Zone-Refining of Phenanthrene and Studies on the Purity[*1]

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There is no available organic solid from commercial products which is in a state of such purity as is enough for the investigation of semiconductive properties. Thus, the purification of a specimen becomes a matter of special importance in the field of organic semiconductors; there have recently begun to appear many papers handling specimens of the utmost purity obtained by zone-refining.[1–5]

This paper deals with the practice of zone-refining of phenanthrene, which was adopted as the specimen of the experiments in the preceding papers,[6,7] and also studies on the purity of the purified specimen.

Experimental

The starting material was phenanthrene of a chemical purpose-grade obtained from Eastman Kodak Co. This material is henceforward denoted as phenanthrene C.

Phenanthrene C was at first recrystallized from an ethanol solution; phenanthrene R stands for the product after the four times recrystallization.

The zone-refining was carried out by using a modified zone-melting apparatus of the type designed by Herington, Handley and Cook.[8,9] The essential features of our apparatus are given in Fig. 1: the cycle of a slow and fast pass of the heater carriage can be continued automatically in our apparatus.

Phenanthrene R was loaded into a Telex-glass tube with an inner diameter of 10 mm, and the tube was sealed under a vacuum after it had been evacuated at 10^{-5} mmHg for eight hours. Then, the phenanthrene in the tube was automatically subjected to a number of zone-passes by the apparatus described above. The

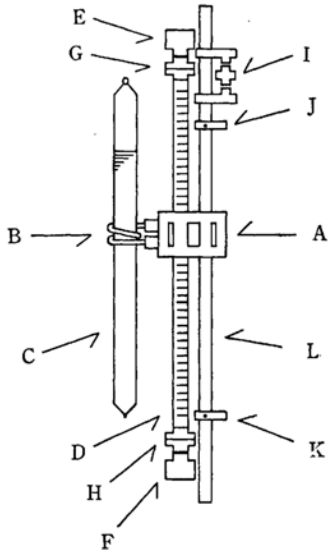

Fig. 1. Automatic zone-melting apparatus.
A: Heater carriage, B: Wire wound heater, C: Zone-tube, D: Drive shaft, E: Slow motor, F: Fast motor, G and H: Solenoid clutch, I: Micro switch, J and K: Limit switch, L: Control rod.

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1) R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).

2) N. Parkyns and A. R. Ubbelohde, *J. Chem. Soc.*, **1960**, 4188.

3) G. P. Brown and S. Aftergut, *J. Chem. Phys.*, **38**, (1963).

4) I. Nakada, K. Ariga and A. Ichimiya, *J. Phys. Soc. Japan*, **19**, 1587 (1964).

5) P. A. Andrews, A. F. Armington and B. Rubin, *Appl. Phys. Letters*, **7**, 86 (1965).

6) S. Matsumoto and T. Fukuda, This Bulletin, **40**, 743 (1967).

7) S. Matsumoto, *ibid.*, **40**, 2749 (1967).

8) E. F. G. Herington, R. Handley and A. J. Cook, *Chem. Ind.*, **1956**, 292.

9) P. Heneage and W. W. Taylor, U. S. Pat. 2990257 (1961).

molten zone about 5 mm long was controlled to move slowly downward at a speed of 20 mm per hour.

The zone-rod of the phenanthrene after being subjected to 130 zone-passes (denoted as phenanthrene Z), with a total length of 130 mm in a Telex-glass tube, was cut into eight sections with a length of about 15 mm, and the phenanthrene of each section was denoted as phenanthrene Z-0, phenanthrene Z-1, ···, and phenanthrene Z-7 from the bottom of the zone-tube.

Results and Discussion

Purification and Electronic Spectra. All electronic spectra were measured in cyclohexane of a spectro-grade with a Cary Model-14 recording spectrophotometer, using 1 cm quartz cells. The variation of the electronic spectrum of phenanthrene Z observed according to distance along the zone-rod is shown in Fig. 2, where the spectra of phenanthrene Z-0, Z-3, Z-5, and Z-7 are represented, and they are accompanied with the spectrum of anthracene of a zone-grade (Tokyo Kasei Co.).

The electronic spectrum of phenanthrene Z near the bottom of the zone-tube, *e. g.*, phenanthrene Z-0, agrees with the spectrum of phenanthrene reported in the literatures,[10,11] while as for the spectrum of the phenanthrene Z in the distance far from the bottom of the tube, *e.g.*, phenanthrene Z-5 and Z-7, there appear four absorptions at 376, 371, 356, and 352 mμ which are not assigned to the spectrum of phenanthrene. These four absorptions become more intensified according to an increase in distance from the bottom of the zone-tube.

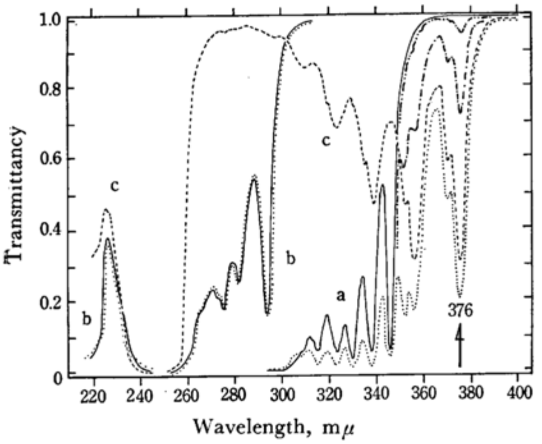

Fig. 2. Variation of the electronic spectrum of phenanthrene Z according to distance along the zone-rod (—— Z-0, —··— Z-3, —·— Z-5, ······ Z-7) and the spectrum of anthracene of a zone-grade purity (----). Symbols a, b for 5.05 $\times 10^{-3}$, 5.05×10^{-5} mol/*l* phenanthrene solutions; symbol c for 4.24×10^{-5} mol/*l* anthracene solution.

Here, it was investigated from which compound among the probable impurities of acenaphthene, anthracene, carbazole, and fluorene, these four absorptions were originated. As a result, these absorptions in question were proved to correspond to the para-bands of anthracene,[11] and further it seemed very improbable spectroscopically that the above-mentioned impurities other than anthracene were present.*[2] Therefore, anthracene may be a main impurity in the phenanthrene R.

Purification and Infrared Spectra. The variation of the infrared spectrum of phenanthrene Z according to distance along the zone-rod was investigated further to confirm the preceding results. The representative spectra of phenanthrene Z-0, Z-3, Z-5, and Z-7 are shown in Fig. 3, together with the spectrum of the zone-grade anthracene; it is observed that the absorption to be assigned to the very intensitive absorption at 882 cm^{-1} which is characteristic of anthracene and belongs to out of plane CH-bending vibrations of

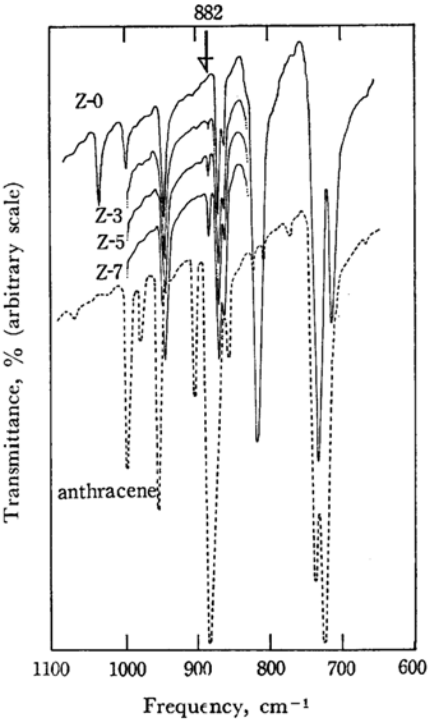

Fig. 3. Variation of the infrared spectrum of phenanthrene Z according to distance along the zone-rod and the spectrum of anthracene of a zone-grade purity.

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10) E. Clar, *Spectrochim. Acta*, **4**, 116 (1950).

11) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," "John Wiley & Sons, Inc., New York (1951).

*[2] The relative intensity of the absorption at 352 mμ among the four absorptions seems to be rather stronger, compared with the corresponding one in the parabands of anthracene, but at the present time a reasonable explanation for it is not available.

it,[12] appaers at the same wave number in the spectrum of phenanthrene Z in the distance far from the bottom of the zone-tube, *e. g.*, phenanthrene Z-5 and phenanthrene Z-7.

The intensity of this absorption at 882 cm^{-1} increases with an increase in distance from the bottom of the zone-tube, while the spectrum of each phenanthrene Z is practically identical with each other except at 882 cm^{-1}. All absorptions other than that at the wave number in question in the spectrum of each phenanthrene Z shown in Fig. 3 coincide with those in the spectrum of phenanthrene reported in the literatures. These observations in the infrared spectroscopy are consistent with the result derived from the electronic spectroscopy, that anthracene is a main impurity in the phenanthrene R.[*3]

The infrared spectra were measured in the region 4000—650 cm^{-1} with a Jasco DS-402 G infrared spectrophotometer, and a potassium bromide disk method was employed.

Concentration-Distribution of Anthracene in the Zone-Rod. The quantity of anthracene as an impurity in each phenanthrene Z was spectroscopically evaluated by employing the absorption at 376 mμ after Beer's law was confirmed to be valid at this wavelength for the cyclohexane solution of phenanthrene containing a minute quantity of anthracene.

Figure 4 shows the resultant concentration-distribution of anthracene in phenanthrene Z; the concentration in moles of anthracene per one mole of phenanthrene (denoted as M) is plotted as the ordinate, and the distance measured from the bottom of the zone-tube is plotted as the abscissa, together with the corresponding position of the section of each phenanthrene Z. As to the concentration of anthracene in phenanthrene Z-0, 7×10^{-6} M was graphically estimated. The result reveals that anthracene travelled in the direction opposite to the direction of zone-travel and aggregated towards the top of the zone-tube.

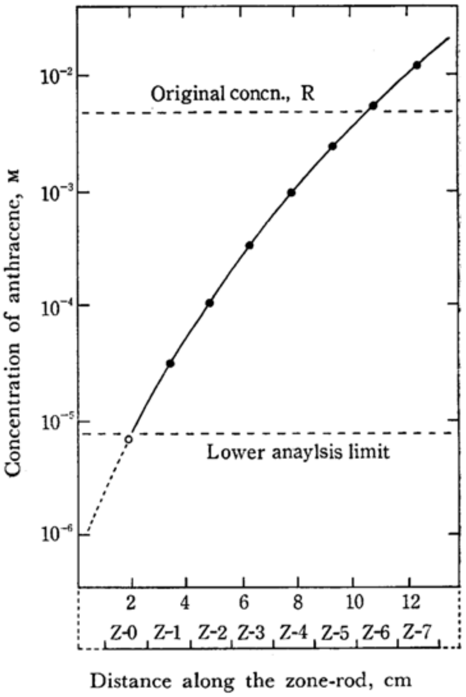

Fig. 4. Concentration-distribution of anthracene in the zone-rod of phenanthrene Z.

As for phenanthrene C and phenanthrene R, the concentration of anthracene was also analyzed spectroscopically; it was evaluated as 1.1×10^{-2} M and 5.6×10^{-3} M, respectively.

The extremely low concentration of anthracene observed at near the bottom of the zone-tube, 10^{-6}—10^{-5} M, indicates the effectiveness of the zone-melting with a sufficient number of zone-passes for the purification of phenanthrene containing anthracene which has been proved to be difficult by the conventional methods of purification.

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[12] M. Randic, *J. Chem. Phys.*, **33**, 710 (1960).

[*3] It should be kept in mind that there is the possible presence of some impurities which could not be spectroscopically detected.