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Single Crystal Phase Transition in the Photoconductor *p*-Diiodobenzene

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Abstract—We have firmly established the presence of a single crystal to single crystal phase transition in *p*-diiodobenzene ($C_6H_4I_2$) using optical microscopy and X-ray diffraction methods. This transition usually occurs at 51 ± 1 °C. The presence of a phase transition in this substance had been suggested by other workers to account for a precipitous drop in the charge carrier mobility in this general temperature vicinity. Our work suggests that this dramatic change in electrical behavior is produced by a rather small molecular reorientation.

The peculiar electrical behavior of photoconductive *p*-diiodobenzene (PDI) has been reported previously in this journal.(1) Both that research and earlier work(2) have suggested the possible presence of a solid–solid phase transition in this substance. In each of those studies, however, there existed a question as to the true nature of the effect being observed. The earlier investigation(2) revealed no change in slope of the heat capacity vs. temperature or thermal conductivity vs. temperature plots for this material. The later work(1) found a sharp discontinuity in plots of carrier mobility vs. temperature, but the temperature at which this discontinuity occurred varied over a range of about 15 °C, depending on sample orientation.

We have conclusively established the existence of a phase transition in single crystals of PDI by means of optical microscopy and X-ray diffraction. The single crystal to single crystal transition occurs at 51 ± 1 °C upon heating from room temperature. The transformation is reversible, though the reverse transformation takes 1–2 hours. The extinction direction of the crystal is not changed by the transition, and the reverse transformation always restores the birefringence to its original value.

Our optical work was carried out using a Vickers M72 polarizing microscope and a Thomas-Kofler hot stage. The accuracy of the hot stage in the temperature range employed is ± 1 °C. The phase transition from the low temperature form of PDI to the high temperature form was signalled by a slight but distinct decrease in the birefringence for light vibrating in the *bc* plane of the crystal.(3) Changes in birefringence were detected as changes in the interference color of a crystal viewed through the polarizing microscope. Because of the subtlety of this phase transition and the high birefringence of PDI, however, the transformation cannot be observed by straightforward observation of ordinary crystal preparations. The change in birefringence accompanying the transition is so small that no color change is detected in ordinary fusion mounts (thin films) of this substance. On the other hand, crystals of this highly birefringent material grown from solution in carbon tetrachloride or absolute ethanol are generally too thick to display interference colors under the polarizing microscope.

One's chance of observing a subtle phase transition in polarized light is enhanced by using a relatively thick crystal; since, when a crystal undergoes a change in birefringence, the magnitude of the change in optical path difference between the slow and fast rays is directly proportional to the thickness of the crystal. Unfortunately, crystals of PDI thicker than about 50 μ display only high order white in polarized light because of the high birefringence. An observable interference color can be obtained in such a situation by the use of an optical compensator. It is easily shown that, although the compensator may reduce the total optical path difference to any desired value, the *change* in path difference accompanying a phase transition is unaffected by the presence of the compensator. Thus, by using a suitable compensator, one can superimpose the large optical effect expected in a thick crystal upon a low order interference color.

We have constructed a special compensator by carefully sandwiching twenty layers of cellophane tape between glass slides. This compensator was calibrated using sodium light ($\lambda = 589.2$ mμ) and a previously calibrated quartz wedge. The cellophane compensator was found to have a path difference of 5545 ± 9 mμ for sodium light. By inserting this compensator between the polarizer and the stage of our microscope, we have been able to observe the sharp phase transition in solution-grown single crystals of PDI on the order of 50–100 μ thick. The decrease in optical path difference accompanying the transition was measured with the calibrated quartz wedge and found to be approximately 2%. Data from several runs are shown in Table 1. Figure 1 shows a plot of path difference vs. temperature for two different PDI crystals.

Sometimes, when a crystal of PDI is heated for the first time, the phase transition does not occur until the temperature reaches as high as 57 °C. However, subsequent transformations of the same crystal almost invariably occur at 51 ± 1 °C. This effect may result from slowness in initially nucleating the high temperature form of the crystal. This point could be clarified by using a hot stage capable of precise temperature control, so that the time variable could be more closely regulated.

TABLE 1 Transition Temperatures and Path Differences[a] for Several PDI Crystals

	Path difference before transition, mμ	Path difference after transition, mμ	Transition temperature, °C
CRYSTAL I			
1st heating	7942	7770	57.5
2nd heating	7962	7787	50.0
CRYSTAL II			
1st heating	6554	6432	50.5
CRYSTAL III			
1st heating	6747	6553	56.5
2nd heating	6708	6560	50.5
CRYSTAL IV			
1st heating	8292	8100	57.0
CRYSTAL V			
1st heating	8667	8471	53.0
2nd heating	8680	8470	51.3
3rd heating	8666	8473	51.0
4th heating	8663	8486	51.5
5th heating	not recorded	not recorded	51.5
CRYSTAL VI			
1st heating	7992	7836	57.0
2nd heating	7992	7829	51.5
3rd heating	7992	7797	51.0
4th heating	7979	7784	50.5

[a] The error in the path differences is about ±20 mμ.

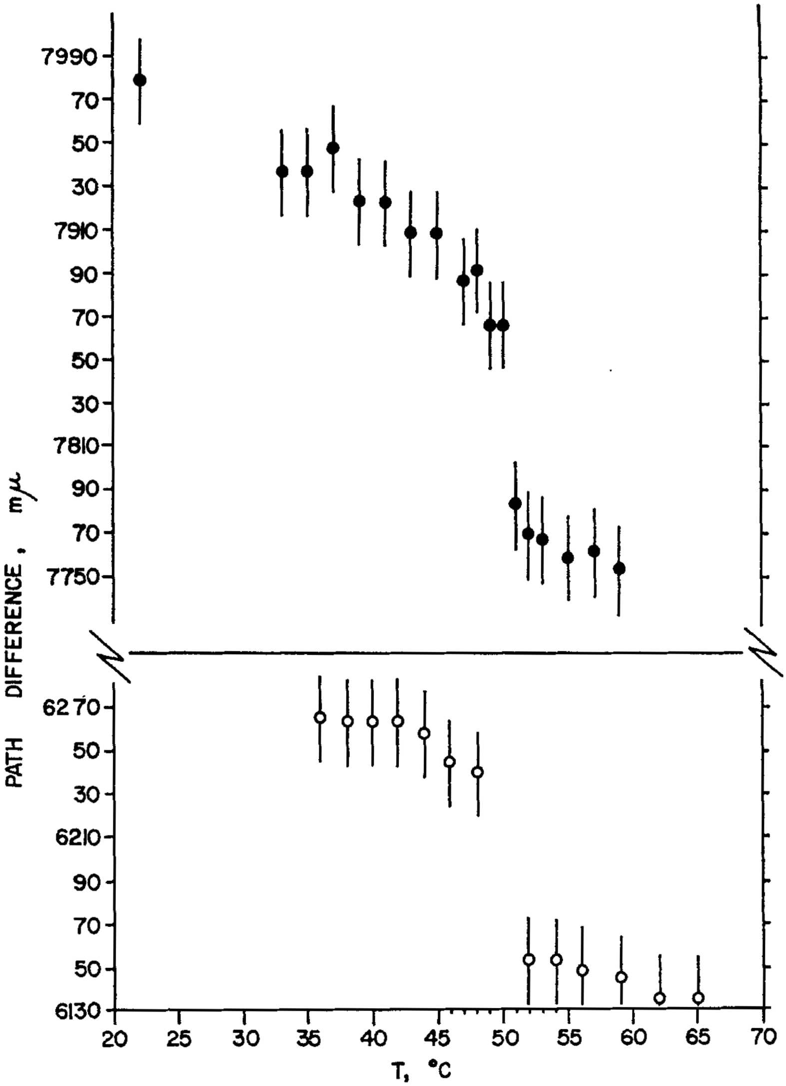

Figure 1. Path difference of two different PDI crystals vs. temperature. Scatter in points is due to uncertainty in positioning the quartz wedge but is within the error limits of reading the wedge (±20 mμ). Open circles refer to the thinner of the two crystals.

We have also measured a discontinuous expansion of the crystal which occurs at the transition temperature. The crystal suddenly elongates by about 1% along the direction of the *b*-axis, while no expansion in the *c*-direction is detected. This result is consistent with the discontinuous increase in molar volume of about 1% reported in Ref. 2.

X-ray diffraction photographs by the Weissenberg method also confirm the presence of a change in phase in PDI.† Comparison of zero-layer Weissenberg photographs of heated and unheated crystals shows a distinctly different pattern of systematically absent reflections for the heated crystals. The zero-layer (*hk*0) Weissenberg photograph of the unheated crystal has absences *hk*0 with *h* odd and 0*k*0 with *k* odd; this is consistent with the space group Pbca given by Dun-Chai and Struchkov.⁽³⁾ The zero-layer Weissenberg photograph of the same crystal after heating has absences *hk*0 with $h+k$ odd.

Both the PDI molecule and the crystal are highly birefringent, and one would expect the observed birefringence for polarized light to be quite sensitive to a general molecular reorientation. The fact that the change in birefringence accompanying the phase transition is observed to be very small suggests that the transition involves only a small reorientation of the molecules. The work described in Ref. 2 is also consistent with this suggestion. Schwartz *et al.*,⁽¹⁾ have found that the hole carrier mobility is relatively high in PDI at room temperature and drops sharply at temperatures in the general vicinity of 50 °C, presumably as a result of the phase transition reported here. Since the molecular reorientation involved in the transition appears to be slight, elucidation of the structural aspects of this phase transition may serve to isolate those structural factors associated with charge transport in this organic crystal.

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