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Photoisomerization Studies in Langmuir Films of Retinal Derivatives

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In this work we examine the effects of the photoinduced *cis* to *trans* isomerization upon the stability conditions of floating monolayers films of *all-trans* retinoic acid and 13-*cis* retinoic acid prepared in an air-water interface. The observed differences between the compression isotherms in hysteresis experiments performed under dark and bright conditions of illumination are interpreted in terms of photoinduced conformational changes of the individual molecules.

Keywords: *all-trans* retinoic acid; 13-*cis* retinoic acid; Langmuir films.

INTRODUCTION

The quest for more efficient molecular optoelectronic devices can benefit from the correct understanding of the microscopic organization of the active medium where the nonlinear optical processes take place. In this context, the study of these phenomena in conjugated molecules organized as thin films represent an important tool for the interpretation of observed macroscopic properties in terms of the intrinsic molecular arrangement.

Of special interest in this regard is the exam of how the macroscopic properties of organized samples of photosensitive molecules such as azobenzene[1], stilbene[2] and retinal[3] derivatives are modified by light. Retinal molecules play a fundamental role in the biochemistry of vision

of the superior vertebrates[4]. Several theoretical and experimental studies[5-7] have examined the effects of photoinduced conformational changes upon the physical properties of retinal derivatives. After the initial step of photon absorption, the retinal molecule is excited and changes conformation along a 3-dimensional path where the main reaction coordinate is the torsion angle in one of the C=C bonds in the main polyenic chain[4].

Although photochemical reactions are usually studied in homogeneous non-organized phases[8], in several biological systems the photophysical and photochemical phenomena of interest occur in organized assemblies[9]. Hence, Langmuir films, i.e. organized floating monolayers prepared in an air-water interface, represent very adequate systems for an initial investigation of the effects of microscopic order upon the macroscopic properties of retinal derivatives.

EXPERIMENTAL

The retinal derivatives examined in this work (Figure 1) - the two isomers 13-*cis* retinoic acid (cRa) and *all-trans* retinoic acid (tRa) - were purchased from Aldrich (USA) and used without further purification.

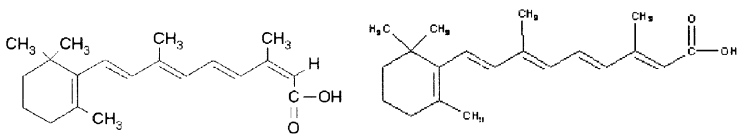

FIGURE 1: 13-*cis* retinoic acid (left) and *all-trans* retinoic acid (right).

After preparation in a dry bag under nitrogen atmosphere, the 0.6mg/mL retinal solutions in chloroform were kept under refrigeration until the moment of spreading. For the compression experiments 100µl of the solution were carefully dispersed in the air-water interface of the Langmuir trough (model 5000, KSV, Finland), under dim red light for the 'dark' experiments, and under normal white fluorescent light for the 'bright' ones. Hysteresis experiments were performed in the usual manner of repeated cycles of isothermal compression until a surface tension close to the collapse of the monolayer was reached, each one followed by a decompression caused by the backward motion of the moving barrier of the instrument.

RESULTS

Two very distinct profiles were observed for the compression hysteresis of the *all-trans* retinoic acid under different illumination situations (Figure 2). Under dark conditions, a small decrease in the mean molecular area is noticeable at each successive compression, in an indication that some degree of molecular rearrangement must be induced on the interface. No such initial reorganization is seen when the experiment is repeated under bright illumination. However, the major difference between the two experiments actually resides in the larger mean molecular areas and surface pressures observed under bright conditions of illumination.

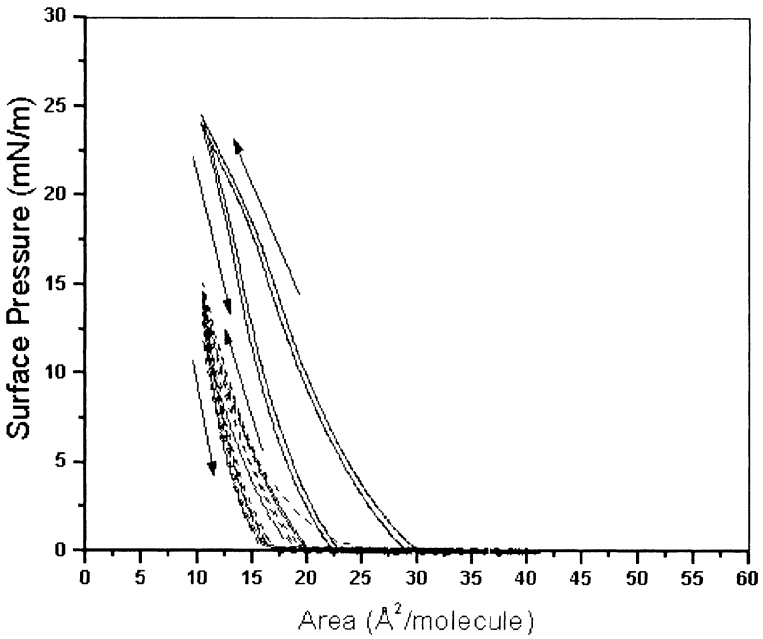

FIGURE 2: Compression hysteresis for the *all-trans* retinoic acid under dark (dashed curves) and bright (solid curves) illumination.

We can assume that light induced disorder plays a role in reorganizing the molecular domains and modifying the average intermolecular forces existent between the *all-trans* molecules in the

dark. A 'liquid-condensed' phase[10] can even be identified in the isotherm compressions under bright conditions. These observations are consistent with the idea that the photoinduced *trans* to *cis* isomerization leads to a different arrangement of the floating molecular aggregates, which because of the interaction with the incident light occupy a larger average area and interact in a stronger manner among themselves than those formed under dark conditions.

This hypothesis is confirmed when we examine the compression experiments for the *cis* isomer (Figure 3), since the differences between the dark and bright hysteresis are now much smaller. Not only are very similar the maximum attained pressures before collapse and the corresponding average molecular areas, but also no consistent reduction of the area under successive compressions is observed under dark conditions.

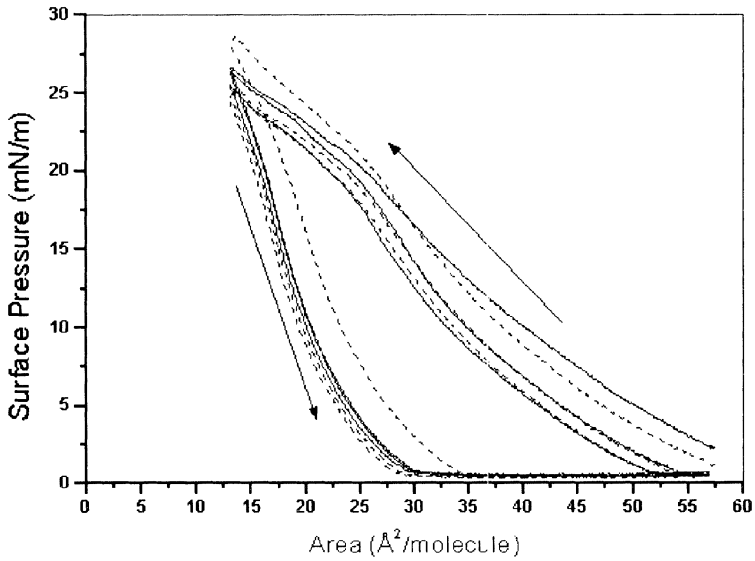

FIGURE 3: Compression hysteresis for the 13-*cis* retinoic acid under dark (dashed curves) and bright (solid curves) illumination.

For both isomers, the monolayers prepared under conditions of white illumination present more stable and reproducible compression isotherms. A possible explanation for such stability could be related to the fact that the UV-Vis absorption spectra of chloroform solutions of

the two isomers are very similar[11] with a broad peak at 370 nm but with a small (~5 nm) red shift for the 13 *cis* molecule. Therefore, under bright conditions there must be a certain degree of dynamic mutual photoconversions between the 13-*cis* and *trans* isomers. As a consequence, successive compressions of these monolayers will not result in progressive reduction of the mean molecular area because of the "free molecular volume"[1] required for such photoconversions.

In spite of this, one should not expect the compression hysteresis for the *all-trans* molecule to be identical to that of the 13-*cis* retinoic acid under bright conditions. It is well known that the photoisomerization of the *all-trans* molecule leads to different types of *cis* isomers[12]. Although 13-*cis* retinal can be the dominant product of this reaction, the mean molecular area in the floating monolayer would be an average of those of the individual *cis* isomers. This large difference in the mean molecular area could represent an important hindrance to the *cis* to *trans* isomerization since a larger overall rearrangement of the monolayer would be involved. Therefore, for any given surface tension the mean molecular area for the *all trans* retinal film under bright conditions is smaller than that of a 13 *cis* isomer monolayer under the same conditions.

Further experiments are under investigation in our laboratory to examine the molecular photoisomerization of retinal derivatives both as organized Langmuir films and as Langmuir-Blodgett (LB) samples prepared by transferring the floating monolayers to solid substrates.

CONCLUSION

We have examined the effect of the illumination conditions upon the molecular arrangement of floating monolayers of 13-*cis* and *all-trans* isomers of the retinoic acid. These results are part of a more complete investigation of the microscopic arrangement and average orientation of the molecular groups in thin films of retinal derivatives. The nonlinear susceptibility of solid films of these compounds prepared by techniques (such as LB) that assure a better organization at the molecular level are expected to be significantly higher than those of the corresponding solutions, since in the latter a random orientation of the individual molecules must reduce the overall optical response of the sample.

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