have undertaken a quantitative study of the temperature dependence of birefringence in phenanthrene.

We have previously reported the use of a specially constructed optical compensator for the polarizing microscope which, in conjunction with a calibrated quartz wedge, allows measurement of birefringence in relatively thick crystal specimens which would otherwise show only the high order white interference color.[11] The advantage of thick specimens is that the measurable change in optical path difference accompanying a change in birefringence is proportional to the sample thickness. This method was applied to phenanthrene single crystals in the present work.

Well-formed single crystals of phenanthrene are difficult to grow by ordinary methods. The crystals used in this study were grown by slow recrystallization from a 70:30 methanol-water solution. An attempt was made to grow phenanthrene crystals in a sodium stearate-methanol gel containing dissolved phenanthrene, by diffusion of water into the gel. The resulting crystals were feathery dendrites, unsuitable for optical study. Ultraviolet spectra of the material used in our work showed the presence of 0.09% anthracene. Sherwood, *et al.*,[12] have recently shown that the impurities in phenanthrene, in which anthracene is the major contaminant, can be reduced to the parts-per-million level by a sequence of chemical and physical puri-

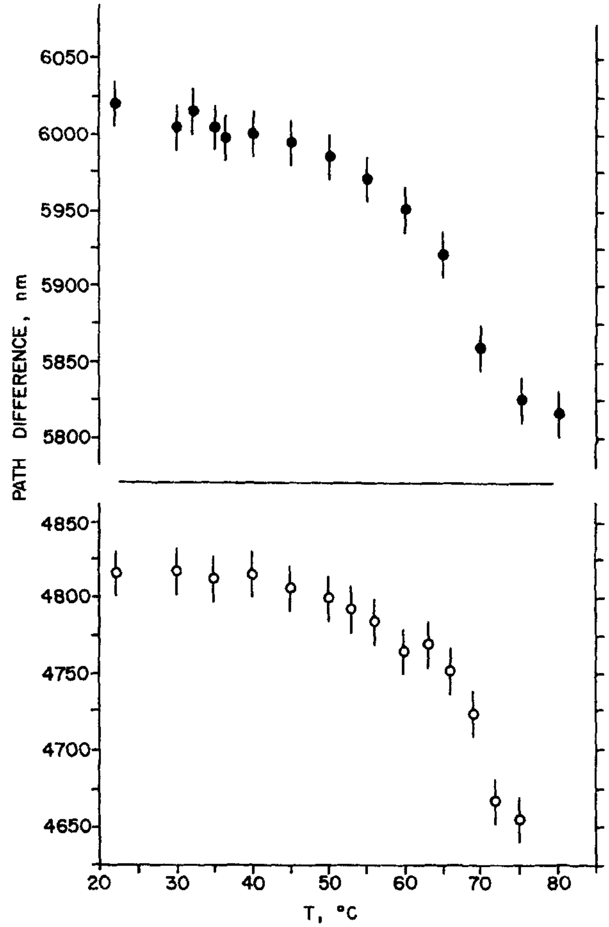

FIGURE 1 Path difference of two different phenanthrene crystals versus temperature. Scatter in points is due to uncertainty in positioning the quartz wedge but is within the error limits of reading the wedge (± 15 nm). Open circles refer to the thinner of the two crystals.

fication steps. Although we have been unable to obtain material of such purity, Sherwood's work indicated that anthracene at the 1000–2500 ppm level did not significantly affect the bulk properties of phenanthrene, although the dislocation mobility was affected.

The crystals selected for study were fairly well-formed pseudohexagonal plates, on the order of 0.05 mm thick. The habit is such that the plates lie on the (001) crystal face. These crystals were observed in the temperature range 21–80°C, using a Vickers M72 polarizing microscope and a Thomas-Kofler heating state in the manner described in Reference 11.

Figure 1 shows the optical path difference versus temperature data for two different phenanthrene crystals. The data follows a profile similar to that seen in other physical measurements on phenanthrene. The slope of the plot begins to change around 45°C, and the region of sharpest descent is near 70°C. For seven trials on various phenanthrene crystals, the average temperature of the sharpest descent was 71°C, with an average deviation of 1°C. Because of the difficulty in controlling the cooling rate of our heating stage, no attempt was made to measure hysteresis.

There is no doubt that the birefringence change seen here is associated with the phase transition in phenanthrene. For comparison, Figure 2 gives comparable data for anthracene, which shows no anomaly in this temperature range. The gradual change in slope for the phenanthrene data in comparison, for example, with the sharp break observed for *p*-diiodobenzene[11] suggests that the transformation in phenanthrene is not an ordinary first order polymorphic phase transition; this has been the conclusion reached by most other workers. The birefringence change does, however, imply a change in molecular orientation, so that possibilities such as a simple order-disorder transformation or an intramolecular conformation change[8,9] are not excluded by our findings.

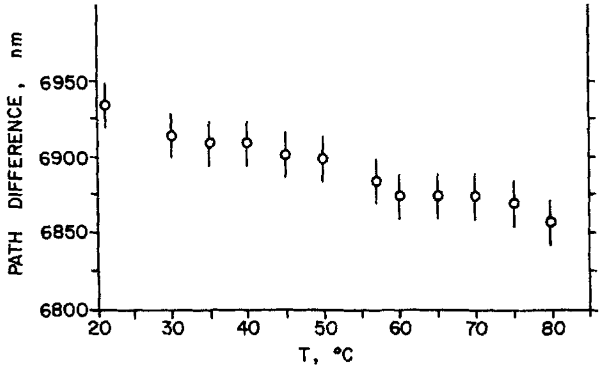

FIGURE 2 Path difference versus temperature for anthracene.

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