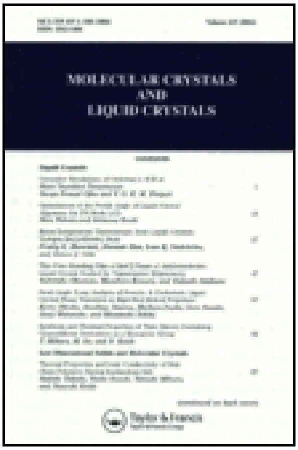

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Purification and Decay Time of Delayed Fluorescence of Chrysene Crystal

Yasuko Ishizuka [a]
[a] National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki, 305, Japan

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Purification and Decay Time of Delayed Fluorescence of Chrysene Crystal

YASUKO ISHIZUKA
National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki 305, Japan

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Chrysene crystal was extensively purified. The decay time of delayed fluorescence was measured with the purified crystal and the triplet exciton lifetime at room temperature was found to be 50 ms.

In a molecular crystal, impurities and defects cause various sorts of traps in the triplet exciton level. As the population at the triplet state decreases effectively through the traps, these traps reduce the triplet lifetime.[1] Benz[2] has observed that the triplet lifetime of naphthalene increases with the number of zone passes upon zone purification. Further, Port *et al.*[3] have shown that the triplet lifetime of naphthalene crystal decreases with an increase of the concentration of anthracene impurity. The triplet lifetime of anthracene crystals has also been examined in relation to purity.[4,5] Thus, in general, the triplet lifetime may be expected to serve as an index of the purity of molecular crystals, particularly in the very low concentration range, where there are no analytical methods to determine the purity. In this connection few data about chrysene crystals have been reported.[6] In this work the triplet lifetime of an extensively purified chrysene crystal was measured at room temperature. Since the chrysene crystal gave no phosphorescence, the decay of its delayed fluorescence was measured. Details about the delayed fluorescence spectra obtained will be reported elsewhere.

EXPERIMENTAL

A 488 nm line of an Ar ion laser was used for the excitation to the triplet state of chrysene. The delayed fluorescence was separated from the prompt fluorescence with a Becquerel-type phosphoroscope, detected with a photomultiplier set behind filters, integrated with a signal analyzer and recorded with an x-y recorder. The decay time of the delayed fluorescence was measured with polycrystalline chrysene contained in a zone-refining Pyrex tube. Impurities in chrysene crystals were examined with a high-speed-liquid chromatography.[7] The optical absorption at 254 nm was used for the detection of impurities with this chromatography.

RESULTS AND DISCUSSIONS

Ten kinds of impurities were detected in crude chrysene crystal (Rutgerswerke) by high-speed-liquid chromatography. Total impurity concentration was estimated to be 4.4% on the assumption that the molar absorption coefficients of all the impurities at 254 nm are equal to that of chrysene. Delayed fluorescence could not be detected with the crude crystal. Before extensive zone-refining, the crude crystal was roughly refined with zone purification where maleic anhydride (0.01 mol) was added to it for the purpose of removing anthracene impurity, and with recrystallization from N, N-dimethylformamide and ethanol with addition of activated charcoal. The roughly refined crystal contained an unknown impurity eluted prior to chrysene in the chromatogram the concentration of which was estimated to be 3×10^{-4} mol/mol. The delayed fluorescence of this crystal could be detected and the decay time was 18 ms. The roughly refined sample was further zone refined up to 343 passes with a zone-melting apparatus with a heater-temperature-controlling mechanism.[8] Figure 1 shows the decay of the delayed fluorescence versus the relative

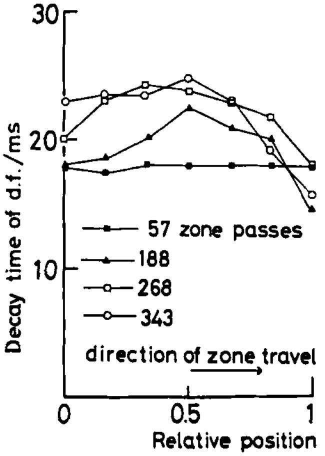

Fig. 1

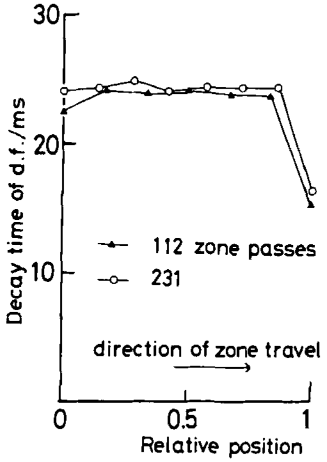

Fig. 2

position of the zone-refined sample column in several zone pass numbers. As the zone pass number increased, the decay times became longer at the central position. After 343 zone passes, no impurity could be detected in the first 4/6 portion of the sample by liquid chromatography, where the detection limit was estimated to be 10^{-6} mol/mol. The longest decay time was obtained at the central portion of the sample column to be 25 ms. After removing of both ends and the portion of which decay time was below 20 ms, the crystal was further zone-refined in another tube. Figure 2 shows that after 231 zone passes, eighty percent of the sample has a decay time above 24 ms, and that the longest decay time is 25 ms. The facts that a marked extension of decay time is not observed in the last stage of purification and that the decay time of eighty percent of the sample is above 24 ms probably shows the limitation of refining. In these processes the purification yield of the chrysene crystal with the decay time above 24 ms was thirteen percent.

It is well known that under weak excitation where the intensity of delayed fluorescence is proportional to the square of the intensity of the excitation light, the decay time of the delayed fluorescence is equal to half of the triplet exciton lifetime.[9] Dependence of the delayed fluorescence intensity on the intensity of the exciting light was examined with neutral density filters. In this case, as the intensity of the delayed fluorescence was proportional to the square of the exciting light intensity, the triplet exciton lifetime of the chrysene crystal was estimated to be 50 ms. This value is far longer than the 30 ms reported by Peter *et al.*[6]

REFERENCES

1. P. Avakian and R. E. Merrifield, *Mol. Cryst.*, **5**, 37 (1968).
2. K. Benz, *Z. Naturforsch.* **24a**, 298 (1969).

3. H. Port, M. Bader, G. Weber and H. C. Wolf, *Z. Naturforsch.*, **30a**, 277 (1975).
4. S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff and W. G. Schneider, *J. Chem. Phys.*, **42**, 330 (1965).
5. K. W. Benz, W. Häkker and H. C. Wolf, *Z. Naturforsch.*, **25a**, 657 (1970).
6. L. Peter, W. Engel and G. Vaubel, *Mol. Cryst. Liq. Cryst.*, **19**, 207 (1973).
7. A zorbax ODS column with the theoretical plates of 6000 was used at 40°C. The optical absorption at 254 nm is integrated with an integrator.
8. Y. Ishizuka, *Bull. Chem. Soc. Jpn.*, **50**, 563 (1977).
9. John B. Birks, *"Photophysics of Aromatic Molecules,"* p. 378, Wiley-Interscience (1970).