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The Apparent Solvent Effect on the Fluorescence Efficiency of 9-Methyl-10-(chloromethyl)anthracene

Fujio TANAKA and Jiro OSUGI
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

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Synopsis. 9-Methyl-10-(chloromethyl)anthracene (I) is immediately transformed into 9-methyl-10-(ethoxymethyl)-anthracene (II) in ethanol, and a very strong fluorescence of II is observed. While I is practically nonfluorescent, II fluoresces strongly in all solvents. These facts explain well a phenomenon misinterpreted by Melhuish as a remarkable solvent effect on the fluorescence efficiency of I.

It was reported by Melhuish that the fluorescence yield of 9-methyl-10-(chloromethyl)anthracene (I) was 0.09 in benzene and 0.73 in ethanol.1) This remarkable difference has received some attention as a typical example of solvent effects on fluorescence yields.2) However, the origin of this interesting phenomenon is not yet well understood. The present authors re-examined the behavior of the fluorescence of I in the course of their studies of the environment effects on the fluorescence yields of anthracene and its derivatives.

As reported by Melhuish, all alcoholic solutions of I fluoresce very strongly, while I is practically nonfluorescent in all solvents except alcohols.3) To clarify the mechanism of the high-fluorescence efficiency in alcoholic solvents, first the spectroscopic nature of I in ethanol and benzene was investigated. The absorption spectrum of an ethanol solution of I shifts toward wavelengths shorter by *ca.* 10 nm relative to that of a benzene solution. This shift is too large compared with the corresponding values (3—4 nm) for anthracene and most derivatives. Therefore, the change in the absorption spectrum suggests the occurrence of a solvolytic reaction in ethanol. Indeed, the residue of an ethanol solution of I was identified as 9-methyl-10-(ethoxymethyl)anthracene (II) by PMR (signals of ethyl group) and mass spectrometry ($M^+=250$). II fluoresces strongly in both ethanol and benzene. Melhuish also reported in the same paper that the fluorescence yields of II are 0.68 in ethanol and 0.71 in benzene.1) As a matter of course, an ethanol solution of II shows the same absorption and fluorescence spectra as an ethanol solution of I. The absorption and fluorescence spectra of I and II in ethanol and benzene are shown in Fig. 1. It is also clear from the similar changes in the absorption spectra that I is transformed into the corresponding alkoxy-compounds in other alcoholic solvents. Accordingly, the following conclusion may be drawn: the high-fluorescence efficiency in alcoholic solutions of I is not due to the solvent effect on the fluorescence efficiency of I itself, but to the transformation of I into II in alcoholic solvents.

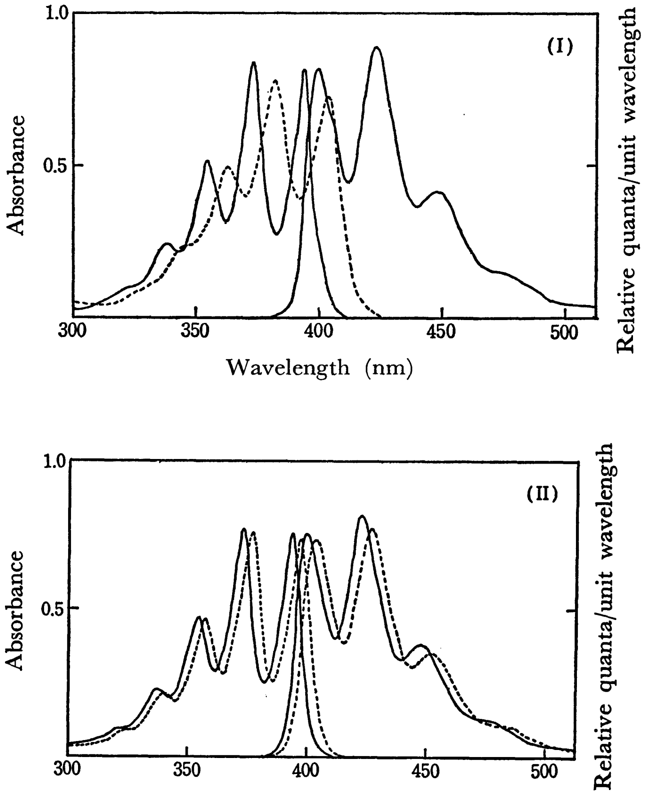

Fig. 1. Absorption and fluorescence spectra of (I) and (II) in ethanol (——) and benzene (----); 8×10^{-5} mol/l for absorption and 8×10^{-6} mol/l for fluorescence. The fluorescence spectra are normalized to the absorption spectra at the 0-0 band.

Further, the above conclusion is confirmed by the fluorescence behavior of I in the acetonitrile–water system, where a solvolytic reaction is likewise possible. Although I is nonfluorescent in acetonitrile, a strong fluorescence appears upon the addition of some water. The residue from this solution was identified as 9-methyl-10-(hydroxymethyl)anthracene (III) by mass spectrometry ($M^+=222$). III also fluoresces strongly in all solvents.

In conclusion, then, the nonfluorescent character of I is an interesting problem. A photolytic process of the C–Cl bond may be considered as the main deactivation process.

Experimental

I was prepared by the chloromethylation4) of 9-methylanthracene5) and was recrystallized three times from benzene. The ethanol and benzene are of a spectroscopic grade. The absorption and fluorescence spectra were measured with a Shimadzu spectrophotometer, UV 200, and a Shimadzu corrected fluorospectrophotometer, RF 502, respectively.

References

1) W. Melhuish, *New Zealand J. Sci. Tech.*, **37B**, 142 (1955).

2) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," John Wiley & Sons, New York, Chapter 11.

3) Indeed, a very weak fluorescence was observed in the benzene solution of I, but its excitation spectrum is different from the absorption spectrum of I; Rather, it resembles the absorption spectrum of III, which seems to be slightly present as impurities.

4) J. L. Adelfang and G. H. Daub, *J. Amer. Chem. Soc.*, **80**, 1405 (1958).

5) A. Sieglitz and R. Marx, *Ber.*, **56**, 1619 (1923).