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Preparation of High-Purity Anthracene: Zone Refining and the Triplet Lifetime†

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Abstract—The triplet lifetime has been used as a monitor to follow the progress of purification during the zone-refining of natural and synthetic anthracene. Chromatography has been found to be a satisfactory initial purification process if a highly pure solvent, e.g. benzene, is used.

A considerable effort has been put forward over the past decade concerning the measurement of optical and electrical properties of molecular crystals. The principal compound used for these studies has been anthracene, and though the techniques for producing the crystals are well known, the quality of the crystals varies considerably. This variation in quality may also be reflected in the reported values for some intrinsic properties of crystal, underlining the necessity to produce a uniformly pure product from which the crystal may be grown.

The use of zone-refining as a primary purification process for metals, semiconductors,[1] insulators and organic[2] substances such as anthracene is now well established. Several investigations have recently been reported in which the zone refining purification process in anthracene has been studied,[3, 4, 5] however only one has attempted to correlate the crystal purity to a crystal property,[5] in this case carrier trapping. Perhaps for studies involving optical properties, the triplet lifetime is a more relevant criterion for purity. The triplet lifetime of anthracene is easily measured from

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the time decay of delayed fluorescence produced by the mutual annihilation of triplet excitons. Sloan[6] has isolated more than a dozen organic, and several inorganic impurities, from commercial anthracene, many of which may have the effect of decreasing the triplet lifetime. Also of course oxygen will rapidly quench anthracene triplet excitons. Thus the triplet lifetime is a sensitive measure of the concentration of many of the probable impurities in an anthracene crystal. Due to our continued interest in producing high quality anthracene crystals, we have studied the effects of zone refining using anthracene which has been commercially produced by different processes. By following these purification processes a consistent quality of anthracene can be obtained, which in turn would provide a primary control for crystal grown by various groups.

The starting materials used were either Eastman X-480 natural anthracene (blue-violet fluorescence) or Eastman H-480 synthetic anthracene[8] from which the common impurities found in the natural anthracene should be absent. The zone refiner used was a commercial unit (Analtech, Inc., Wilmington, Del.), similar in design to that described in the report "Automatic Zone Refiner for Organic Compounds[9]". The zone length was kept approximately equal to the inside diameter of the tube, $\sim\frac{1}{2}$ inch. Interzone spacing was approximately 2 inches and the travel rate 1 inch per hour unless noted otherwise. The ingot length was kept at about 15 inches.

The triplet lifetime was measured from an analysis of the time decay of the delayed fluorescence. A helium-neon laser, Spectra-Physics Model 125, was used as the source of exciting light, and a blue-sensitive photomultiplier as the detector, the signal being displayed on an oscilloscope. The zone refining tube entered a circular, disc-type phosphoroscope at right angles to the laser beam and the detector. By using light baffles, the excitation was confined to a length of less than $\frac{1}{2}$ inch along the refining tube. A rod attached to the tube allowed specific positions of the refining tube to be moved into the laser beam and their relevant lifetimes measured.

Natural anthracene was first chromatographed through alumina using benzene as solvent. Most of the solvent was removed by first vacuum pumping for several hours, then melting the anthracene in the presence of an inert gas and reevacuating while the anthracene was still hot, ~ 150°C. After a vacuum of 10^{-5} mm pressure was reached, the pyrex zone refining tube was refilled with 20 cm pressure of nitrogen (prepurified grade) and sealed with a hook.

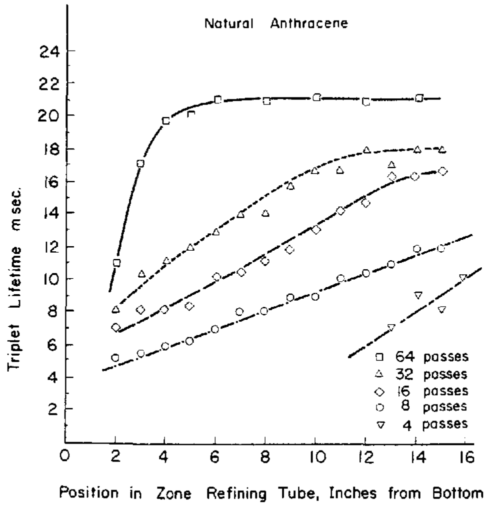

Figure 1. Variation of the triplet lifetime of natural anthracene with position in the zone-refining tube following 4, 8, 16, 32 and 64 passes.

The triplet lifetime was then monitored throughout the ingot length following a specific number of zone passes. The results are shown in figure 1 for 4, 8, 16, 32 and 64 passes. Initially the lifetime throughout is too short to be measurable, < 1 msec. After 4 passes a coloration appears at the bottom of the tube and at the tube top lifetimes of $\leqslant 5$ msec are measured. After 32 passes there is a consistent lifetime decrease from top to bottom of the refining tube, however the maximum lifetime measured is only slightly less than that measured after 64 passes, although in the latter case it is obvious that most of the impurities have been removed to the lower zones, the lifetime through most of the tube being constant. Any increase in the triplet lifetime following more than 64 passes is within the experimental accuracy of the measurements.

Figure 2 illustrates the results obtained using synthetic anthracene (Eastman H-480) as starting material. Though there seems to be no difference between the ultimate triplet lifetime reached by either X-480 or H-480, the synthetic anthracene (H-480) reaches a constant, high triplet lifetime throughout the zone refining tube in far fewer passes. Thus there is a clear difference between the average segregation coefficient of the impurities in natural and synthetic anthracene. The highest value of triplet lifetime measured in tubes from different batches of anthracene varies between 20–22 msec if these zone refining procedures are followed. The lifetime of the corresponding crystals grown by a Bridgeman

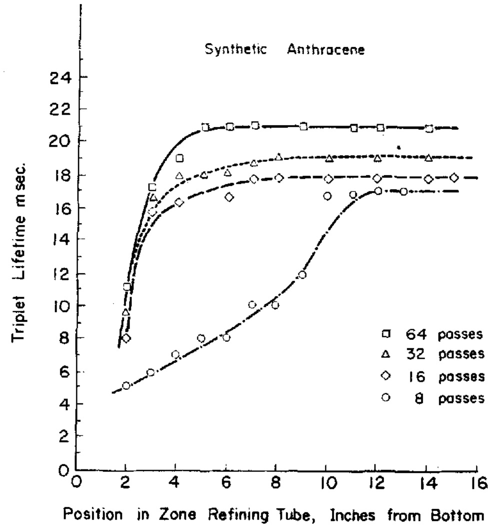

Figure 2. Variation of the triplet lifetime of synthetic anthracene with position in the zone refining tube following 4, 8, 16, 32 and 64 passes.

technique is normally slightly greater than that measured for the zone refined anthracene, namely 22–24 msec. Crystals of deuterated anthracene have also been produced following this purification-technique, the triplet lifetime showing a marked deuteration effect, being approximately 40 msec.

We have also studied the effect of purification processes before zone refining, and varying the travel-rate during the zone refining. Natural anthracene (blue-violet fluorescence grade) contains glycol as an impurity remaining from an azeotropic distillation. This may be removed either by sublimation or by chromatography, however, the solvent used in the chromatography can also add impurities that must be removed by zone refining. Although the vacuum process described earlier was used to remove most of the solvent, the change in triplet lifetime during the zone refining of

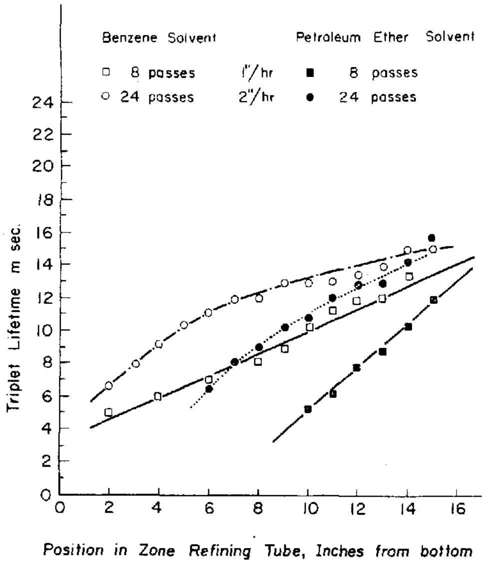

Figure 3. Change in triplet lifetime of natural anthracene after zone-refining following the use of benzene or petroleum-ether 60–80°C as chromatographic solvent.

anthracene showed considerable dependence on this initial solvent. For example, in figure 3 the lifetime changes following chromatography using benzene and petroleum-ether (60–80°C) are compared. The purifying efficiency of these two solvents is also evident from a visual analysis of the alumina support of the chromatographic column in which a band of impurities appears only following the use of benzene.

Figure 4 illustrates the triplet lifetime along the zone refining tube in which blue fluorescence grade anthracene has been prepurified by different processes before zone refining. It can be seen that chromatography with benzene followed by sublimation is the most efficient, though chromatography alone is able to remove most impurities. The lifetime reached after 64 passes is the same for both of these pretreatments.

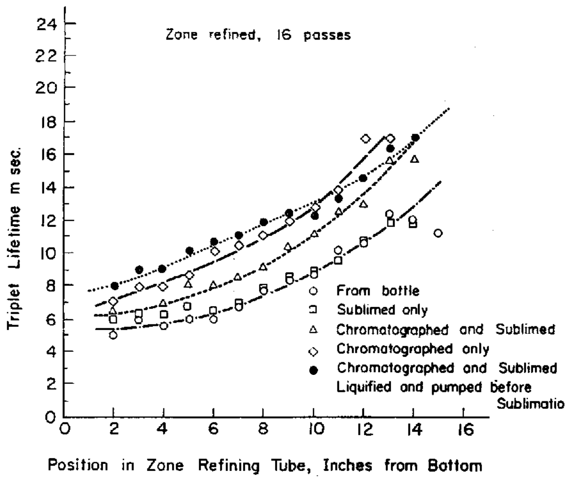

Figure 4. Variation of the triplet lifetime measured along a zone-refining tube after 16 passes, using anthracene initially prepurified by different techniques.

It has also been found that using the apparatus described, a rate of travel of 1 in/hr. seems to be optimum; increasing the rate tends to cause the segregation coefficient to approach unity.

Thus by using chromatography followed by a zone refining procedure, a uniformly pure sample of polycrystaline anthracene can be produced from either synthetic or natural anthracene. Crystals grown with care from these zone refined ingots have a long triplet lifetime, 22–24 msec, showing a high degree of purity with respect to compounds which quench triplet excitons. This use of triplet lifetime as a quality control affords a simple non-destructive measurement from which crystals grown by different techniques can be compared with respect to at least the one optical property which in certain experimental circumstances may be most relevant.

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