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Diyas A. Myrzakozha<sup>a</sup>, Takeshi Hasegawa<sup>b</sup>, Jujiro Nishijo<sup>b</sup>, Toyoko Imae<sup>c</sup>, Katsuhiko Takagi<sup>d</sup> & Yukihiro Ozaki<sup>a</sup>

<sup>a</sup> School of Science, Kwansei Gakuin University, Nishinomiya, Japan

<sup>b</sup> Kobe Pharmaceutical University, Kobe, Japan

<sup>c</sup> Faculty of Science, Nagoya University, Nagoya, Japan

<sup>d</sup> Faculty of Engineering, Nagoya University, Japan

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## Photocyclodimerization of Cinnamic Acid in a Langmuir-Blodgett Film Investigated by Infrared Spectroscopy

DIYAS A. MYRZAKOZHA<sup>a</sup>, TAKESHI HASEGAWA<sup>b</sup>, JUJIRO NISHIJO<sup>b</sup>, TOYOKO IMAE<sup>c</sup>, KATSUHIKO TAKAGI<sup>d</sup>, YUKIHIRO OZAKI<sup>a</sup>

<sup>a</sup>School of Science, Kwansei Gakuin University, Nishinomiya, Japan;

<sup>b</sup>Kobe Pharmaceutical University, Kobe, Japan; <sup>c</sup>Faculty of Science, Nagoya University, Nagoya, Japan; <sup>d</sup>Faculty of Engineering, Nagoya University, Japan

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Monolayer Langmuir-Blodgett (LB) films of octadecyldimethylamine oxide ( $C_{18}$ DAO), dioctadecyldimethylammonium chloride ( $2C_{18}$ DAC) and their mixtures with cinnamic acid were prepared on gold evaporated glass slides by use of the LB technique and their structures were investigated by infrared spectroscopy. The infrared study indicates that cinnamic acid exists as a monomer and its C=O group is nearly perpendicular to the substrate surface in the LB film of  $2C_{18}$ DAC mixed with cinnamic acid, while the C=O group is nearly parallel the substrate surface in the case of mixed film with  $C_{18}$ DAO. The irradiation of UV light causes a marked change in the C=O stretching band of the film of  $2C_{18}$ DAC mixed with cinnamic acid, indicating that the acid is changed into the dimeric form.

**Keywords** photoreaction; LB films; monolayer; infrared spectroscopy

### INTRODUCTION

Langmuir-Blodgett (LB) films have been the topic of extensive research in the recent years for their fundamental importance in the surface science together with their potential industrial application as thin barriers, membranes and material for the optoelectronics<sup>[1]</sup>. One of the authors (T.I.) has been investigating photocyclodimerization and molecular

arrangement of cinnamic acid in reaction matrices such as micelles, vesicles and LB films of double-tailed cationic amphiphile, dioctadecyldimethylammonium chloride ( $2C_{18}DAC$ ) and of single-tailed nonionic amphiphile, octadecyldimethylamine oxide ( $C_{18}DAO$ )<sup>[2,3]</sup>. In the present study we investigate the molecular orientation and structure in the LB films of  $2C_{18}DAC$  and  $C_{18}DAO$  mixed with cinnamic acid before and after the irradiation of UV light (254 nm) by use of infrared spectroscopy.

## EXPERIMENTAL

$C_{18}DAO$ ,  $2C_{18}DAC$  and cinnamic acid (Figure 1) employed in the present study were the same as those previously used<sup>[2,3]</sup>. The instrumentation and techniques for the fabrication of LB films of  $C_{18}DAO$ ,  $2C_{18}DAC$ , and their mixtures with cinnamic acid on gold evaporated glass slides were described elsewhere<sup>[3]</sup>. The infrared reflection-absorption (RA) spectra were obtained at a  $4\text{ cm}^{-1}$  resolution with a Nicolet Magna 550 IR

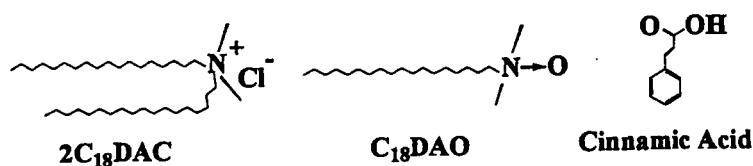


FIGURE 1. Chemical structures of  $2C_{18}DAC$ ,  $C_{18}DAO$  and cinnamic acid

spectrometer with an MCT detector. To generate the spectra with a high signal-to-noise ratio, 1000 interferograms were added.

## RESULTS AND DISCUSSION

Figure 2A shows infrared RA spectra of the monolayer LB films of  $2C_{18}DAO$  and  $C_{18}DAO$  mixed with cinnamic acid. Bands near  $2924$  and  $2855\text{ cm}^{-1}$  are assigned to  $CH_2$  antisymmetric and symmetric stretching modes of the alkyl chains. Their frequencies and relative intensities indicate that the alkyl chains contain some *gauche* conformers and are tilted considerably with respect to the surface normal in both LB films.

There observe marked differences in the  $1750\text{--}1600\text{ cm}^{-1}$  region between the two spectra in Fig. 2A. The spectrum of the LB film of  $2C_{18}DAC$  mixed with cinnamic acid shows an intense band at  $1739\text{ cm}^{-1}$  assignable to a  $C=O$  stretching mode of cinnamic acid. Judging from its frequency, it seems that the acid takes a monomer form in the film. The strong intensity of the  $C=O$  stretching band suggests that the  $C=O$  group is nearly perpendicular to the substrate surface in the LB film of  $2C_{18}DAC$  mixed with cinnamic acid. In contrast to the film of  $2C_{18}DAC$  mixed with cinnamic acid, that of  $C_{18}DAO$  mixed with cinnamic acid does not give a band assignable to the  $C=O$  stretching mode, implying that the  $C=O$  group is nearly parallel to the substrate surface in the LB film of  $C_{18}DAO$  mixed with cinnamic acid.

In Fig. 2B are shown infrared RA spectra of the monolayer LB films of  $C_{18}DAO$  and  $2C_{18}DAC$  mixed with cinnamic acid after the

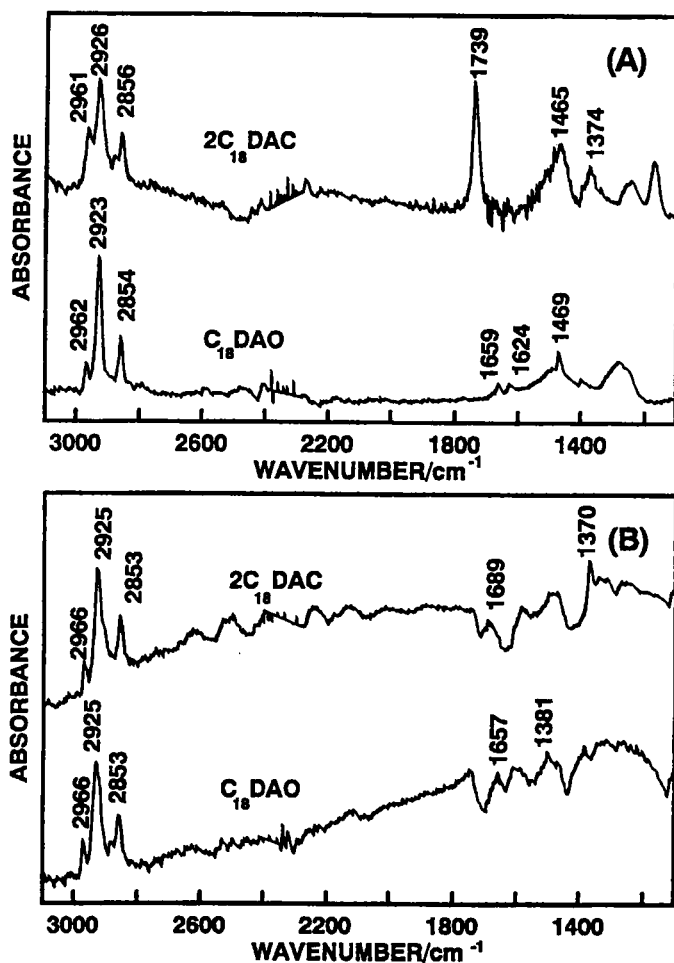


Figure 2. Infrared RA spectra of one-monolayer LB films of  $2\text{C}_{18}\text{DAC}$  and  $\text{C}_{18}\text{DAO}$  mixed with cinnamic acid before (A) and after (B) irradiation.

irradiation of UV light (254 nm). The relative intensities and frequencies of the two  $\text{CH}_2$  stretching bands change little with the irradiation. Therefore, it is very likely that the molecular orientation and structure of the alkyl chains in the LB films do not undergo a significant change upon the UV irradiation. The photo-irradiation brought about a marked change in the  $1750\text{--}1600\text{ cm}^{-1}$  region of the spectrum of the LB film of  $2\text{C}_{18}\text{DAC}$  mixed with cinnamic acid. Probably, monomeric cinnamic acid changes into dimeric forms via the photoreaction<sup>[2,3]</sup> and the  $\text{C}=\text{O}$  group is nearly parallel to the substrate surface in the LB film after the irradiation.

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