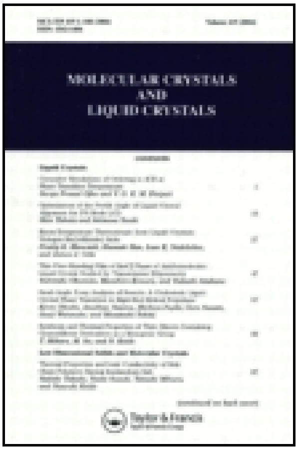

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A Controlled Photodimerization of Cinnamic Acid in a Composite Bilayer of Dioctadecyldimethylammonium Bromide

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Investigations of the photochemistry of cinnamic acid (CA) were carried out in a form of 1 : 1 composite solids with dioctadecyldimethylammonium bromide (DODAB) or chloride (DODAC). UV irradiation of the composite solids with DODAB resulted in the highly selective formation of the *syn*-Head-to-Head dimer, suggesting the parallel orientation of CA within the complex. Studies of X-ray diffraction, DSC, and IR spectra revealed the formation of a composite bilayer assembly showing the interaction between polar groups of CA and DODAB as well as the incorporation of CA into the alkyl regions of DODAB. On the other hand, the mixture of CA and DODAC showed less and non-selective photodimerization reaction, which could be ascribed to a disordered molecular arrangement, judging from a weak and broad endothermic peak at around reaction temperature in the DSC curve.

Keywords: composite bilayer; controlled photodimerization; cinnamic acid; dioctadecyldimethylammonium bromide

INTRODUCTION

The photodimerization of various aromatic olefins in the crystalline state has been established as a topochemical reaction.[1-4] There have been a number of studies[5-11] dealing with the topochemical photoreactions in anisotropic media, especially with regard to photodimerization in a variety of organized media such as micelles, vesicles, and Langmuir-Blodgett films. In previous literature,[6, 7] we have reported that the irradiation of cinnamate or 2-indenecarboxylate ions incorporated into self-assembled molecular aggregates results in the selective formation of Head-to-Head dimers (*syn*-HH and *anti*-

HH). The photoreactivity and stereochemistry of cyclodimers are extremely sensitive to the morphologies and structural rigidity of the molecular aggregates.

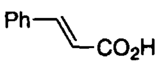
Recently, some kinds of amphiphilic molecules have been found to form complexes with aromatic molecules in a crystalline state.[12,13] For example, molecular discrimination occurs between ammonium amphiphiles and phenol derivatives, and separation of a phenol isomer is accomplished. It is important to clarify the morphologies of the complexes and interaction between the component molecules.

In the present work, the photodimerization of cinnamic acid (CA) as the molecular aggregates with dioctadecyldimethylammonium bromide (DODAB) or chloride (DODAC) has been investigated and characterization of the molecular aggregates has been carried out. Recently, it has been shown that the cast films prepared by drying an aqueous bilayer dispersion on a solid plate have multibilayer structures with macroscopic orientation,[14-16] and can be utilized as a template for the preparation of two-dimensional networks of organic[17] and inorganic polymers.[18] The cast films prepared from aqueous dispersions of CA and DODAB (or DODAC) were analyzed by X-ray diffraction, DSC, IR spectra, and by the stereochemistry of resulting cyclodimers.

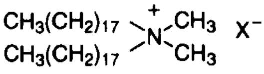
RESULTS AND DISCUSSION

Irradiation of Solid Mixture of Cinnamic Acid (CA) with Dioctadecyldimethylammonium Salts.

To 2.5×10^{-2} mol dm^{-3} aqueous dispersions of dioctadecyldimethylammonium bromide (DODAB) or chloride (DODAC) was added an equimolar cinnamic acid (CA), and translucent crystalline solid films were obtained by developing on glass slides. The photochemical reaction of CA was examined to observe the molecular arrangement of cinnamic acid moieties in the crystalline films. UV irradiation of the films through a Pyrex filter (> 280 nm) under ambient atmosphere resulted in an appearance of *syn*-Head-to-Head dimer (*syn*-HH), *anti*-Head-to-Head dimer (*anti*-HH), *syn*-Head-to-Tail dimer (*syn*-HT) and

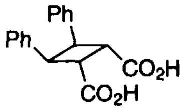


CA

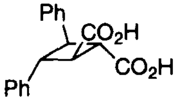


$X^- = Br^-$ or Cl^-

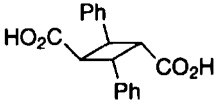
DODAB or DODAC



syn-HH



anti-HH



syn-HT

TABLE I Photoirraditaion of CA in the composite films with DODAB or DODAC.

Amphiphiles	Irr. / h	Conv. / %	Yield[a] / % *cis*	*syn*-HH	*anti*-HH	*syn*-HT
DODAB	1/6	27.0	4.1	22.6	0	1.2
	1	63.6	9.8	49.5	0	2.8
DODAC	1	41.7	24.7	4.7	2.5	0
	10	81.6	10.3	16.8	10.4	0

[a]Irradiated with a 300 W medium-pressure Hg lamp, λ > 280 nm, under ambient atomosphere.

cis-isomer as shown in TABLE I. It is interesting to note that the predominant photoproduct in the complex with DODAB was found to be the *syn*-HH, in contrast to the reporet of CA in the α-form crystal of which the sole yield was the *syn*-HT. On the other hand, *cis*-isomer was the major product in the complex with DODAC. The difference of the photoreactivities would result from the effect of counter ions on complexation, as mentioned below.

Characterization of the Solid Film of CA and Dioctadecyldimethylammonium Salts.

The translucent crystalline solid films of an equimolar mixture of CA and DODAB (or DODAC) were investigated by X-ray diffraction measurments. The cast film of DODAB alone exhibits a series of peaks due to a spacing of d = 35 Å up to the tenth order. DODAB has been reported to form a bilayer structure as a single crystal where the molecules are tilted 45° from the layer normal.[19] The composite film of CA and DODAB gave a series of peaks due

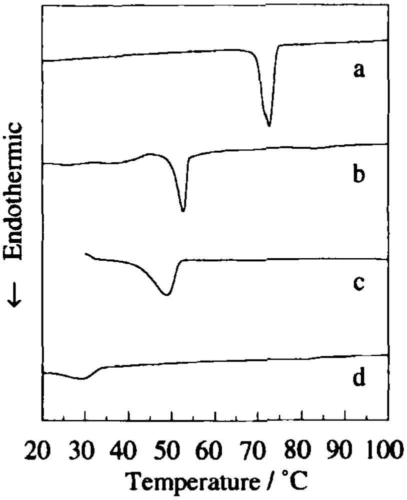


FIGURE 1 DSC curves of composite films; (a) DODAB, (b) CA and DODAB, (c) DODAC, and (d) CA and DODAC.

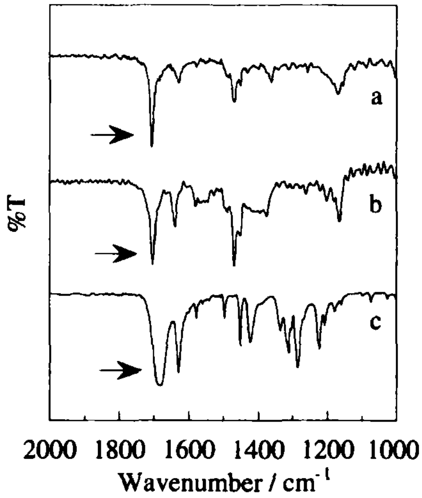


FIGURE 2 The C=O stretching vibrations, indicated by arrows, of carboxyl group of CA in the complex with (a) DODAB or (b) DODAC, or (c) in α-form crystal.

to a spacing of d = 30 Å up to the seventh order. The smaller spacing in the complex implies a larger inclination of the molecules of DODAB from the layer normal or interdigitation of the alkyl chains of DODAB. Anyway, the results suggest the incorporation of CA into a bilayer of DODAB.

In the cast film of DODAC, a series of peaks up to the third order were obtained with a spacing of d = 33 Å. The composite film of CA and DODAC gave only one peak with a spacing of d = 39 Å. It implies that the complex with DODAC has less regularity in a bilayer structure than the complex with DODAB, which could be the cause of the difference of the photoreactivities.

Analyses of differential scanning calorimetry (DSC) gave clear evidence of the regularity in a bilayer structure. FIGURE 1 shows the DSC curves of the composite films of CA and DODAB (or DODAC) together with the cast films of DODAB or DODAC alone. A single component of DODAB exhibited an endothermic peak at T_c = 72 °C (ΔH = 21.3 kcal mol^{-1}), which is ascribed to the crystal-to-liquid crystal phase transition of the bilayer structure.[20] In contrast, the 1 : 1 composite film of CA and DODAB showed an endothermic peak at T_c = 52 °C (ΔH = 16.3 kcal mol^{-1}). The peak at 52 °C can be attributed to the phase transition of the 1 : 1 aggregate of CA and DODAB since this peak increased steadily by the addition of CA with the suppression of the peak at 72 °C (data is not shown). No peak was observed in the range of 20-100 °C with DSC analysis of CA (α-crystal). The shift of the T_c value from 72 to 52 °C is due to the incorporation of CA into the alkyl regions of DODAB. These observations indicate that CA molecules interacts with DODAB to form the stable and regular composite bilayer. The cast film of DODAC gave an endothermic peak at T_c = 49 °C (ΔH = 17.1 kcal mol^{-1}). On the other hand, an only weak and broad peak was observed at T_c = 29 °C (ΔH = 6.6 kcal mol^{-1}) in the 1 : 1 film of CA and DODAC, suggesting that this complex has a disordered bilayer structre and is in liquid crystalline state at reaction temperature. This is why an non-selective photodimerization was observed in the complex of DODAC.

The IR spectra of the 1 : 1 complex provided further information on the structure of the aggregates as shown in FIGURE 2. The composite solid of CA and DODAB exhibits the carboxylic acid C=O stretching vibration at 1705 cm^{-1}, which was found to be much higher than that of the α-form crystal of CA at 1684 cm^{-1} assigned to the dimeric structure by the hydrogen bonding between the carboxyl groups. This suggests that CA in the composite solid may be present in a different circumstance from the dimeric form of CA in α-crystal. Toda et al.[12] reported on the formation of 1 : 1 complex of phenols and alkylammonium halides through a hydrogen bond between the acidic OH group and halide ion. We can see that the hydrogen bonding between the OH group of CA and Br^- of DODAB plays an important role in the complex formation. This interaction also can been seen in the mixture of DODAC.

Considering the above results, a mixture of CA and DODAB is concluded to form the 1 : 1 composite crystal with a highly regular multibilayer structure without phase separation into each component, CA and DODAB, whereas a mixture of CA and DODAC do not form a composite bilayer with regular sunucture. These features decisively influence on a controlled photodimerization.

Acknowledgements

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References

[1.] G. M. J. Schmidt, J. Chem. Soc., **1964**, 2014.
[2.] G. M. J. Schmidt, Pure Appl. Chem., **27**, 647 (1971).
[3.] M. D. Cohen, Angew. Chem., Int. Ed. Engl., **14**, 386 (1975).
[4.] V. Ramamurthy and K. Venkatesan, Chem. Rev., **87**, 433 (1987).
[5.] K. Takagi, B. R. Suddaby, S. L. Vadas, C. A. Backer, and D. G. Whitten, J. Am. Chem. Soc., **108**, 7865 (1986).
[6.] K. Takagi, M. Itoh, H. Usami, T. Imae, and Y. Sawaki, J. Chem. Soc., Perkin. Trans. 2, **1994**, 1003.
[7.] T. Imae, T. Tsubota, H. Okamura, O. Mori, K. Takagi, M. Itoh, and Y. Sawaki, J. Phys. Chem., **99**, 6046 (1995).
[8.] I. Weissbuch, L. Leiserowitz, and M. Lahav, J. Am. Chem. Soc., **113**, 8941 (1991).
[9.] X.-M. Zhao, J. Perlstein, and D. G. Whitten, J. Am. Chem. Soc., **116**, 10463 (1994).
[10.] M. Yamamoto, N. Furuyama, and K. Itoh, J. Phys. Chem., **100**, 18483 (1996).
[11.] a) Y. Ito, B. Borecka, J. Trotter, and J. R. Scheffer, Tetrahedron Lett., **36**, 6083 (1995); b) Y. Ito and G. Olovsson, J. Chem. Soc., Perkin Trans. 1, **1997**, 127.
[12.] a) F. Toda, K. Tanaka, T. Okada, Su. A. Bourne, and L. R. Nassimbeni, Supramol. Chem., **3**, 291 (1994); b) K. Tanaka, T. Okada, and Toda, Angew. Chem., Int. Ed. Engl., **32**, 1147 (1993).
[13.] K. Tanaka, K. Tamura, and F. Toda, J. Chem. Soc. Perkin Trans. 2, **1995**, 1571.
[14.] T. Kunitake, M. Shimomura, T. Kajiyama, A. Harada, K. Okuyama, and M. Takayanagi, Thin Solid Films, **121**, L89 (1984).
[15.] T. Kunitake, Angew. Chem., Int. Ed. Engl., **31**, 709 (1992).
[16.] K. Okuyama and M.Shimomura, New Developments in Construction and Function of Organic Thin Films, ed by T. Kajiyama and M. Aizawa, Elsevier Science B. V. (1996), pp. 39-70.
[17.] a) S. Asakuma, H. Okada, and T. Kunitake, J. Am. Chem. Soc., **113**, 1749 (1991); b) M. Marek, K. Fukuta, and T. Kunitake, Chem. Lett., **1993**, 291.
[18.] a) K. Sakata and T. Kunitake, J. Chem. Soc., Chem. Commun., **1990**, 504; b) N. Tsutsumi, K. Sakata, T. Kunitake, Chem. Lett., **1992**, 1465.
[19.] K. Okuyama, Y. Soboi, N. Iijima, K. Hirabayashi, T. Kunitake, and T. Kajiyama, Bull. Chem. Soc. Jpn., **61**, 1485 (1988).
[20.] K. Okuyama, K. Hoso, N. Maki, and H. Hamatsu, Thin Solid Films, **203**, 161 (1991).