

Fourier Transform Infrared Spectroscopy Evidence of a Two-Dimensional Hydrogen-Bonded Structure in Langmuir–Blodgett Films of a Novel Azobenzene Compound

J. Zhao, Z. Y. Wu, J. Zhang, T. Zhu, A. Ulman,[†] and Z. F. Liu*

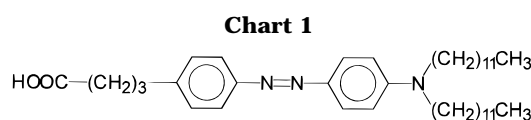
Centre for Intelligent Materials Research (CIMR), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received September 9, 1996. In Final Form: February 10, 1997[⊗]

Langmuir–Blodgett (LB) multilayers of a novel azobenzene derivative were fabricated and studied by polarized transmission Fourier transform infrared spectroscopy. The dichroism in two perpendicular polarizations revealed that there exist two types of hydrogen-bonded carboxyl groups, which are orientated in planes perpendicular to each other, forming a two-dimensional intermolecular hydrogen-bonded structure in the LB film.

Highly organized Langmuir–Blodgett (LB) films have been attracting much attention during last decades because of their prospective applications in fabricating molecular electronic devices.^{1–6} Many efforts have been made up to now on expanding the LB film family by attaching different functional groups and on correlating the film structure with its functionalities.^{7–12} One has recognized by these studies that it is very important to introduce specific interactions for stabilizing the highly ordered film structures.^{13–17} Generally speaking, intermolecular interactions within LB films mainly include hydrophobic interactions between alkyl chains, aromatic interactions between π -conjugation systems, and hydrogen bonding between specific groups. Hydrogen bonding is the strongest one among them, which has a direction-specific property.

In this paper, we report our studies on LB monolayers of a novel azobenzene compound with two alkyl chains attached to the aromatic ring through one amide group (Chart 1). We expect that the strong aromatic, hydrogen-bonding, and hydrophobic interactions between alkyl chains may greatly improve the ordered film structure



and its stability. To evaluate the structure of LB monolayers, we employed a polarized Fourier transform infrared (FTIR) spectroscopic technique, which is known to be powerful in determining the orientations of functional groups and the local environments surrounding them.^{17–19} Our experimental results showed that a unique two-dimensional hydrogen-bonded structure has been formed in the LB films.

The azobenzene monolayers were deposited onto CaF₂ substrates using a commercialized Langmuir–Blodgett trough (FACE Co. Ltd., Japan). Milli-Q water with a resistance of >17 M Ω cm was used as the subphase solution. The azobenzene compound was dissolved in chloroform and spread onto the air/water interface with a microsyringe. The CaF₂ plate was cleaned by heating at 70 °C in a mixture of K₂Cr₂O₇ and concentrated H₂SO₄ for 1–2 min. All the LB films were prepared at a constant surface pressure of 20 mN/m, and the subphase temperature was kept at 20 °C. At the experimental conditions, the molecules formed Z-type multilayer films, and the transferring ratio was nearly unity. Figure 1 shows the surface pressure–molecular area isotherm of the monolayer on water at 20 °C, in which three main characteristics can be seen obviously: (1) this π -A curve does not bear the three-stage feature like most other monolayers; (2) the slope of the curve is rather large (\sim 367 mN/(m²·mm⁻²)); (3) the collapse pressure of the monolayer is very high (\sim 46 mN/m). All these features indicate the existence of strong interaction between the azobenzene molecules inside the monolayer on the air/water interface. One may expect a highly ordered structure in the LB films transferred to the solid substrate.

The FTIR spectra were measured with a Perkin-Elmer System 2000 FTIR spectrometer, equipped with a deuterate triglycine sulfate (DTGS) detector. The resolution of the system was set to be 4 cm⁻¹, and usually, 500 interferograms were collected to achieve a good signal to noise ratio. The infrared probe radiation was normally incident on the films.

* To whom correspondence should be addressed: telephone and fax, +86-10-62757157; e-mail, cimr@chemms.chem.pku.edu.cn.

[†] Department of Chemistry and Polymer Research Institute, Polytechnic University, Brooklyn, NY 11210.

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

(1) Ulman, A. *An Introduction to Ultrathin Organic Films: from Langmuir-Blodgett to Self-assembly*; Academic Press: Boston, MA, 1991.

(2) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658.

(3) Schildkraut, J. S.; Penner, T. L.; Willand, C. S.; Ulman, A. *Opt. Lett.* **1988**, *13*, 134.

(4) Yamada, S.; Nakano, T.; Matsuo, T. *Thin Solid Film* **1994**, *245*, 196.

(5) Saito, A.; Wajima, T.; Yamamoto, M.; Itoh, K. *Langmuir* **1995**, *11*, 1277.

(6) Büchel, M.; Sekkat, Z.; Paul, S.; Weichart, B.; Menzel, H.; Knoll, W. *Langmuir* **1995**, *11*, 4460.

(7) Wang, R.; Yang, J.; Wang, H.; Tang, D.; Jiang, L.; Li, T. *Thin Solid Films* **1995**, *256*, 205.

(8) Sato, T.; Ozaki, Y.; Iriyama, K. *Langmuir* **1994**, *10*, 2363.

(9) Yokoyama, S.; Kakimoto, M.; Imai, Y. *Langmuir* **1994**, *10*, 4594.

(10) Yokoyama, S.; Yamada, T.; Kajikawa, K.; Kakimoto, M.; Imai, Y.; Takezoe, H.; Fukuda, A. *Langmuir* **1994**, *10*, 4599.

(11) Kawai, T.; Umemura, J.; Takenaka, T. *Langmuir* **1990**, *6*, 672.

(12) Azumi, R.; Matsumoto, M.; Kuroda, S.; Crossley, M. T. *Langmuir* **1995**, *11*, 4495.

(13) Smith, E. L.; Alves, C. A.; Anderegg, J. W.; Porter, M. D.; Siperko, L. M. *Langmuir* **1992**, *8*, 2707.

(14) Sun, L.; Crooks, R. M.; Antonio, J. R. *Langmuir* **1993**, *9*, 1775.

(15) Sun, L.; Kepley, L. J.; Crooks, R. M. *Langmuir* **1992**, *8*, 2101.

(16) Creager, S. E.; Steiger, C. M. *Langmuir* **1995**, *11*, 1852.

(17) Miyashita, T.; Suwa, T. *Langmuir* **1994**, *10*, 3387.

(18) Nakahara, H.; Fukuda, K. *J. Colloid Interface Sci.* **1979**, *69*, 24.

(19) Umemura, J.; Hishiro, Y.; Kawai, T.; Takenaka, T.; Gotoh, Y.; Fujihira, M. *Thin Solid Films* **1989**, *178*, 281.

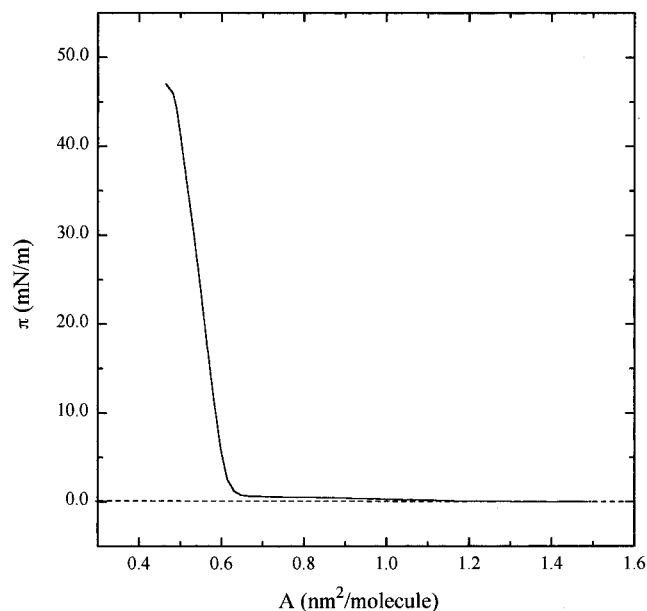


Figure 1. π - A isotherm of the monolayer on water at 20 °C.

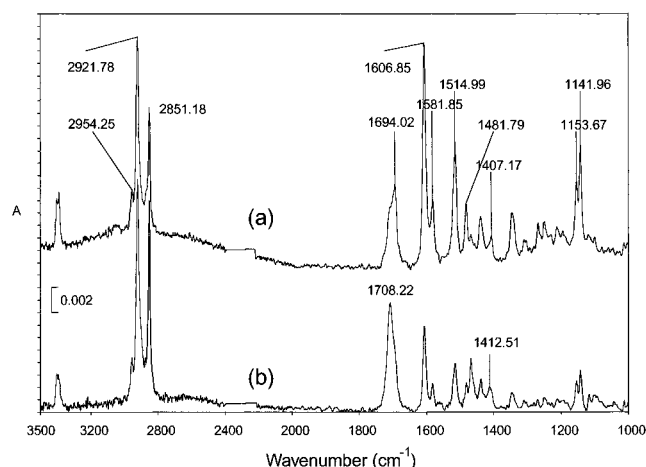


Figure 2. Polarized FTIR transmission spectra of a nine-monolayer azo LB film: (a) polarization parallel to the dipping direction; (b) polarization perpendicular to the dipping direction.

Figure 2 is the polarized transmission spectra of the nine-monolayer LB film on CaF_2 substrate, which were taken with an incident radiation polarized parallel to (a) and perpendicular to (b) the dipping direction, respectively. Attention was paid on the two absorption bands of the carboxyl group, located in the frequency ranges of 1690–1710 and 1405–1415 cm^{-1} , which correspond to the stretching vibration mode of its carbonyl group ($\nu(\text{C}=\text{O})$) and the in-plane bending vibrating mode of its hydroxyl group ($\delta(\text{OH}, \text{ip})$), respectively.^{20,21} The peak position of $\nu(\text{C}=\text{O})$ for parallel polarization was 1694 cm^{-1} , while for perpendicular polarization, it was 1708 cm^{-1} . This dichroism implies that the carbonyl groups were located in different microenvironments, or say, two different types of carbonyl groups were existing in the LB film. Generally, the frequency of $\nu(\text{C}=\text{O})$ in free carboxyl group falls into a range of 1735–1760 cm^{-1} . When the carboxyl group is in a hydrogen-bonded environment, the $\nu(\text{C}=\text{O})$ vibration shifts to lower frequency, and the stronger the hydrogen bond is, the lower frequency the $\nu(\text{C}=\text{O})$ peak has.^{16,21}

(20) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975.

(21) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic: Boston, MA, 1991.

Obviously, the $\text{C}=\text{O}$ groups in the LB monolayers were all in the hydrogen-bonded states, but the bonding strength with the adjacent OH groups was not the same: the $\text{C}=\text{O}$ group with its projection on the substrate surface being along the dipping direction was in a stronger hydrogen-bonded state than that along the direction perpendicular to dipping. A similar conclusion can also be drawn by analyzing the in-plane bending vibration of the hydroxyl group ($\delta(\text{OH}, \text{ip})$) involved in the carboxyl group. This vibration mode is also greatly influenced by the intermolecular interactions. In contradiction to the $\text{C}=\text{O}$ group, the $\delta(\text{OH}, \text{ip})$ vibration shifts to higher frequency when the OH group is hydrogen-bonded. The stronger the hydrogen bond is, the higher frequency the $\delta(\text{OH}, \text{ip})$ mode has.²² It is seen from Figure 2 that the frequency of the $\delta(\text{OH}, \text{ip})$ was 1407 cm^{-1} for parallel polarization, and 1412 cm^{-1} for perpendicular polarization, showing similar dichroism behavior. The former corresponds to the OH groups weakly hydrogen bonded to the adjacent $\text{C}=\text{O}$ groups and the latter to the OH groups strongly hydrogen bonded to the neighbor $\text{C}=\text{O}$ groups. Combining the $\text{C}=\text{O}$ and OH spectral data, we can imagine that in such monolayers, the $\text{C}=\text{O}$ and OH of the carboxyl group are all in the hydrogen bonded states: the $\text{C}=\text{O}$ group parallel to the dipping direction forms a strong hydrogen bond with the OH group perpendicular to the dipping direction; whereas the OH group parallel to the dipping direction forms a weak hydrogen bond with the $\text{C}=\text{O}$ group perpendicular to the dipping direction.^{25,26}

To obtain more experimental evidence, the polarization angle dependence of the FTIR spectra was studied using the same LB film, where the polarization of the incident radiation was changed from -30° to 110° at a step of 10° , referring to the dipping direction. Figure 3a shows the spectra obtained in the range of 1650–1750 cm^{-1} , and the absorption intensities of $\nu(\text{C}=\text{O})$ at 1694 and 1708 cm^{-1} versus the polarization angle are sketched in Figure 3b. It can be seen that the intensity at 1694 cm^{-1} has its maximum around 0° and reaches its minimum around 90° , while the intensity at 1708 cm^{-1} has its minimum around 0° and gets to its maximum around 90° . With these spectral data, numerical simulation was performed, based on a model of two transition dipole moments of the $\nu(\text{C}=\text{O})$ mode in two directions (see the solid and dashed curves in Figure 3b). The orientation angles of the $\nu(\text{C}=\text{O})$ transition dipoles at 1694 and 1708 cm^{-1} were found to be -2° and 87° , respectively, referring to the dipping direction.²³ This indicates that two differently hydrogen bonded $\text{C}=\text{O}$ groups are orientated nearly perpendicular to each other.

The above dichroism phenomenon of the $\text{C}=\text{O}$ and OH

(22) Hadzi, D.; Bratos, S. In *The Hydrogen Bond: Recent developments in theory and experiment II. Structure and spectroscopy*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Press: Amsterdam, 1976; Chapter 12.

(23) The absorption intensity is proportional to the square of the transition dipole moment's projection to the electric field vector ($\Delta I \propto |\mu \cdot \mathbf{E}|^2$, where μ is the transition dipole moment and \mathbf{E} is the electric field of the radiation). Although these numerical results of the orientation angle are not strictly precise due to the experimental errors, they do provide information of orientation of two different types of carbonyl groups.

(24) Gerdy, J. J.; Goodard, W. A., III *J. Am. Chem. Soc.* **1996**, *118*, 3233.

(25) The in-phase and out-of-phase of the carbonyl and hydroxyl groups in the hydrogen-bonded chain may also result in the doublet feature. However, for the $\text{C}=\text{O}$ groups orientating in the same direction, their dipoles reinforce if they vibrate in-phase, and therefore bring about an increase in intensity and a decrease in frequency. And the out-of-phase vibration case will result in a decrease in intensity and an increase in frequency. The spectroscopic data in this study lie in contradiction to this prediction and therefore exclude the factor group splitting mechanism.

(26) Taylor, P. J. *Spectrochim. Acta* **1976**, *32A*, 1471.

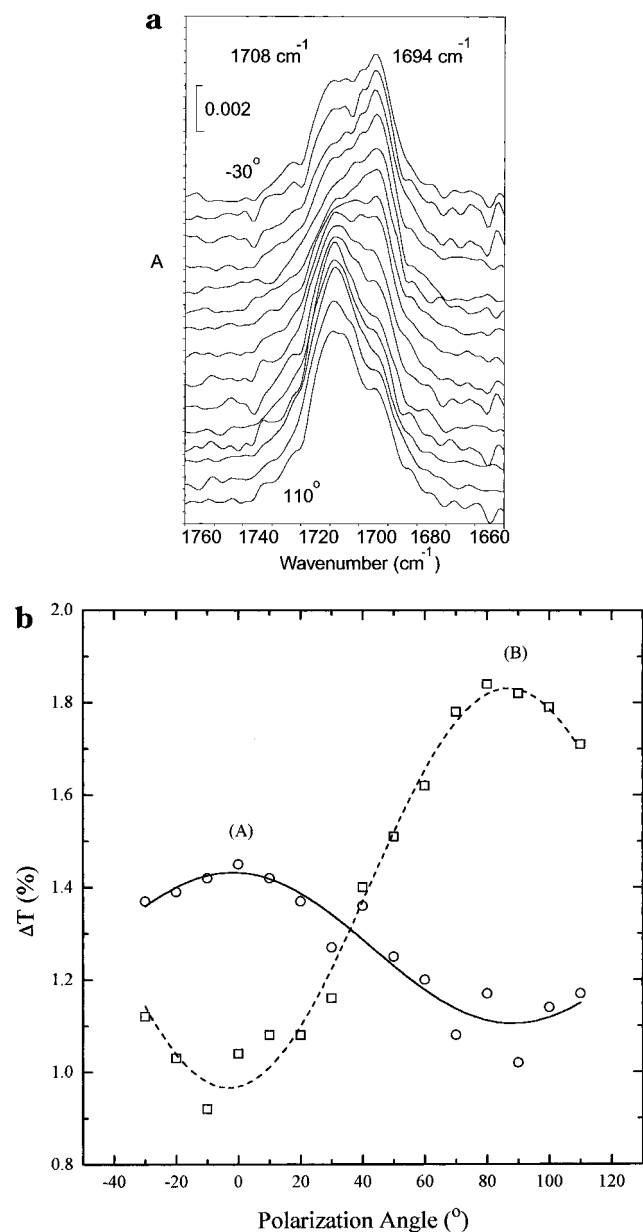


Figure 3. (a) FTIR spectra of a nine-layer LB film collected as the polarization angle varied from -30° to 110° at a step of 10° . (b) The relationship between the absorption intensities of the $\nu(\text{C}=\text{O})$ mode at 1694 cm^{-1} (A) and 1708 cm^{-1} (B) and the polarization angles of the incident radiation. The solid and dashed curves represent the theoretical simulation results.

vibrations of the carboxyl group was also observed in LB films having different monolayers. As an example, Figure 4 gives the FTIR results of three, six, and nine monolayers in the frequency range of $\nu(\text{C}=\text{O})$ mode.

From the spectra shown in Figure 2, additional information can be obtained. The first feature is the dichroism of the in-plane vibration mode of the aromatic ring, located at 1606 , 1581 , 1515 , and 1481 cm^{-1} . The absorbances of these modes have larger values in the parallel polarization case than in the perpendicular case. A polarization dependence of the ring breathing mode at 1606 cm^{-1} is shown in Figure 5, which indicates the parallel orientation of the aromatic ring to the dipping direction. Secondly, regarding the symmetric and asymmetric stretching mode of the CH_2 group, located at 2921 and 2851 cm^{-1} , both $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ modes have larger absorbance in the perpendicular polarization. As we know, the directions of the transition dipole moments of $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ are perpendicular to each other, and therefore, to achieve

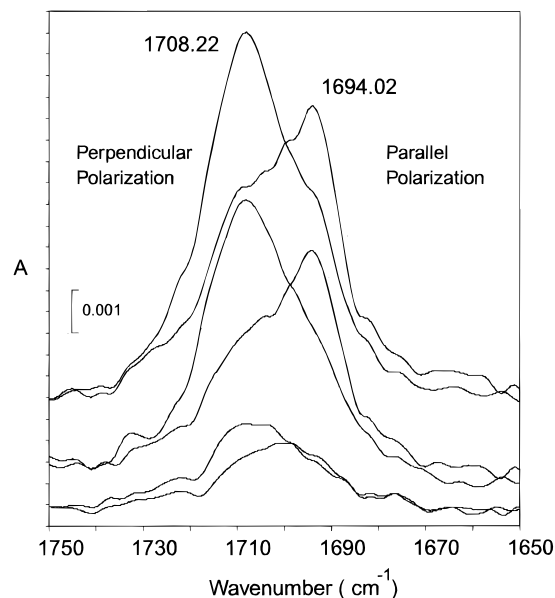


Figure 4. FTIR dichroism of $\nu(\text{C}=\text{O})$ on three-, six-, and nine-layer LB films in two perpendicular polarization. The peak frequencies of this mode were 1694 cm^{-1} in the parallel polarization and 1708 cm^{-1} in the perpendicular polarization.

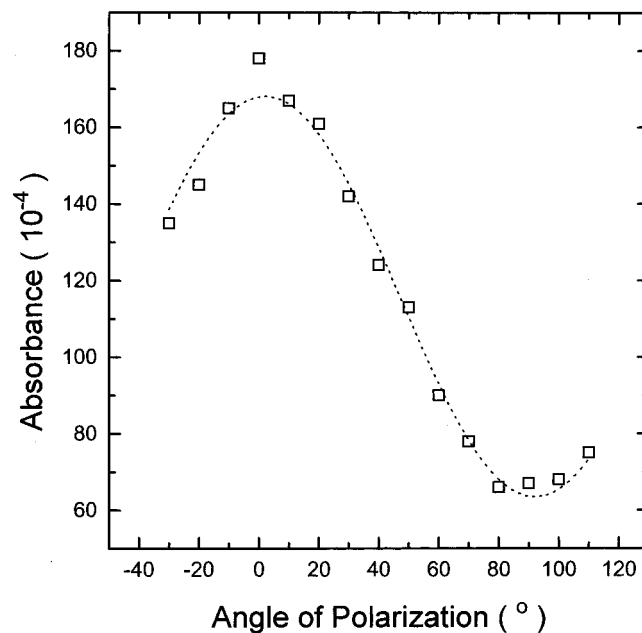


Figure 5. Dichroism of the breathing stretching mode of the aromatic ring at 1606 cm^{-1} , indicating the orientation of the aromatic rings is parallel to the dipping direction.

the above spectroscopic feature of CH_2 group, two kinds of alkyl chains with different orientation would be required. It could be suggested that one kind of the alkyl chain have its $\text{C}-\text{C}-\text{C}$ plane orientating along the dipping direction and the chain tilt in this plane. The other kind would have its $\text{C}-\text{C}-\text{C}$ plane perpendicular to that of the alkyl chain described above and its $\text{C}-\text{C}-\text{C}$ plane also have a tilting angle with respect to the substrate surface. We suggest that the two alkyl chains of one molecule have their $\text{C}-\text{C}-\text{C}$ planes perpendicular to each other. Similar suggestion can be found in ref 24.

Apart from the FTIR data, UV-vis spectra of the molecules in LB monolayer and in solution were also measured, in which a $\sim 40\text{ nm}$ blue shift of the absorption peak around 380 nm was observed for the LB monolayer compared with that for solution, which indicated the

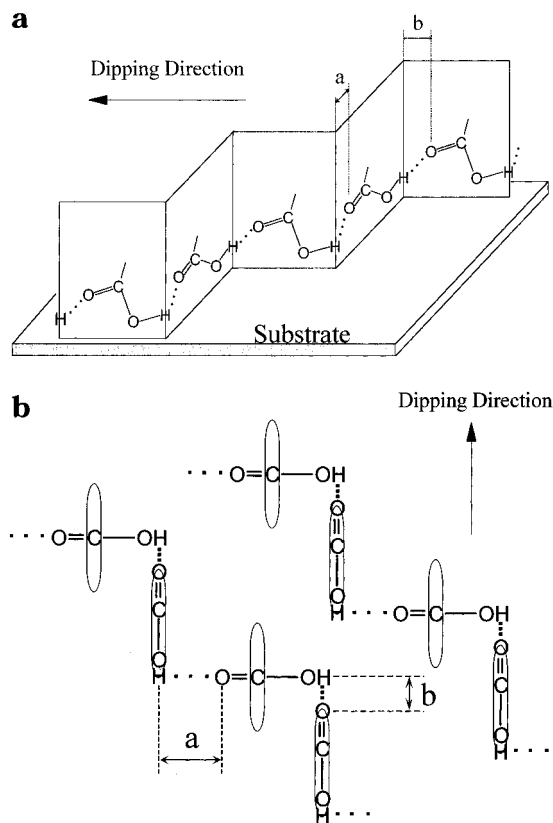


Figure 6. (A) Steric conformation of neighboring carboxyl groups which create four hydrogen bonds. The different packing densities are displayed by two distance values between the O and H atoms, a and b , where $a > b$. (B) Projection of the two-dimensional hydrogen-bonded structure on the substrate surface, where the narrow shuttle patterns represent the azobenzene group.

existence of H-aggregated state of the molecules in monolayers.

The above observation demonstrates in-plane dichroism in IR absorption and, more importantly, the in-plane

anisotropy in molecular orientation. It is noted that in-plane dichroism in other LB systems has previously been reported, for example, in IR absorption¹⁷ and UV-vis spectroscopy,^{27,28} and the in-plane anisotropic molecular orientation has been studied indirectly by other methods (e.g., X-ray technique).²⁹

Figure 6 illustrates the possible structural model of the LB film, where (a) represents the steric conformation of three carboxyl groups which create two hydrogen bonds and (b) is the projection of the two-dimensional hydrogen-bonded carboxyl group on the substrate surface. For simplicity, the molecular backbone was omitted from the structural model. In this model, each carboxyl group links two other carboxyl groups of different molecules via hydrogen bonds and the adjacent hydrogen-bonded carboxyl groups are perpendicular to each other in projection, leading to a zig zag structure. As can be seen from this model, the parallel orientating aromatic rings form H-aggregates in the LB monolayer. The larger absorption intensity of $\nu(\text{C}=\text{O})$ in perpendicular polarization suggests a closer molecular packing distance in the direction parallel to dipping, which results in the stronger hydrogen bonding between the C=O group along the dipping and the OH group perpendicular to dipping. On the other hand, the weaker H-bonds between the perpendicular C=O and the parallel OH is originated from the less close packing in the perpendicular direction. Such a structural model gives a satisfactory explanation of our FTIR results. A more detailed study on this two-dimensional hydrogen-bonded structure is in process.

Acknowledgment. This work was supported by the State Science & Technology Committee, the State Education Committee, and the National Natural Science Foundation of China (NSFC).

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(27) Fu, Y.; Lever, A. B. P. *J. Phys. Chem.* **1991**, *95*, 6979.

(28) Ionov, R.; Angelova, J. *J. Phys. Chem.* **1995**, *99*, 17606.

(29) Weissbuch, I.; Majewski, J.; Kjaer, K.; Als-Neilsen, J.; Lahav, M.; Leiserowitz, J. *J. Phys. Chem.* **1993**, *97*, 12848.