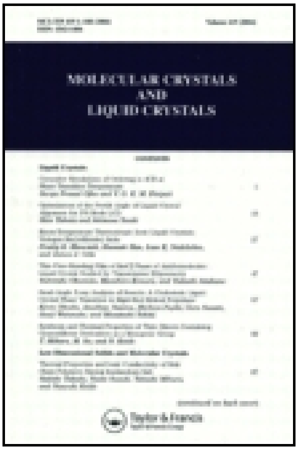

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Study on the Orientation of Benzodixanthene Analogue Having Alkyl Chain in Langmuir-Blodgett Film

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Study on the Orientation of Benzodixanthene Analogue Having Alkyl Chain in Langmuir-Blodgett Film

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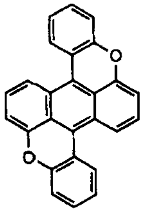
Xantheno[1′, 9′ : 4, 5, 6]benzo[1, 2, 3-*kl*]*N*-(1-dodecyl-2-pyridynium)-acridine iodide (**2a**) was synthesized from 1, 5-dichloroanthraquinone in six steps. The polarized UV-VIS spectra of the LB film of (**2a**) on CaF_2 were compared with the transition moments of (**2a**) calculated by semi-empirical molecular orbital method to discuss the orientation of (**2a**) in the LB film. The plane of the skeleton structure of the polycondensed aromatic ring of (**2a**) on CaF_2 in the LB film was rather oblique, not parallel to the CaF_2 surface.

Keywords: Photochromism; Benzodixanthene; Langmuir-Blodgett film; orientation; polarized UV-VIS spectra; semi-empirical molecular orbital method

INTRODUCTION

Benzo[1, 2, 3-*kl* : 4, 5, 6-*k'l'*]dixanthene (**1**) [1] and its analogues [2-13] are typical photochromic compounds. Derivatives and heterocyclic analogues of (**1**) have been studied.[2-9] The molecular design [10], and X-ray crystallographic analysis [11] were reported. Furthermore, we have been interested in monolayers and Langmuir-Blodgett (LB) films of analogues of (**1**) having alkyl chain.[12,13] The LB film is one of the sophisticated systems in which molecular orientations can be highly controlled. The orientations of analogues of (**1**) in LB films have not been studied.



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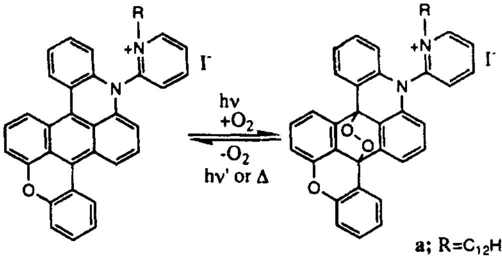


2 **3**

a; R=$C_{12}H_{25}$

b; R=$C_{10}H_{21}$

In the present work, the compound (**2a**) was synthesized and its photochromic properties in the LB film on CaF_2 were studied from the point of the orientation of (**2a**) in the film.

METHOD

Compound (**2a**) was prepared in six steps starting from 1, 5-dichloroanthraquinone, as described in the reference.[12] Monolayers were spread from the benzene solution on the distilled water surface and the surface pressure–area (π–A) isotherms were measured by using a Lauda film balance. The built-up films with an X-type structure on CaF_2 were prepared at 10 mN/m by the horizontal lifting method. Polarized UV-VIS spectra of (**2a**) on CaF_2 in the LB film were measured by spectrophotometer (Hitachi, U-3210). Molecular structure was optimized with AM1 procedure [14] and transition moments were calculated by INDO/S.[15]

RESULTS AND DISCUSSION

Monolayers on water surface and LB films on CaF_2

The π–A isotherms at different temperatures for the monolayer of (**2a**) on distilled water under the dark condition are shown in FIGURE 1. The compound (**2a**) having dodecyl chain forms condensed monolayers in which the limiting area has a tendency to decrease from 44 to 38 Å²/molecule with increasing the temperature of the aqueous subphase from 5 to 20 °C. The molecular areas of the monolayers of (**2a**) were larger than those of (**2b**) [12] with the limiting areas of 30-21 Å²/molecule at 10-20 °C. These values seem to be too small for the skeleton structure of polycondensed aromatic rings of (**2a**) or (**2b**).

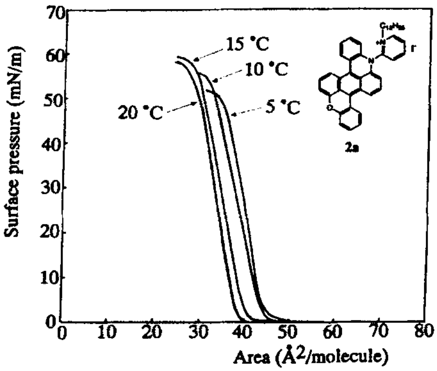


FIGURE 1 Surface pressure-area isotherms of (**2a**) on distilled water under dark condition.

Therefore, it is considered that the chromophore (**2a**) is oriented with the skeleton structure somewhat slanting on water surface.

The values of absorbance for 58 layers of (**2a**) on CaF_2 in the visible region at 580, 537, and 418 nm were 0.0611, 0.0372, and 0.0247, respectively. Spectral changes accompanied with the photochromic reactions of **2a**$\rightleftarrows$**3a** in the LB film (58 layers) on CaF_2 under irradiation of light (500 W Xe lamp at a distance of 40 cm) above 500 nm or dark and thermal condition, are shown in FIGURE 2.

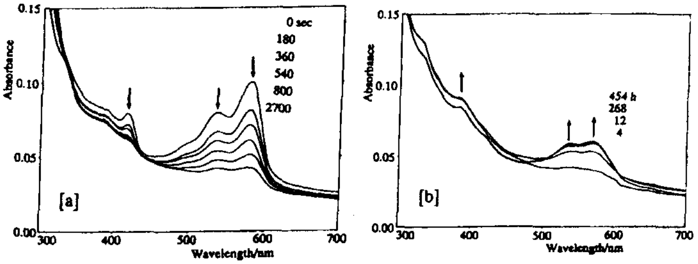


FIGURE 2 Spectral changes accompanied with
[a] the reaction **2a->3a** upon exposure to visible light (>500 nm), or
[b] its reverse reaction **3a->2a** under dark and N_2 atmosphere at 45 °C.

Polarized UV-VIS Spectra and Semi-empirical Molecular Orbital Calculation

The polarized UV-VIS spectra of (**2a**) on CaF_2 in the LB film are shown in FIGURE 3. When the direction of UV-VIS incident light is perpendicular to the film surface, the band shapes of s- and p-polarized UV-VIS absorption spectra in the range of 350 nm and 700 nm are similar to each other. On the other hand, in the polarized UV-VIS absorption spectra of the LB film at 45° incidence, the p-polarized absorption band around 530 nm is stronger than the corresponding s-polarized absorption band. The electronic transition moment of the increased visible band, calculated by INDO/S, is indicated in FIGURE 4. Therefore, it is found that the direction of the transition moment of (**2a**) is rather oblique, not parallel to the film surface.

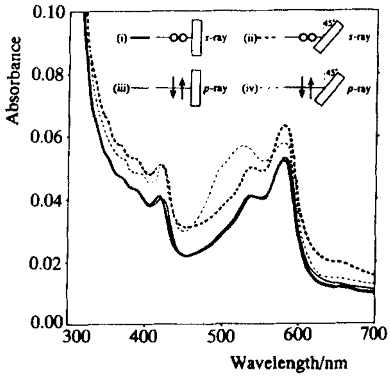
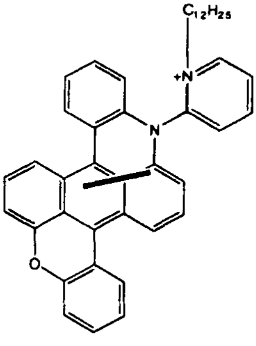


FIGURE 3 Polarized UV-VIS absorption spectra in the LB film of (**2a**).



2a

FIGURE 4 Transition moment of (**2a**) around 530 nm absorption band.

CONCLUSION

In conclusion, from the π-A isotherms of the monolayer on water surface and the polarized UV-VIS spectra of the LB film on CaF_2 plate, the present paper has demonstrated that the chromophore of (**2a**) is oriented with the plane of the skeleton structure of the polycondensed aromatic rings rather slanting, not lying flat on the film surface.

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