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Photodimerization of Anthracene Derivative in Langmuir-Blodgett Films

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Mixed Langmuir-Blodgett (LB) films of (10-butyl-9-anthryl)-3-propanoic acid (1) and arachidic acid were prepared and their UV-Vis spectra were measured. Photodimerization of 1 in these LB films was successfully performed with monochromatic light.

When the Langmuir-Blodgett (LB) films are used as photo-functional materials, they are expected to possess some splendid optical properties because the chromophores are packed compactly in super thin layers. Furthermore, some specific photoreactivities can be expected because the environments of the reacting molecules could be considered as a quasi-solid state, the existence of highly systematic arrangements and orientations of the molecules in the films. So far, in spite of these expectations, only a few fundamental studies have been reported for the photochemical reactions in LB films.$^{1)}$ In this line, we have been studying some photodimerizations of anthracenes in LB films. Although anthracene dimerizations have been studied extensively for a long time,$^{2)}$ to the best of our knowledge, the reactions have not been conducted in LB films. In this communication, we wish to report the intermolecular photodimerizations of (10-butyl-9-anthryl)-3-propanoic acid (1)$^{3)}$ in mixed LB films with arachidic acid (C20).

For the pure 1 and for the mixtures of 1 and C20 in various ratios, the measurements of surface pressure-area (F-A) curves of the monolayers and depositions of these on quartz plates were performed with a Lauda Filmwaage at 17 °C. All the samples were dissolved in $CHCl_3$ to give 10^{-3} M (1 M=1 mol dm^{-3}) solution and spread on the subphases which were 2.5×10^{-4} M $CdCl_2$ aqueous solution at pH 4.01 for the pure 1 and 4.0×10^{-4} M $CdCl_2$ at pH 6.0 for other cases. The adjustment of pH was made with HCl for the former solution and with 5×10^{-5} M $KHCO_3$ for the latter. F-A curves of some samples are shown in Fig. 1. The average limiting areas for the mixtures of 1 and C20 were smaller than that of pure C20 (20Å^2). This result suggests partial squeezing out of molecule 1 from monolayers. Nevertheless, the UV-Vis absorption of LB films gave a linear relationship with the number of layers deposited on a quartz plate.

UV-Vis absorption spectra were measured for unsubstituted anthracene in methanol (10^{-6} M) and for 1 in methanol (10^{-6} M) and in LB films (Fig. 2). In case of LB films, UV-Vis spectra of 1 were measured for pure and for mixed

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films. A distinct red shift of absorption bands was observed for the solution of **1** when compared with that of the unsubstituted anthracene. Comparisons of UV-Vis spectra have revealed that the extent of red shift is dependent on the concentration of **1** in the LB films. However, in our experiment, the degree of red shift in the UV-Vis spectrum of pure **1** in the LB film was smaller than that of the reported literature. This result is probably reflecting some extents of disorder in the systematic structure of the film.[4]

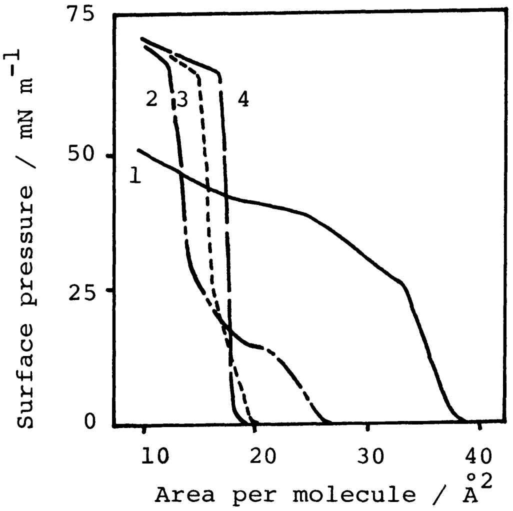

Fig. 1. Surface pressure-area isotherms of mixed layers of **1** and arachidic acid.
1: pure **1**
2: **1**:C20=1:1
3: **1**:C20=1:3
4: **1**:C20=1:10
C20=arachidic acid

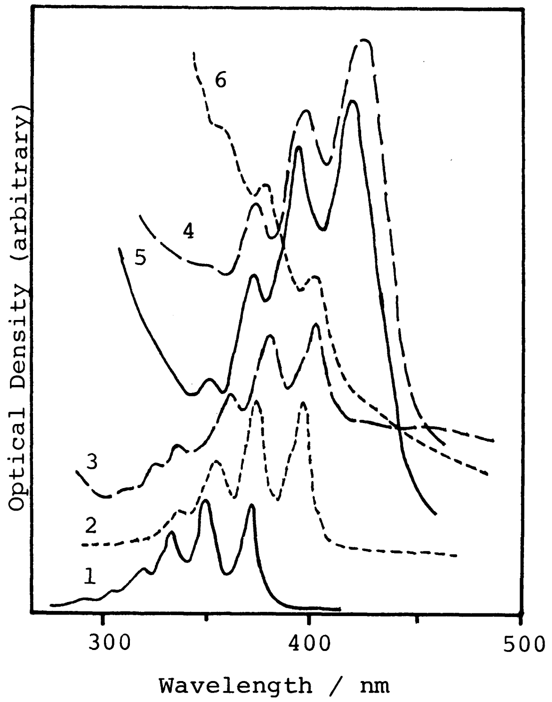

Fig. 2. UV-Vis spectra of anthracene derivatives.
1: Anthracene in MeOH (10^{-6}M)
2: **1** in MeOH (10^{-6}M)
3: LB Film (pure **1**)
4: LB Film (**1**:C20=1:1)
5: LB Film (**1**:C20=1:3)
6: LB Film (**1**:C20=1:10)
C20=arachidic acid

There are two plausible photochemical reaction pathways for **1** when the reaction is conducted in air. One is a [4+4] photochemical cyclodimerization (**2**) and the other is an addition of oxygen to the anthracene nucleus (**3**) (Fig. 3).[2]

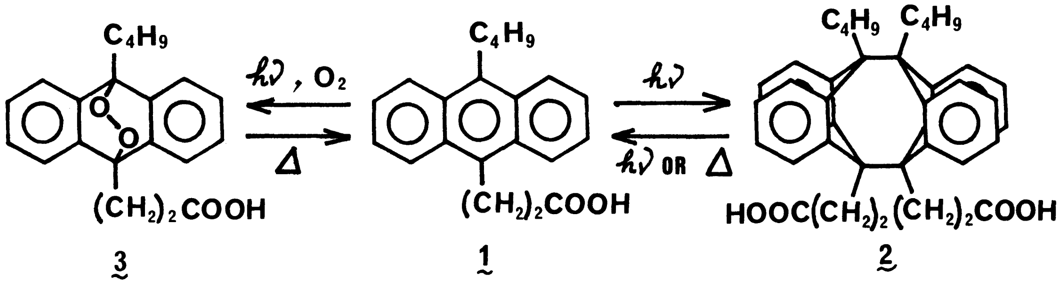

Fig. 3. Plausible reaction pathways of **1**.

Photochemical reactions of 1:1 and 1:3 mixtures of **1** and C20 in LB films were conducted with 422 ± 2.5 nm (0.968 mW/cm^2) and 416 ± 2.5 nm (1.131 mW/cm^2) light, respectively. The extent of reactions was monitored with an UV-Vis spectrophotometer. The photochemical reactions in mixed LB films gave an analogous results. The spectrum change of a 1:1 mixture in the course of the irradiation is illustrated in Fig. 4. These changes in spectra are similar to those of dimerizations of several anthracene derivatives.$^{5)}$ In addition, an appreciable increase in the absorption of the oxygen addition product was not observed during the irradiation.$^{6)}$ From these results, it can be concluded that the major reaction in the film was not an oxygen addition but a dimerization reaction.

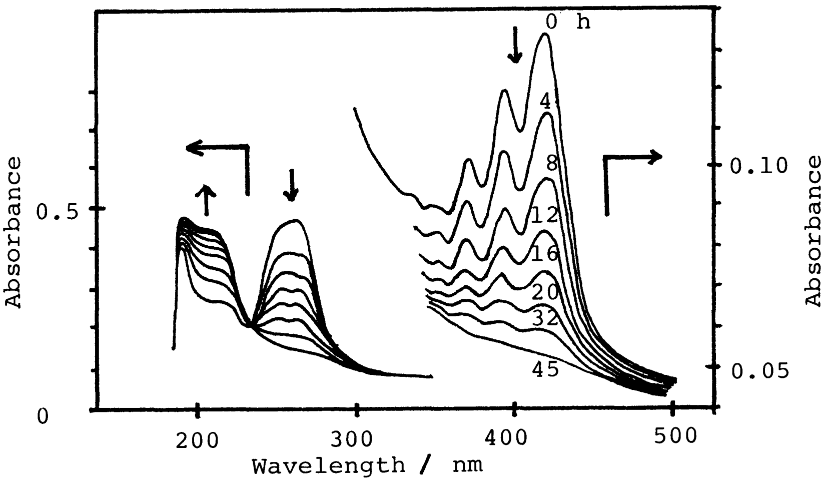

Fig. 4. UV-Vis spectra of **1** and arachidic acid (1:1) mixture in LB film. Irradiated with 422 ± 2.5 nm light.

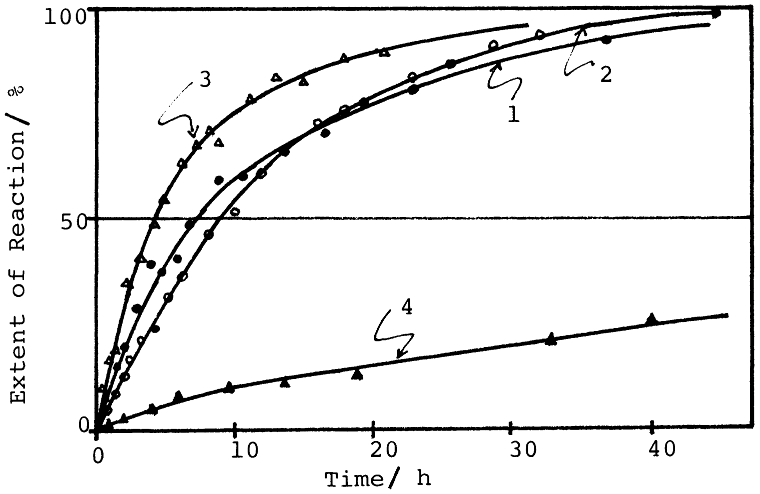

Fig. 5. Photochemical reactions of **1** and anthracene.
1: LB film (**1**:C20=1:3)
2: LB film (**1**:C20=1:1)
3: **1** in MeOH (10^{-6} M)
4: Anthracene in MeOH (10^{-6} M)
C20=arachidic acid

The extent of dimerization of **1** against irradiation time is shown in Fig. 5. The rates of dimerization of **1** in LB films were somewhat slower when compared with that in the solution, but it was much faster than that of the unsubstituted anthracene in methanol. Furthermore, it is very surprising to see that the reaction have proceeded to completion in mixed LB films.

The diffusion of the molecule is strongly suggested for the interpretation of the forementioned results. If the mobility of the molecules is restricted in the film, termination of the reaction should be observed before the complete consumption of 1, which is inconsistent with our results. Besides, there is another interpretation which can explain the completion of the reaction. When 1 is perfectly dispersed in the film as an intimate pairs prior to the irradiation, the reaction is expected to follow the first order kinetics because it can be regarded as an intramolecular reaction. However, the kinetic experiment has revealed that it was not a first order reaction, which can be regarded as a negative evidence for the latter case. In consequence, as mentioned previously, the existence of diffusion is suspected in the films.

At the initial stage of the reaction, the occurrence of a topochemical reaction is probable in the film. That is, reaction between neighboring 1 can proceed without much movements in multilayers.

Finally, the reversible reaction was tested for dimer 2 in the LB films. However, according to the UV-Vis spectra, reversible reaction was not observed when they were left in the dark at room temperature for a week or irradiated with 254 nm light of a 10 W low pressure mercury lamp for ca. 14 h. Further researches for the reversible reactions are in progress.

References

1) D.G.Whitten, Angew. Chem., Int. Ed. Engl., 18, 440 (1979) and the references cited therein.

2) A.Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York (1968), Chap.9; C.H.Wells, "Introduction to Molecular Photochemistry," Chapman and Hall Ltd., London (1972), Chap.5.

3) 1 was synthesized by the reported method: F.H.C.Stewart, Aust. J. Chem., 13, 478 (1961). The purity was checked by NMR, IR, and TLC. The sample was spectroscopically pure and developments on TLC with several solvent systems showed a single spot.

4) For this compound (1), several authors have reported the difficulties of monolayer formations on the subphase and deposition of these on a glass plate: P.S.Vincett, W.A.Barlow, F.T.Boyle, J.A.Finney, and G.G.Roberts, Thin Solid Films, 60, 265 (1979); F.H.C.Stewart, Aust. J. Chem., 14, 57 (1961). To perform photochemical reactions, we have used quartz plates for the deposition of monolayers, which are different from those of previous authors.

5) For example: M.Nowakowska, Makromol. Chem., 179, 2959 (1978); T.Tamaki, Chem. Lett., 1984, 53; M.Daney, C.Vanucci, J-P.Desvergne, A.Castellan, and H.Bouas-Laurent, Tetrahedron Lett., 1985, 1505.

6) UV-Vis spectrum of methanolic 1 (10^{-6} M) was measured after an irradiation with 398 ± 2.5 nm light. The reaction was conducted in oxygen and in air. In an oxygen atmosphere, a new absorption band appeared at 270 nm region after the irradiation.

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