

PREPARATION AND GROWTH OF PHENANTHRENE CRYSTALS

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Single crystals of phenanthrene have been grown from the melt following extensive purification efforts including adsorption column chromatography, sublimation and zone-refining in specially designed crystal growing tubes. The important factors which governed the successful growth of single crystals of phenanthrene by the moving vessel technique (Bridgman Crystal Growth System Type 365), have been investigated, viz, the purity of the phenanthrene, the temperature gradient, the shape of the growth vessel and the growth rate.

1. Introduction

1.1 Melt-grown crystals

Growth of organic crystals from the vapour phase usually results in slow growth of very thin crystals¹⁻⁵). Thus, when large single crystals are required, these must be grown from the melt, or from saturated solution. In the case of phenanthrene, the latter method is of doubtful applicability, because the limiting factor in growth from solution⁶) is solubility. Solubilities of 20—50% by weight are required for tolerable growth rates, and phenanthrene solubilities are much lower. There is also the disadvantage of possible solvent occlusion.

Growth from the melt has none of these disadvantages and reports⁷⁻¹⁵) are available on the growth of organic crystals by this method. Though the Kyropoulos procedure^{16,17}) may not be of use because of the volatility of phenanthrene and the likelihood of atmospheric oxidation, the moving vessel^{15,18-20}) and the stationary vessel techniques^{18,21,22}) can be used. These have the advantages that

crystals can be grown from highly purified material in an inert atmosphere. The moving-vessel technique: Bridgman Crystal Growth System Type 365 from the Cambridge Instrument Ltd., U. K., was used for the present study: The investigation is concerned with several important criteria to be observed before crystals may be grown successfully, namely, the purity of materials, the temperature gradient, the rate of crystal growth, and the shape of the growth vessel.

1.2 Problems of impurity

Phenanthrene may be extracted from coal-tar distillates or synthesized. Material from both sources is commercially available. The total impurity content of both synthetic phenanthrene and good samples of chemically purified phenanthrene is approximately 1%. However, the major difference between the two materials is the type of impurity present. Anthracene ($C_{14}H_{10}$), 9, 10-phenanthraquinone ($C_{14}H_{12}O_{12}$), carbazole ($C_{12}H_9N$), fluorene ($C_{13}H_{10}$) and traces of other aromatic hydrocarbons are found in commercially available phenanthrene²³). Synthetic phenanthrene²⁴) is contaminated with phenanthraquinone ($C_{14}H_8O_2$), anthrone ($C_{14}H_{10}O$), and 9, 10-dihydrophenanthrene ($C_{14}H_{12}$). Segregation coefficients (ratio of the impurity concentration in the solid to the impurity concentration in the liquid in equilibrium with that solid) have been determined for some of these impurities²⁵). Unfortunately, the coefficients are themselves concentration dependent. At high concentrations most of the impurities segregate efficiently from the solid during normal freezing. The impurity content can therefore be reduced by zone-refining (Sec. 2.1.3). In some cases, however, the segregation process becomes rather inefficient at low impurity concentrations, and long periods of zone-refining yield only a small increase in over-all purity. This is particularly true for carbazole, which forms solid solutions with phenanthrene²⁴).

The most efficient method for the removal of carbazole^{22, 26, 27}) is adsorption column chromatography²⁷). This process has the added advantage that other polar impurities are removed, and the impurity level generally is reduced thus making the task of subsequent zone-refining somewhat easier. When this process is followed by distillation or sublimation under reduced pressure and, finally, zone-refining, material of total impurity content less than 1 ppm can be obtained²⁴). However, in addition to the necessity for highly pure starting material, it is essential to provide seed crystals and arrange for their propagation in the desired orientation^{14, 15}). This is usually effected by the design of the containing tube, and controlled cooling in a precision-controlled furnace (Sec. 2.1.2 and 2.1.3).

2. Experimental

2.1 Purification of phenanthrene

2.1.1 Adsorption column chromatography

The chromatographic separation of mainly 9, 10-dihydrophenanthrene from synthetic 'BDH' grade phenanthrene was carried out by adopting the procedure which consisted of carrying out the following steps in sequence: (i) Preparation of

adsorbent column, (ii) Adsorption of the mixture of compounds over the column and (iii) Sublimation and recrystallization.

(i) *Preparation of adsorbent column*

The material used for adsorption of mainly 9, 10-dihydrophenanthrene was silica gel. A burette type glass tube (1m long, 18mm OD, 15mm ID) having a narrow portion with a stop-cock at the base was used for the packing of the column. A cotton-wool plug was inserted in the narrow portion of the tube near the stop-cock and a layer of neutral sand was used to cover the cotton-plug. A slurry of about 80g of adsorbent material silica gel was prepared in solvent-acetone (to be used later on for dissolving phenanthrene) and this was then poured carefully into the tube held vertically with the help of a clamp. The solvent was also taken in a dropping funnel clamped just above the tube. As soon as the slurry of the adsorbent material settled in the tube, a disc of filter paper was placed above it and the solvent was allowed to run slowly down the adsorbent column (Fig. 1). The solvent coming out of the tube was collected in a conical flask. Precaution was taken to ensure that the top of the column was always covered with the solvent.

(ii) *Adsorption*

The mixture of compounds to be separated i. e., 'BDH grade' phenanthrene, was dissolved in the least amount of solvent-acetone, and the solution was allowed to run through the column with the help of the dropping funnel. Different components of the mixture got adsorbed at different distances from the top in the form of bands. The strongly adsorbed impurity due to 9, 10-dihydrophenanthrene moved slowly and formed light yellow bands near the top while weakly absorbed impurities due to tarry materials moved faster and formed light brown bands near the bottom (Fig. 1). The crystallized phenanthrene from the solution in the conical flask was filtered off and the remaining phenanthrene obtained by evaporating the solvent.

The yield of 1m long column was about 8 g of phenanthrene in about five hours, and in order to avoid photo-oxidation of the phenanthrene, the process was carried out in the dark. Since it was difficult to assess the true position of the lower end of the brown impurity, the process was repeated in order to insure the removal of all strongly absorbed impurities and particularly 9, 10-dihydrophenanthrene.

(iii) *Sublimation and recrystallization*

The most important and perhaps the most delicate method of purification of solid organic compounds is the process of sublimation and recrystallization. It consisted of dissolving the chromatographed phenanthrene in minimum amount of hot solvent n-hexane : in which the substance was more soluble than in the

* Reagent-grade n-hexane was purified by shaking with a 1 : 1 v/v mixture of concentrated nitric and sulphuric acids, washing the separated n-hexane several times with dilute sodium hydroxide solution and then with water, and finally drying the wet solvent over a solid desiccant and distilling prior to use.

cold n-hexane. The impurities were removed by filtering the hot solution using a hot water funnel, and was allowed to cool when crystals of pure phenanthrene were obtained (Fig. 1). These were filtered and again dissolved for the recrystallization. It was observed that quick cooling of the filtrate formed tiny but purer crystals whereas slow cooling formed bigger but impure crystals. The mother liquor was concentrated by evaporation and cooled to obtain a fresh crop of crystals of pure phenanthrene which were further subjected to recrystallization. This process was repeated several times to recover maximum amount of pure phenanthrene.

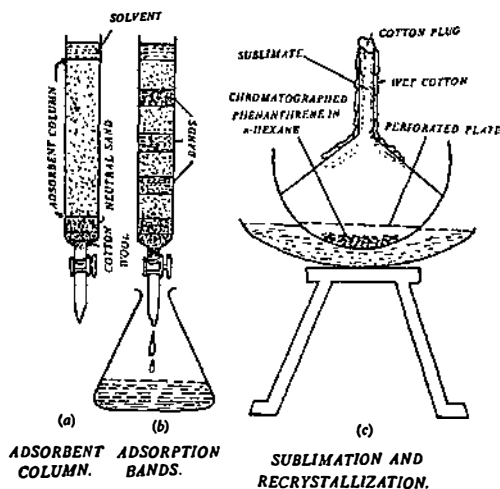


Fig. 1. Adsorption column chromatography.

The 9, 10-dihydrophenanthrene-free phenanthrene from the chromatographic purification still contains those non-polar impurities soluble in hexane, along with a high proportion of solvent. To remove these contaminants a combination tube assembly type-A as shown in Fig. 2 was used^{1,4)}.

About 10 g of chromatographed phenanthrene was loaded into the lowest section (a) of the thoroughly cleaned pyrex glass combination tube assembly type-A, and slowly evacuated to a residual pressure of 0.1 Pa using nitrogen gas filling apparatus as shown in Fig. 3. Pure nitrogen was admitted to normal atm. pressure and the combination tube assembly was again slowly evacuated to 0.1 Pa. The process was repeated two times. A pyrex glass tube (130 mm long, 15 mm OD, 13 mm ID) carrying a heating coil, was then pushed over the lowest tube of type A to sublime the phenanthrene under continuous evacuation into the second section (b) slowly over a period of one hour. In this process, the most volatile impurities should have been pumped off and trapped. When approximately 90–95% of the phenanthrene had passed over into (b), the constriction between (a) and (b) was melted and section (a) with its remnant of impure phenanthrene discarded.

* All glass tubes were cleaned by the fumes from a nitric acid/alcohol reaction, repeatedly rinsed with distilled water, and finally vacuum-baked at about 350 °C and backing pressure.

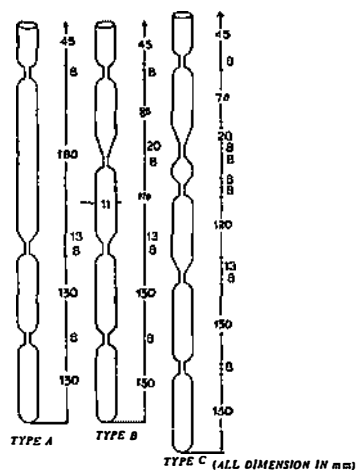


Fig. 2. Combination tube assembly for the growth of phenanthrene crystals.

At this stage the cold sublimed phenanthrene in (b) had a light yellow colour due to phenanthraquinone carried over during the sublimation. This was particularly noticeable at the tail end of the sublimate (the light yellow colour of pure, hot phenanthrene should not be confused with that due to impurity).

The material in section (b) was then resublimed into the section (c), zone-refining tube, and this section sealed at the constriction. Pure nitrogen was now added to normal atm. pressure and the phenanthrene melted into the bottom of the

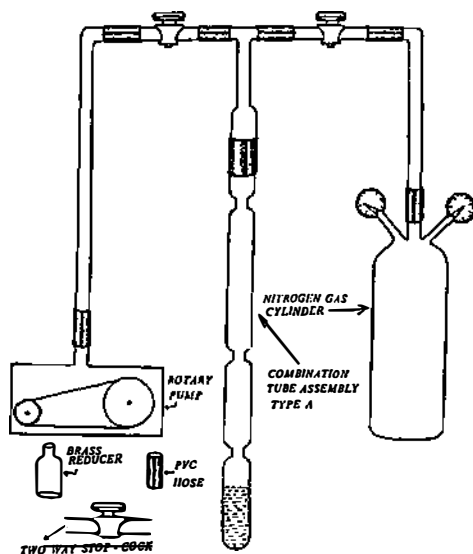


Fig. 3. Nitrogen filling apparatus.

tube (c). While the material was still liquid the pressure was reduced to 50 kPa. The phenanthrene was then allowed to solidify and the tube (c) sealed off at the constriction above it and a glass hook formed. It was always found essential to wind a few turns of asbestos cord on both sides of the constriction before melting to avoid decomposition of phenanthrene.

The whole process was carried out in the blacked-out laboratory with only a red lamp for illumination to safeguard against photo-oxidation.

2.1.2 Zone-refining

After the chromatographic and sublimation processes, the phenanthrene was finally purified by zone-refining. Zone-refining involves the repeated passage of a molten zone through an ingot to achieve purification by continuous crystallization from the melt. Only those impurities can be removed for which the segregation coefficient is finite. Organic compounds are best refined in vertical systems, since in horizontal tubes, their melts tend to underrun and contaminate the purified solid²⁸⁾.

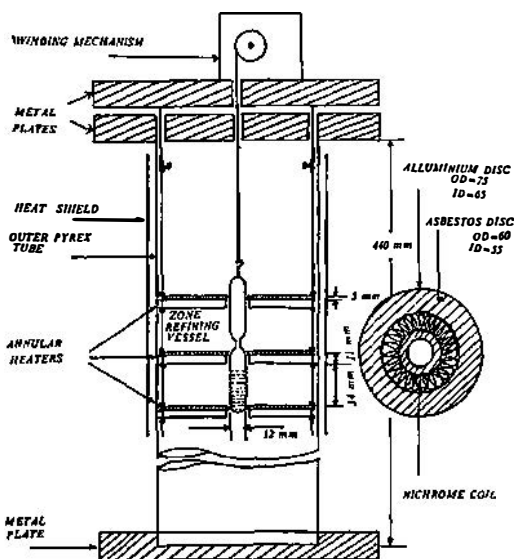


Fig. 4. Travel mechanism including annular heaters for reciprocal motion after Sloan and McGowan (1963).

The passage of n zones can be effected by $(n + m - 1)$ reciprocating runs through a battery of m heaters at intervals of icm with an ingot $(m - 1) icm$ long (Fig. 4); at the end of each run; the ingot is returned manually to its starting position. The apparatus used was the Bridgman Crystal Growth System Type 365 from the Cambridge Instruments Ltd., U. K., and carried a 'home-made' zone-refining stack, manufactured to the pattern of the original zone-refining stack designed by Sloan especially for anthracene²⁹⁾. The zone heater separation was 35 mm, and the zone thickness about 10 mm.

The usual practice was to pass 21—24 zones down a 80 mm long column of phenanthrene. This took about 385 hours. The travel rate during melting (sample tube raised) was 1 mm hr^{-1} . The sample tube was, however, lowered manually to its starting position at the completion of three zones at a time. The temperature of the heaters was adjusted so that the melting point (99.5°C) was only just reached, to minimize thermal decomposition of the material. The presence of nitrogen at 50 kPa, pressure in the tube prevented serious sublimation of phenanthrene up the tube. The perspex shield of the apparatus was placed in position in order to minimize photo-reaction in the hot liquid.

The most obvious change in the appearance of the material during zone-refining was the concentration of yellow phenanthraquinone at the lower end of the tube, together with some dark brown material.

When the required member of passes had been completed, the tube was cracked open and the upper and lower extremes of the ingot were rejected. The central portions of two such ingots were combined to give about 8 g, and loaded into the bottom section of a combination tube assembly type B (Fig. 2). The whole process of sublimation and zone-refining was then once more repeated. However, on this occasion, no yellow phenanthraquinone was observed in the sublimed material, and during zone-refining the phenanthrene formed large clear crystals, a good indication of the high purity of the material.

After completion of the final zone-refining, the upper portion ($3/4$ of the ingot) was melted into the crystal growing tube under controlled heating in the dark, and sealed off. In this way, the transfer was effected without exposing the phenanthrene to the atmosphere, and the crystal grown (section 2.1.3) in the same ambient.

2.1.3 Resistance heated furnace

The apparatus used for crystal growth was resistance heated furnace type 365 from the Cambridge Instrument Ltd., U. K. The furnace was protected against mechanical vibration by standing it on a heavy slate plate resting on brick pillars but isolated from them by 25 mm foam rubber pads. The optimum condition found for phenanthrene growth in preliminary trials was a steep gradient, with the upper and lower sections of the furnace at 180°C and 75°C , respectively. The temperature was uniform for 20 mm above and below the lower end of the heating element, but it changed by 105°C within the length of the heating element viz., 105 mm.

The tube containing the purified phenanthrene was placed in the resistance heated furnace with the help of a graphite pedestal which in turn was located by 12.5 mm counter bore on the Bridgman lowering rod so that the tip was just below the melting-point isothermal: the system was then allowed to come to thermal equilibrium. After five hours, the lowering mechanism was switched on and the vessel lowered at the rate of 1 mm hr^{-1} . Continued lowering through the temperature gradient resulted in crystal growth. However, it was found essential to initiate crystal seeds prior to inserting the growth vessel into the furnace by electrically heating the tip of the vessel to melt the phenanthrene and allowing it to cool naturally. Attempts to grow crystals from 'unprimed' charges always resulted in super cooling, and the consequent formation of multi-crystals.

When the crystallization was complete, the lowering motor was switched off and the temperature in both hot and cold sections of the furnace manually lowered to 60°C and 35°C, respectively, in about ten hours. The tube was then further lowered down to attain the room temperature in about twenty hours.

The type-C vessel (see Fig. 2) was also used in the same way as the type-B vessel for growing phenanthrene crystals, but with type-C single crystals of phenanthrene were seldom obtained. The type-B vessel was found to be the most suitable for growing phenanthrene crystals, provided the wall of the growth vessel above the constriction sloped fairly gradually—rather than abruptly outwards to the full diameter.

2.1.4 Preparation of specimens

The growth vessel was cut open to tip out the ingot. Examination of the crystal boule usually revealed the positions of cleavage cracks. By placing a sharp 'Eveready' razor blade against one of these and applying a steady pressure in the direction of the crack the crystal cleaved apart readily along an *ab* plane³⁰). The dimensions of the cleaved phenanthrene plates aimed at were 5 mm × 5 mm × 0.35 mm. Attempts to prepare plates less than 0.35mm thick proved unsuccessful.

As a precaution against the photo-oxidation of phenanthrene to phenanthraquinone, when exposed to ultraviolet light in air, all crystals were stored in a desiccator in dark under vacuum. When crystals had to be handled in daylight in air, this was done as quickly as possible.

3. Discussion and conclusions

3.1 Crystal orientation

The factors which affect crystal orientation during crystal growth had been discussed in detail by Scott, Hutchinson and Lapage¹⁸). It was experimentally found by Saleh^{14,31}), and the present authors that for phenanthrene, if the angle of the capillary to the vessel axis is less than 45°, then the *ab* cleavage plane will grow parallel to the vessel axis, but if the angle is greater than 45°, this plane will grow perpendicular to the vessel axis. This was probably the result of using highly purified material, and growing the crystals very slowly. For the purpose of the present study, crystals were usually grown in which the *ab* cleavage planes were horizontal.

3.2 Rate of crystal growth

The rate of crystal growth sets an upper limit to the rate at which the crystal growing vessel can be lowered in the furnace. A rate of 1-2 mm hr⁻¹ has been recommended¹⁸) as an upper limit for organic crystals, in contrast to 20mm min⁻¹ for metals²⁹), and 1-4 mm hr⁻¹ for ionic crystals^{17,32}).

The crystal growing tube was lowered by means of a synchronous motor. It was found that rates greater than 1-2 mm hr⁻¹ always resulted in the formation of multi-crystals, whereas lower rates resulted in satisfactory growth (Sec. 2.1.3). Large crystals could be grown in about five days at 1mm hr⁻¹.

3.3 Purity and perfection of phenanthrene crystals

The successful growth of single crystals depends partly on the production of the highly purified phenanthrene and on the shape of the growth vessel. The over-all impurity of the final crystal should, therefore, be considerably less than 0.1 ppm (Sec. 2.1.2). This will be distributed along the crystal in a manner determined by the segregation coefficients of the separate impurities. The lower end of the boule will always be the most pure portion. The type-B vessel was found to be the most suitable for growing phenanthrene crystals, provided the wall of the growth vessel above the constriction sloped fairly gradually rather than abruptly-outwards to the full diameter (Sec. 2.1.3). The crystals in the form of boules 30 mm long and 11 mm in diameter could be cleaved easily along the 001 plane into plates 5 mm × 5 mm × 0.35 mm. Attempts to prepare plates less than 0.35 mm thick proved unsuccessful (Sec. 2.1.4). These plates were examined for singularity under polarizing microscope, and were found to be free of all striations and visible imperfections.

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PREPARACIJA I RAST KRISTALA FENANTRENA

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Monokristali fenantrena dobiveni su iz taljevine Bridgmanovom metodom. Da bi se dobili što čišći uzorci upotrebljene su metode adsorpcione kolumnarne kromatografije, sublimacije i zonskog čišćenja u specijalno disajnriranim cijevima. Ispitivani su faktori koji su bitni za uspješan rast monokristala tom metodom, kao što su čistoća uzorka, temperaturni gradijent, oblik posude u kojoj kristal raste, te brzina rasta kristala.