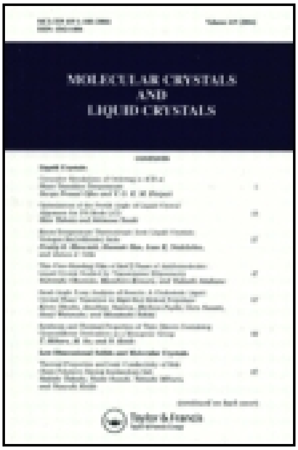

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PHOTO-EXCITED HYDROGEN TRANSFER IN THE LB FILMS OF LONG-CHAIN ANILS

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Abstract Long-chain anils of salicylaldehyde, 2-hydroxy-1-naphthaldehyde and *ortho*-nitrobenzaldehyde were newly synthesized and the photo-excited hydrogen transfer in the LB films of these compounds was investigated. Hydrogen transfer occurred in all the LB films. The back reaction in the LB films of anils of salicylaldehyde, 2-hydroxy-1-naphthaldehyde was markedly suppressed in comparison with the corresponding solutions. No back reaction was observed in the LB films of derivatives from *ortho*-nitrobenzaldehyde.

INTRODUCTION

Some anils of salicylaldehyde, 2-hydroxy-1-naphthaldehyde and *ortho*-nitrobenzaldehyde are reported to exhibit photochromism.[1-3] The photochromism in these compounds is based on the intramolecular hydrogen transfer and the reaction in the systems is markedly dependent on the molecular environment where the molecules are present. Langmuir-Blodgett method is suitable for the control of the molecular arrangement. In this work, these functional groups were introduced into the LB films and their molecular arrangements and behaviors to the light irradiation were studied.

EXPERIMENTAL

The structures, abbreviations and the melting points of the anils (including those from the ortho-nitrobenzaldehyde and fatty amine) with long alkyl chain are shown in Figure 1 and Table 1, respectively. These compounds were synthesized by the condensation of cor-

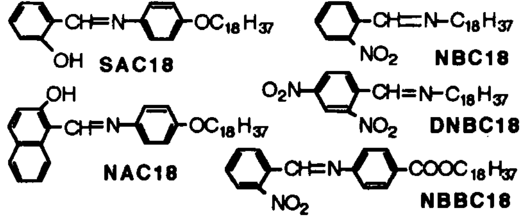

FIGURE 1 Structures of long-chain Schiff bases.

Table1 Melting points of the compounds

Abbrev.	mp (°C)
SAC18	93.0-94.0
NAC18	83.0-84.0
NBC18	50.0-51.0
DNBC18	68.0-69.0
NBBC18	74.0-74.5

responding aldehydes and primary amines and recrystallized from ethanol. The monolayers of the compounds were formed by spreading a chloroform solution on water surface and the surface pressure-area isotherms were recorded by a Langmuir-type film balance (FW-1). The LB films were transferred by a horizontal lifting method. The UV spectra of the solution and the film were recorded by a Shimadzu UV-190 double-beam spectrophotometer. The transient absorption spectra of the solution and the films were recorded by a flash photolysis system assembled in our laboratory. All the experiments were done at room temperature.

RESULTS AND DISCUSSIONS

Surface pressure-Area Isotherms

Figure 2 shows the surface pressure-area isotherms of the monolayers of the compounds on pure water surface. The monolayers of SAC18 and NAC18 show the limiting areas of 0.24 and 0.36 $nm^2 molecule^{-1}$, respectively. Taking into consideration of the dimensions of these groups, it can be suggested that the long axis of these groups is nearly vertical to the water surface. These results are very similar to that reported for an amphiphilic salicylideneaniline derivative.[4] For the monolayers of the long-chain Schiff bases from the nitrobenzaldehyde, by comparison the limiting areas of the NBC18 and NBBC18 with that of DNBC18, it can be suggested that the long axes of the functional groups in the NBBC18 and NBC18 are rather parallel to the water surface.

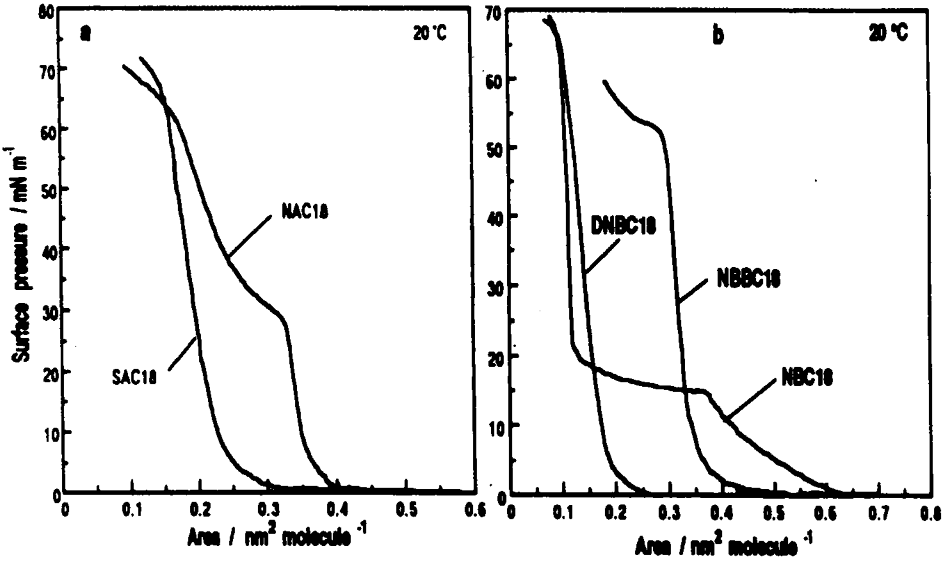

FIGURE 2 Surface pressure -area isotherms of the long-chain Schiff bases.

Photo-excited Hydrogen Transfer in the LB Films of SAC18 and NAC18

In Figure 3 (left part), the absorption spectrum of the built-up multilayer of SAC18 (30 mN/m, 100 layers on quartz plate) is compared with that of an ethanol solution. The film shows the major absorption band at 334 nm, which is 16 nm blue shifted in comparison with the solution. This result suggests the vertical arrangement of the functional group in the LB films. When the solution or LB film of SAC18 was excited by a light beam (355 nm, Nd:YAG), transient absorption bands were observed at about 480 nm in solution and 470 nm in the LB film, as shown in the right part of Figure 3. The peak at around 470-480 nm can be considered as the *trans*-keto form of the salicyldeneaniline formed by the intramolecular hydrogen transfer upon irradiation.[3] In the LB films, an additional peak is observed at around 510 nm, which may be due to the intermolecular coupling of the SA groups.[1] The back reaction can occur in these systems. By monitoring the decay of the absorption band at 480 nm in solutions and 470 nm in the LB film, the rate of the back reaction can be estimated. It was found that the rate of the back reaction is in the order of 10^{3-4} s^{-1} in solution, depending on the solvent, while it was of 10^{-3} s^{-1} in the LB films. The hydrogen transfer can also occur upon irradiation in the NAC18 solution and LB films in a similar manner. However, in the case of NAC18, hydrogen transfer can even occur in polar solvents without irradiation.

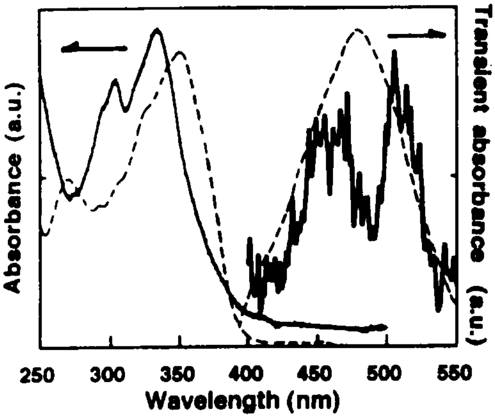

FIGURE 3 Absorption spectra (left) and transient absorption spectra (right) of SAC18 in ethanol solution (dashed lines) and in LB films (30 mN m^{-1}, 100 layers) recorded at 100 ns after excitation by a laser pulse (355 nm, Nd:YAG laser).

Photo-excited Hydrogen Transfer in LB Films of *ortho*-nitrobenzaldehyde Derivatives

When the LB film of NBBC18 was subjected to an UV light, the film changed color from pale yellow to red. Such color change was followed by the UV measurement, as shown in Figure 4 (a). The peak intensity at 290 nm decreased and absorption at longer wavelength increased after irradiation (330 nm). Such change in the LB film is also reflected in the corresponding FT-IR spectra, as shown in Figure 4 (b). The most important changes in the IR spectra are that the stretching vibration of nitro group at 1334 cm^{-1} in the multilayer disappeared, while a peak at 3302 cm^{-1}, which can be assigned to

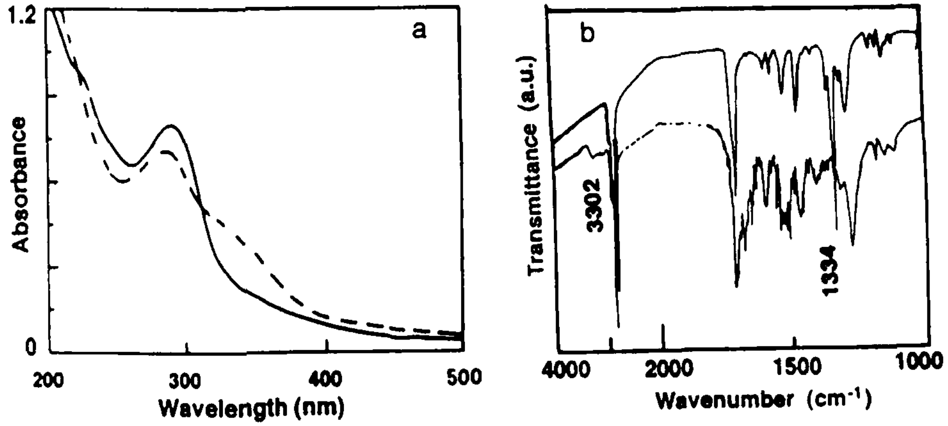

FIGURE 4 Absorption (a) and FT-IR (b) spectra of NBBC18 LB film before (solid lines) and after (dashed lines) irradiation (330 nm).

the OH stretching vibration, appeared after irradiation. This result indicates that the hydrogen transfer occurred when the NBBC18 LB film was subjected to the UV irradiation. Similar results were obtained for NBC18. With respect to the DNBC18 having nitro group in ortho and para positions, the irradiation caused the decrease of the nitro vibration, but not the disappearance of the band. From the fact, it is understood that the ortho nitro group is important in hydrogen transfer reaction. For these compounds, however, no back reaction was observed in the multilayers.

In summary, it is suggested that hydrogen transfer occurred in all the LB films. The back reaction in the LB films of anils of salicylaldehyde, 2-hydroxy-1-naphthaldehyde was markedly suppressed in comparison with the corresponding solutions. No back reaction occurs in the LB films of the derivatives from *ortho*-nitrobenzaldehyde.

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