A Phase Transition in Phenanthrene Crystal*

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In a previous paper,[1] we reported that phenanthrene shows an anomaly at around 64—71°C in the temperature dependence of its electrical conductivity; the resistivity increases abruptly with the rising temperature and becomes 6—7 times greater than that below 64°C, while the linear relationship between the logarithm of resistivity and the reciprocal absolute temperature remains kept both below and above the anomaly. We also suggested in that paper that this anomaly may be attributed to a phase transition of the crystal.

In this paper, a differential thermal analysis and a dilatometric investigation of phenanthrene will be presented, and the phase transition confirmed by the results will be discussed.

Experimental

Material.—Phenanthrene of a chemical purpose-grade (Eastman Kodak Co.) was recrystallized three times from an ethanol solution, and then purified further by the zone-melting technique.

The recrystallized specimen was introduced into a Telex-glass tube with a diameter of 10 mm., and the tube was sealed under a vacuum after it had been evacuated for about 12 hr. Then the tube was subjected to forty-five passes in an automatic zone refiner, clamped in a vertical position. The molten zone about 5 mm. long was controlled to move downward at the speed of 20 mm. per hour.

Differential Thermal Analysis (DTA).—The measurements were performed with a recording differential thermal analysis apparatus (Shimadzu DT-10B), using α-alumina powder as the reference substance. In order to avoid possible effects by oxygen and humidity, the procedure was carried out, with nitrogen gas passed through slowly. For most measurements, the specimen was heated at the rate of 4—6°C per minute.

Dilatometric Measurements. — A dilatometric investigation was made by using a modified differential dilatometer of the type originated by Chevenard.[2] Our dilatometer was designed to magnify the differential expansion between a specimen and an equal length of fused silica used as the standard specimen 2000 times.

In this study, the heating rate was about 0.8°C per minute, except in the vicinity of the anomalous point, where temperature was raised as slowly as possible. The temperatures were measured by means of a calibrated chromel-alumel thermocouple; they were accurate to ± 0.2°C.

Samples were prepared by casting molten rods of zone-refined phenanthrene, rods which were 9 mm. both in length and in diameter.

Results and Discussion

In the DTA investigation, upon heating we found a new endothermic peak at about 71°C on the thermogram of phenanthrene. A typical thermogram is shown in Fig. 1.

The endothermic peak at 71°C is very small, compared with the peak beginning at 100°C, which is the melting temperature of the substance, the area of this endothermic peak for each thermogram is approximately one-seventeenth of that for melting.

TABLE I. THE OBSERVED VALUES FOR ENDOTHERMIC PEAKS ON THE DTA THERMOGRAMS OF PHENANTHRENE

Trial	T_1, °C	T_p, °C	T_2, °C
Sample A-2	61	72	78
Sample A-3	59	70	76
Sample B-1	60	70	75
Mean	60	71	75

Table I lists the results observed in heating, where T_1 and T_2 show the temperatures at a point of intersection between the base line and the tangential line on the left side of the peak, and the

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[1] S. Matsumoto and T. Tsukada, This Bulletin, **38**, 2023 (1965).

[2] P. Chevenard, *Rev. Met.*, **14**, 610 (1917).

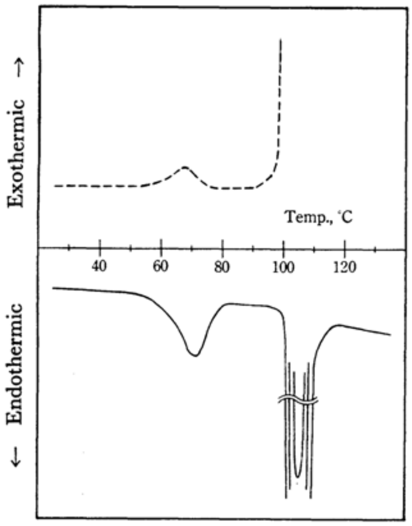

Fig. 1. A typical example of the thermogram of phenanthrene (Sample B-1 in Table I). The continuous curve for heating, the dashed one for cooling.

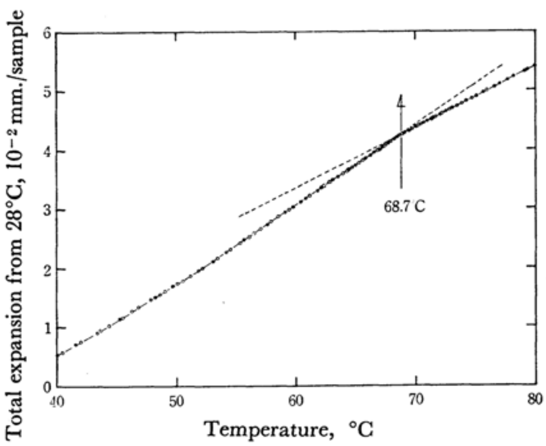

Fig. 2. The linear expansion-temperature relation of phenanthrene (sample 11-11 in Table II), showing a distinct discontinuity at 68.7°C. The open circles for heating, the black ones for cooling.

one on the right of it. T_p is the temperature at the vertex of the peak.

In the dilatometric study, we found a distinct discontinuity in the expansion-temperature relation of phenanthrene at 68.7°C. Figure 2 gives, as a typical example, a graphical representation of the total linear expansion of Sample 11-11 plotted aginst the temperature, where the curve consists of two distinct lines; the lines intersect at 68.7°C, although the slope below about 50°C gradually becomes smaller. These phenomena were quite reversible with the temperature. These features of the expansion-temperature relation show that the thermal expansion coefficient of the specimen is almost constant below or above 68.7°C, but that it undergoes a conspicuous, abrupt change at that temperature. Each expansion coefficient can be evaluated from the slope of each line. The results are summarized in Table II, where $\beta_{\rm I}$ is the mean coefficient of the linear thermal expansion between the temperature of 50°C and $T_{tr.}$, the transitional point, and where $\beta_{\rm II}$ is the coefficient between $T_{tr.}$ and 80°C.

TABLE II. THE MEAN COEFFICIENT OF LINEAR THERMAL EXPANSION OF PHENANTHRENE MEASURED WITH A DILATOMETER

Trial	$T_{tr.}$, °C	$\beta_{\rm I}$	$\beta_{\rm II}$
Sample 11-11	68.7	1.67×10^{-4}	1.05×10^{-4}
Sample 11-12	68.8	1.61×10^{-4}	1.08×10^{-4}
Sample 11-13	68.7	1.66×10^{-4}	1.03×10^{-4}
Average	68.7	1.65×10^{-4}	1.05×10^{-4}

Generally, a substance with a phase transition shows an endothermic peak corresponding to the transition on a thermogram of DTA, and the transition point exists between the T_1—T_p temperatures. The thermogram obtained for phenanthrene shows the presence of an endothermic peak with $T_1=60$°C and $T_p=71$°C, as is summarized in Table I. This result, in addition to the anomaly in the temperature dependence of the electrical conductivity,[1] reveals the presence of a phase transition in the phenanthrene crystal; this transition point is expected to exist between the temperature of 60 and 71°C.

The present attempt to make dilatometric measurements of phenanthrene indicates that the coefficient of the thermal expansion definitely undergoes a conspicuous change at 68.7°C; the value of 1.67×10^{-4} abruptly changes to 1.05×10^{-4} at this point, as is shown in Table II. This result shows that the transition point of phenanthrene crystal is 68.7°C.

In order to determine the heat associated with this phase transition, the ratio of the area of the endothermic peak at the transition to that for melting observed on the thermogram of DTA, 1 : 17, was conveniently applied. Phenanthrene melts at 100°C with a latent heat of fusion, $\Delta H=4.45$ kcal./mol.,[3] so the heat of the transition was evaluated as $\Delta H=0.26$ kcal./mol., while the associated entropy change at the transition was estimated to be $\Delta S=0.77$ e.u.

The estimated entropy change at this transition is much smaller than the change for the melting, $\Delta S=11.9$ e. u. This indicates that the modification of phenanthrene above the transition point is at least not a so-called plastic crystal. It is not exactly clear at the present stage that what other kind of phase transition this transition belongs to, but as the shape of a graphical representation of

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[3] Landalt - Börnstein, Physikalisch - Chemischen Tabellen, 6 Auflage, II Band, 4 Teil.

the expansion plotted against the temperature and its reversibility with temperature, as is shown in Fig. 2, are characteristic of what is called a high-order transition, it seems that the phase transition of the phenanthrene crystal is not polymorphic.

For an accurate treatment of this transition from the point of view of structural chemistry, it is necessary to determine the crystal structure above the transition point. For this purpose, an X-ray analysis of the structure is now being made in our laboratory.