SUBSTITUENT EFFECT IN THE PHOTODIMERIZATION OF AMPHIPHILIC ANTHRACENES: REACTIONS IN MONOLAYER ASSEMBLIES AND IN SOLUTIONS

Akihiko Ouchi,[*] Hiroyuki Niino, Yasujiro Kawabata,
Motoo Tanaka, and Akira Yabe
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

The rate of intermolecular photodimerization of amphiphilic anthracenes was largely affected by the substitution to anthracene nucleus, both in monolayer assemblies and in MeOH solutions. A larger substituent effect was observed in monolayer assemblies compared with those in solutions.

Chemical reactions in a rigid, organized environment, such as crystals, have attracted the deep interest of researchers particularly, in organic photochemistry.[1] However, there are many compounds which cannot become crystal states; and for crystal states, the relative orientation of molecules is fixed by the nature of the molecules and is usually unchangeable. Recently, it was shown that almost any kind of molecule — by modification with introduction of hydrophobic and hydrophilic moieties — can be made into an organized structure by arranging it into a monolayer assemby; and chemical reactions in such assemblies have been reported.[2]

It was expected that the relative orientation of the reaction centers in monolayer assemblies could be controlled by varying the position of the substitution to the reaction center; the difference in the relative orientation should be reflected to the reaction rate. In the course of our investigation of the effect of substitution, we report here the photodimerization of some differently substituted anthracene derivatives in monolayer assemblies and in solutions.[3]
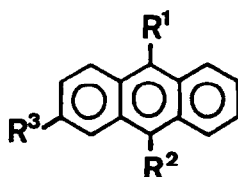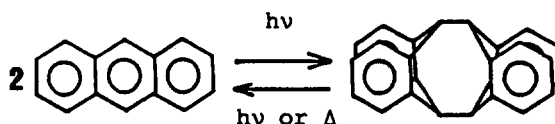
1 $R^1 = n\text{-}C_6H_{13}$, $R^2 = H$, $R^3 = (CH_2)_5COOH$
2 $R^1 = R^2 = H$, $R^3 = (CH_2)_{11}COOH$
3 $R^1 = n\text{-}C_{11}H_{23}$, $R^2 = R^3 = H$
4 $R^1 = R^2 = R^3 = H$
5 $R^1 = n\text{-}C_4H_9$, $R^2 = (CH_2)_2COOH$, $R^3 = H$

Two amphiphilic anthracenes with different substitution were synthesized: 6-(2-(10-hexyl)anthryl)-1-hexanoic acid 1 and 12-(2-anthryl)-1-dodecanoic acid 2.[4] Figure 1 shows π-A curves of 1 and 2.[5] Two limiting areas were observed for 1, 26.2 and 86.6 Å^2/molecule; the result suggests the existence of two different arrangements in the monolayer assembly. Compound 2 showed a limiting area of 28.6 Å^2/molecule with a shoulder at 51.4 Å^2/molecule. Preparation of the monolayer assemblies[6] was carried out at surface pressure of 25 (LP: low pressure) and 40 mN/m (HP: high pressure) for 1, and at 30 mN/m for 2. Figure 2 shows the UV spectra of 1 and 2, both in MeOH solutions and in monolayer assemblies.[7].

The photochemical reactions of 1, 2, 3,[4] and 4 in 10^{-5} M MeOH solutions were performed by using a quartz cell with 10 mm optical path. The irradiations were conducted with monochromatic light corresponding to the 0—0 component of the first singlet vibronic transition of anthracenes: 390.0±5.0 nm, 0.30 mW/cm^2 for 1; 379.0±5.0 nm, 0.27 mW/cm^2 for 2; 385.0±2.5 nm, 0.03 mW/cm^2 for 3; and 374.0±2.5 nm, 0.99 mW/cm^2 for 4. The reactions were monitored by UV-Vis spectroscopy and the product was identified
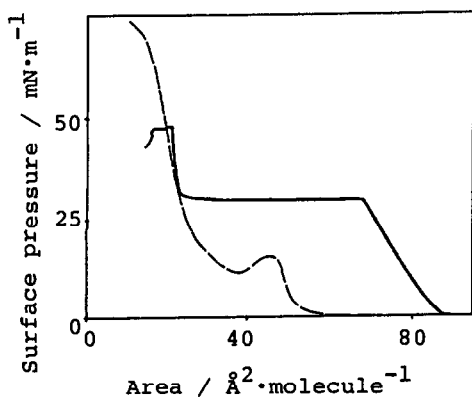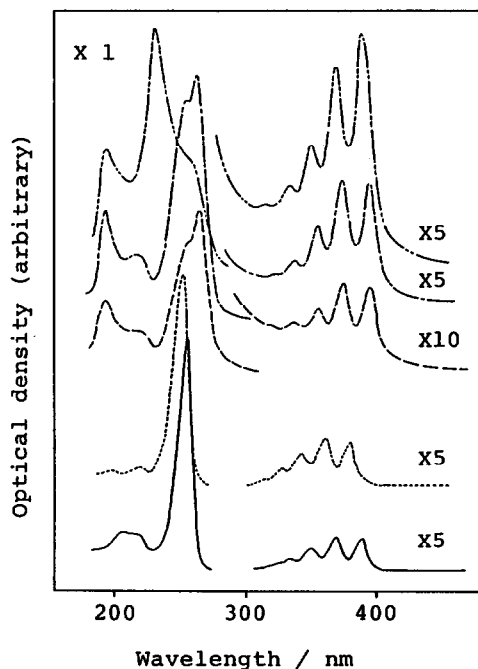

Fig. 1. Surface pressure-area (π-A) curves of 1 (—) and 2 (--).

Fig. 2. UV spectra of anthracene derivatives in MeOH solutions and in monolayer assemblies;
——: 1, MeOH soln (10^{-5} M);
••••: 2, MeOH soln (10^{-5} M);
----: 1-LP, monolayer assembly;
-•-•: 1-HP; monolayer assembly;
-•••-: 2, monolayer assembly.

by comparison with the reported UV spectra.[8] The photochemical reactions in the monolayer assemblies were conducted similarly with the monochromatic light: 397.0±5.0 nm, 0.30 mW/cm^2 for 1 (both HP and LP); and 392.0±5.0 nm, 0.30 mW/cm^2 for 2.

The extent of reactions as a function of reaction coordinate — the irradiation time normalized with the flux of photons and the extinction coefficient — for 1, 2, 3, and 4, both in solutions and in monolayer assemblies, is shown in Fig. 3. In solutions, compounds 1, 2, and 3 showed considerable retardation in the photodimerization compared with 4; the relative rates to 4 were ca. 1/6.7, 1/20, and 1/2.7 for 1, 2, and 3, respectively at the primary stage of the reaction. The result can be explained by the steric repulsion during the reaction. In spite of higher substitution, 1 reacted faster than 2; both compounds give pairing of the molecules by hydrogen bonding[9] prior to the photodimerization, and 1 have suitable chain lenght to give favorable orientation of the two anthracene moieties for the photodimerization, resulting in faster reaction.

As shown in the figure, greater acceleration of the reaction was observed in the monolayer assemblies compared to those in the solutions; ca. 80 to 110-fold of acceleration for 1 and ca. 35-fold for 2. The substituent effect was more apparent in the monolayer assemblies because of the closer location of the molecules. The similar limiting areas for 1-HP and 2
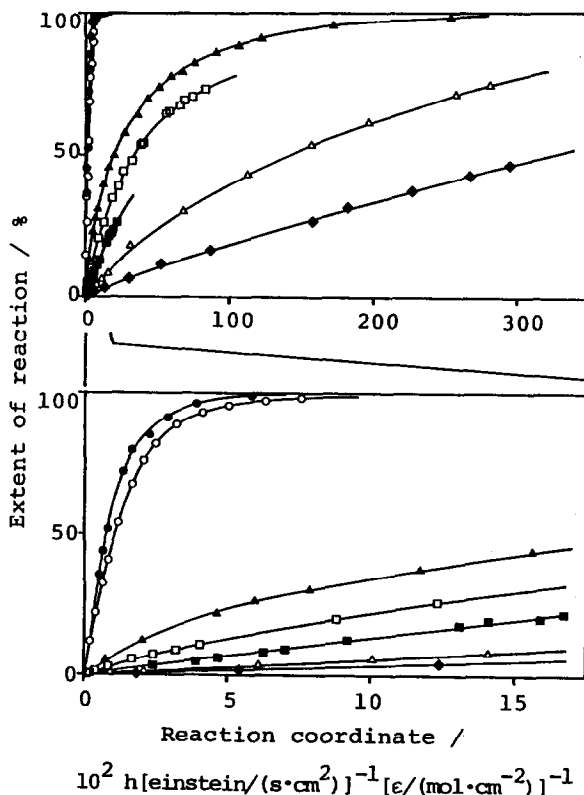

Fig. 3. Extent of reactions for 1 and 2 as a function of reaction coordinate:

●: 1-LP; monolayer assembly;

O: 1-HP; monolayer assembly;

▲: 2, monolayer assembly;

△: 1, MeOH soln (10^{-5} M);

◆: 2, MeOH soln (10^{-5} M);

■: 3, MeOH soln (10^{-5} M);

□: 4, MeOH soln (10^{-5} M).

Reaction coordinate /

10^2 h[einstein/(s·cm^2)]$^{-1}$[ε/(mol·cm^{-2})]$^{-1}$

suggest that the distance between two molecules in these assemblies is comparable. However, *ca.* 7-fold acceleration of the rate was observed between 1-HP and 2; the result implies the difference in the relative orientation of the chromophores, favoring photodimerization in 1-HP monolayer assembly.

It is interesting to see that, in spite of the larger limiting area in the monolayer assembly, thus greater separation of the two chromophores, 1-LP reacted *ca.* 9-fold faster than 2. The reason is still not clear; however, it suggests preferable orientation for photodimerization in 1-LP monolayer assembly compared with that of 2. The comparable reaction rate in 1-HP and 1-LP monolayer assemblies, *ca.* 1.3-fold faster in that of 1-LP, implies that the relative orientation of anthracene chromophores is very similar in these films.

References

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3 Photodimerization of 3-(9-(10-butyl)anthryl)-1-propanoic acid 5 in the mixed monolayer assemblies with arachidic acid has been reported; however, the assembly was suspected to have less organized structure: A.Ouchi, M.Tanaka, T.Nakamura, M.Matsumoto, Y.Kawabata, S.Tomimasu, and A.Yabe, *Chem. Lett.*, 1986, 1833.

4 Compound 1 was synthesized by the reaction of n-$C_6H_{13}MgBr$ and anthrone, followed by Friedel-Crafts reaction with $MeOOC(CH_2)_4COCl$, and Wolff-Kishner reduction. Compound 2 was synthesized by Friedel-Crafts reaction of anthracene and $EtOOC(CH_2)_{10}COCl$, and successive Wolff-Kishner reduction. Compound 3 was synthesized by the reaction of n-$C_{11}H_{23}MgBr$ and anthrone. NMR, IR, MS spectra of 1, 2, and 3 were consistent with the structure. The purities were checked by TLC and HPLC; developments of samples on silica gel TLC with several solvent systems and HPLC analyses showed a single spot and peak, respectively, for each compound.

5 The measurement of surface pressure-area (π-A) curves and the deposition of films were performed with a Lauda Filmwaage at 17°C. The subphase utilized was 4.0×10^{-4} M $CdCl_2$ aqueous solution at pH 6.0, which was adjusted with 5×10^{-5} M $KHCO_3$ aq.

6 The monolayer assemblies were prepared by deposition of ten monolayers on both sides of a quartz plate which is precoated with five layers of arachidic acid on each side.

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