J. Am. Chem. Soc. 1987, 109, 1297-1301

durene, on the basis of the $\sim$2-kcal/mol endothermicity one estimates that at equilibrium the concentration of triplet durene would only be 3% of that of triplet acetone (at equal concentrations of ground-state acetone and durene). Even if subsequent energy transfer from triplet durene to DBA took place with unit efficiency, the typical second peak of the decay curves (see Figures 4 and 6) would not be observed.[34] A similar argument is even stronger in the case of triplet cyclohexanone and *o*-xylene[6] where the equilibrium concentration of triplet *o*-xylene would be only 0.1% of that of triplet ketone. Thus, energetic as well as spectral considerations rule out the aromatic triplet as the excited donor species detected in these experiments.

While the analysis presented above clearly rules out the excited aromatic as the species detected in the experiments, one can still ask whether the small concentration present could affect the observable decay of the exciplex through a leakage mechanism, fed through the excited-state equilibria. Quite clearly, the equilibrium concentration of triplet durene *must* be present in the system, in equilibrium with triplet acetone, and therefore with the exciplex as well. When in addition to the $\sim$2 kcal/mol energy difference with acetone (vide supra) we take into account k_{AE} and k_{EA}, the concentration of triplet durene would be four orders of magnitude lower than that of the exciplex, far too low to play any role in determining the exciplex decay kinetics. Finally, we envision the mechanism proposed as applicable not only to alkanones but also to the quenching of triplet benzophenone by benzene, which has been proposed to proceed via an exciplex intermediate[36] and where energy transfer can clearly be ruled out on energetic grounds.[37]

Exciplex formation may nevertheless be coupled with endothermic energy transfer. For the sake of discussion, a possible rationalization of the results goes as follows. Triplet acetone and durene first form an encounter complex. Although the solvent cage is usually considered to allow sufficient time for the collision partners to explore all possible mutual orientations, here the preconditions for exciplex formation must be very restrictive, since most encounter complexes simply come apart ($k_{EA} \simeq 5 \times 10^7$ M^{-1} s^{-1}). Conceivably, the solvent cage may actually reduce the probability of reaching the desired orientation. In any case, sometimes proper orbital overlap and nuclear distance are achieved, through repeated collisions within the complex, and a stabilized exciplex is formed. The possibility of a stabilized complex along the path of an electron-exchange energy-transfer process has been discussed by Turro.[31] Studies of other ketone–aromatic pairs, in solvents of different viscosities, may lead to an understanding of the factors apparently at play here.

Registry No. DBA, 523-27-3; acetone, 67-64-1; durene, 95-93-2.

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(36) Wolf, M. W.; Brown, R. E.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 526–531.

(37) E_T(benzophenone) = 69 kcal, hence ΔE_T = 15 kcal.

Davydov Splitting in 7-(2-Anthryl)-1-heptanoic Acid Langmuir–Blodgett Films

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Abstract: 7-(2-Anthryl)-1-heptanoic acid (I) forms a monolayer at pH 4.9 and 6.0 ([Cd^{2+}] = 5.5 $\times$ 10^{-4} M) with a zero-pressure area of 26 Å^2/molecule. Monolayers of I transfer at 21 mN/m to hydrophobic surfaces to form Y-type Langmuir–Blodgett multilayers. Low-angle X-ray diffraction of multilayers of I reveals a periodic distance normal to the film plane of 36.0 (pH 4.9) and 37.1 Å (pH 6.0). The absorption spectrum in the 420–250-nm range shows a polarization effect for the first and second singlet vibronic transitions of the anthracene moiety that is analogous to that seen for the *ab* face of single-crystal anthracene. For multilayers prepared at pH 6.0 the first singlet vibronic transition is split by $\sim$360 cm^{-1} (measured at the 0–0 transition) into two orthogonally polarized components with a polarization ratio of $\sim$2.5. This polarization effect is attributed to multilayer polycrystallinity and a transfer-induced preferred orientation for the unit cell.

The last 10 years have seen a tremendous increase in the number of basic[1a] and applied[1b] studies of Langmuir–Blodgett (L–B) films. In order to understand such diverse phenomena as, for example, conductivity[2] or the electronic spectroscopy of dye molecule aggregates[3] in L–B multilayers, structural information, especially in-plane structure, is essential. Polarized IR spectroscopy and electron diffraction, in particular, have been used extensively to determine in-plane structure. Recent studies by Swalen and co-workers[4] and Allara and Swalen,[5] for instance, made use of grazing incidence and transmission Fourier transform IR to determine the orientation and crystalline packing arrangement of cadmium arachidate monolayers. Several of the earliest applications of electron diffraction[6,7] showed that some fatty acid L–B films deposited anisotropically on metal surfaces. More recent electron diffraction studies,[8-11] in some cases complemented by polarized IR spectroscopy,[8,12] have determined unit cell parameters and orientation for a number of fatty acids on various metal

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(1) For a review see: (a) Kuhn, H. *Thin Solid Films*, **1983**, *99*, 1. (b) Roberts, G. G. *Adv. Phys.* **1984**, *34*, 475.

(2) Roberts, G. G.; McGinnity, T. M.; Barlow, W. A.; Vincett, P. S. *Thin Solid Films* **1980**, *68*, 223.

(3) Bird, G. R.; Debuch, G.; Möbius, D. *J. Phys. Chem.* **1977**, *81*, 2657.

(4) Rabolt, J. F.; Burns, F. C.; Schlotter, N. E.; Swalen, J. D. *J. Chem. Phys.* **1983**, *78*, 946.

(5) Allara, D. L.; Swalen, J. D. *J. Phys. Chem.* **1982**, *86*, 2700.

(6) Germer, L. H.; Storks, K. H. *J. Chem. Phys.* **1938**, *6*, 280.

(7) Germer, L. H.; Storks, K. H. *Proc. Natl. Acad. Sci. U.S.A.* **1937**, *23*, 390.

(8) Bonnerot, A.; Chollet, P.-A.; Firsby, H.; Hocket, M. *Chem. Phys.* **1985**, *97*, 365.

(9) Stephens, J. F.; Tuck-Lee, C. *J. Appl. Crystallogr.* **1969**, *2*, 1.

(10) Peterson, I. R.; Russell, G. J. *Philos. Mag. A.* **1984**, *49*, 463.

(11) Peterson, I. R.; Russell, G. J.; Roberts, G. G. *Thin Solid Films* **1983**, *109*, 371.

(12) Chollet, P.-A.; Messier, J. *Chem. Phys.* **1982**, *73*, 235.

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surfaces. Long-range order over macroscopic distances was also recently detected by Vogel and Wöll[13] in a LEED study of L–B fatty acid monolayers on Cu, Ag, and Au(111) metal surfaces.

In this investigation we use polarized UV-visible spectroscopy to demonstrate the anisotropic deposition of L–B films of 7-(2-anthryl)-1-heptanoic acid (I). This compound, which originally found application in the construction of molecular devices for the light-induced injection of charge carriers into molecular crystals,[14,15] displays a polarization effect in the region of the lowest energy singlet vibronic transition of the anthracene moiety that is analogous to that observed for the *ab* face of single-crystal anthracene.[16] We attribute this to Davydov splitting and to the presence of crystallites in the L–B multilayer in which the unit cell displays a preferred orientation relative to the direction of transfer onto the hydrophobic substrate.

Experimental Section

7-(2-Anthryl)-1-heptanoic acid (I) was prepared by the method of Kaplun et al.:[17] mp 163–164 °C (lit. mp 162–164 °C). 3-(9-(10-Dodecyl)anthryl)-1-propionic acid (II) was prepared by the method of Stewart:[18] mp 113–114 °C (lit. mp 112–113 °C).

All solvents and reagents used for the preparation of L–B films were of analytical purity. The water used was refluxed for several hours over $KMnO_4$/NaOH and then triply distilled in a quartz apparatus. The preparation of the hydrophobic quartz and glass slides has been previously described.[14]

Monolayers were formed with use of a Lauda Film Waage Langmuir–Blodgett trough and were transfered at a constant film pressure of 21 mN/m and a transfer speed of either 8 or 22 mm/min. The subphase pH was adjusted by the addition of HCl.

Spectroscopic measurements were performed at room temperature on a Perkin-Elmer 555 UV–visible spectrophotometer with use of a slit width corresponding to a 1.0 nm wavelength resolution. The reference and sample beams were polarized with use of a matched pair of Glan polarizers (Halle). Samples were mounted in a holder that could be rotated up to 45° away from the perpendicular for experiments with p-polarized light.

Low-angle X-ray diffraction was performed on a powder diffractometer. Cu Kα (Ni-filtered) radiation (λ = 1.542 Å) was produced with use of an accelerating voltage of 40 kV at 30 mA. Data were collected with a proportional counter by the $\theta/2\theta$ method. The electron density along the surface normal was calculated with use of data corrected for Lorentz and polarization effects and phases determined by a Fourier deconvolution computer program written by Pape[19] and modified by us. It was first pointed out by Hosemann and Bagchi[20] that the Fourier transform of the corrected intensity data from a system composed of a small number of unit cells is not an ideal infinite periodic function (a Patterson function), as in the case of single crystals where the number of unit cells is effectively infinite, but is rather a so-called Q-function that vanishes for $X < -D$ and $X > D$ (where X = coordinate normal to the film plane and D = overall thickness of the bilayer stack). If the number of unit cells (bilayers) is known one can determine the Q-function for one bilayer (Q_0-function) using the methods of Kreutz[21] and Lesslauer and Blasie.[22] The Q_0-function is the convolution square of the electron density across one bilayer perpendicular to the film plane and was used as the input for the deconvolution program.

Results

1. Pressure–Area (Π–*A*) Behavior. Monolayers of I were formed by using subphase pH values of 4.9 and 6.0 with [Cd^{2+}] = 5.5 × 10^{-4} M. The Π–*A* curves in Figure 1 show a slight pH variation with films formed at the higher pH collapsing at somewhat lower pressures. All curves extrapolate to a zero-pressure area of 26 ± 0.5 Å^2/molecule, however. The Π–*A* characteristics of II have been previously described.[23]

Y-type deposition[24] was observed at pH 4.9 and 6.0 for I and at pH 6.0 for II at a constant film pressure of 21 mN/m. The transfer ratio (substrate area/area removed from the surface of

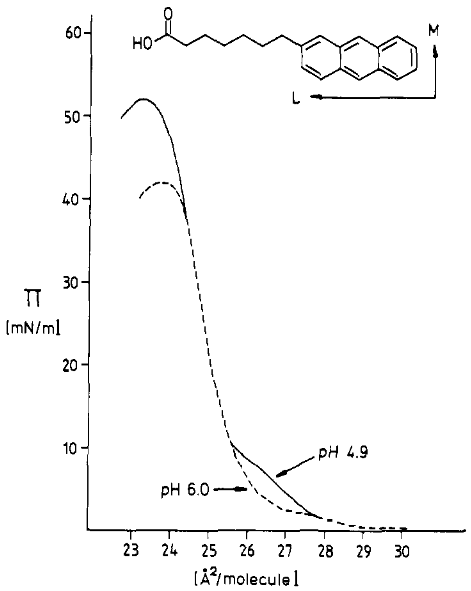

Figure 1. Pressure–area (Π–*A*) curve for I at pH 4.9 and 6.0 ([Cd^{2+}] = 5.5 × 10^{-4} M).

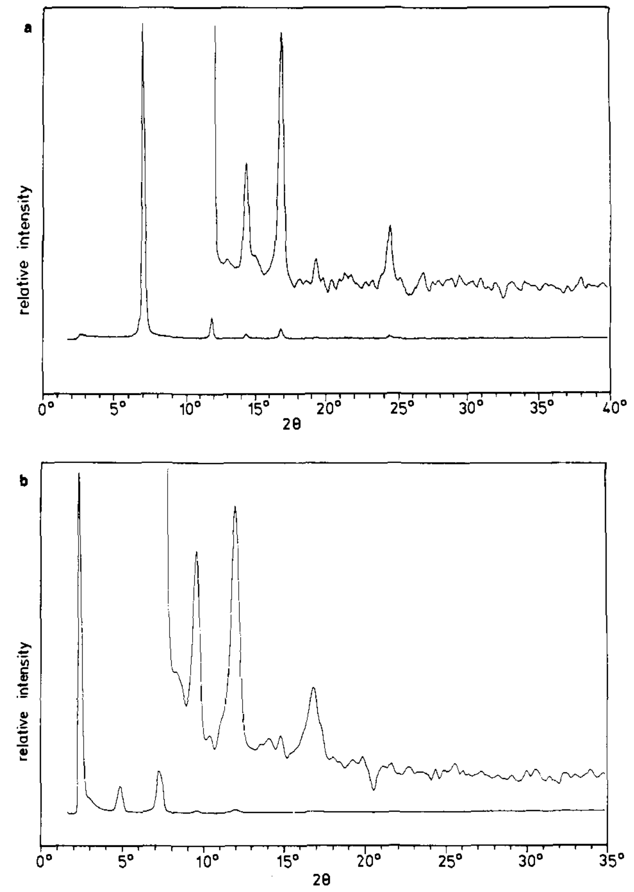

Figure 2. Low-angle X-ray diffraction patterns for 20 monolayers of I deposited on hydrophobic glass at (a) pH 4.9 and (b) pH 6.0 ([Cd^{2+}] = 5.5 × 10^{-4} M, Π = 21 mN/m and transfer speed = 7.7 mm/min).

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[13] Vogel, V.; Wöll, C. *J. Chem. Phys.* **1986**, *84*, 5200.

[14] Van der Auweraer, M.; Willig, F. *Isr. J. Chem.* **1985**, *25*, 274.

[15] Van der Auweraer, M.; Willig, F.; Charlé, K.-P. *Chem. Phys. Lett.* **1986**, *128*, 214.

[16] For a review see: Philpott, M. R. *Advances in Chemical Physics*; Prigogine, I., Rice, S., Eds.; Wiley: New York, 1973; p 227.

[17] Kaplun, P. A.; Basharuli, V. A.; Shchukina, L. G.; Shvets, V. I. *Bioorg. Khim.* **1979**, *5*, 1826.

[18] Stewart, F. H. C. *Aust. J. Chem.* **1960**, *13*, 478.

[19] Pape, E. H. *Biophys. J.* **1974**, *14*, 284.

[20] Hosemann, R.; Bagchi, S. N. *Direct Analysis of Diffraction by Matter*; North-Holland: Amsterdam, 1962.

[21] Kreutz, W. *Advances in Botanical Research*; Preston, R. D., Ed.; Academic: London, 1970; Vol. 3, p 53.

[22] Lesslauer, W.; Blasie, J. K. *Biophys. J.* **1972**, *12*, 175.

[23] Vincett, P. S.; Barlow, W. A. *Thin Solid Films* **1980**, *71*, 305.

[24] Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.

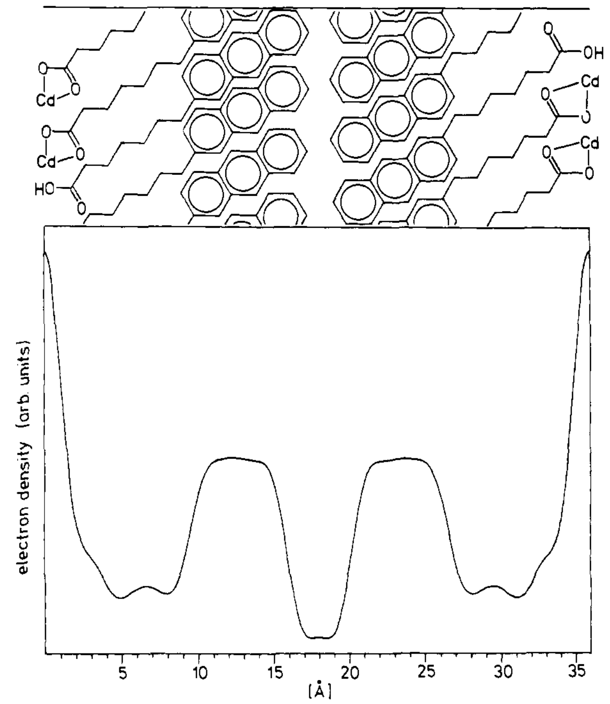

Figure 3. Electron density parallel to the surface normal for 20 monolayers of I (pH 4.9, $[Cd^{2+}] = 5.5 \times 10^{-4}$ M, $\Pi = 21$ mN/m and transfer speed = 7.7 mm/min).

the aqueous subphase) was always within a few percent of 1.0.

2. X-ray Diffraction. As Cd^{2+} is a much stronger X-ray scatterer than C, H, or O, low-angle X-ray diffraction can be used to measure the periodic distance normal to the plane of the multilayers between Cd^{2+}–carboxylate groups. Figure 2a shows the (001) diffraction peaks as a function of the angle 2θ for 20 monolayers of I deposited on hydrophobic glass at a pH of 4.9 and a film pressure of 21 mN/m. The most intense peak at $2\theta = 7.4°$ corresponds to the 003 reflection while the 001, 002, and 004 are totally absent. Diffraction as high as 10th order is seen at $2\theta = 24.7°$. A distance of 36.0 Å across the double layer was calculated with use of the Bragg equation ($2d \sin \theta = n\lambda$). Figure 3 shows the electron density across the bilayer at a resolution of 3.6 Å and clearly indicates Y-type films.

The diffraction pattern for films prepared at pH 6.0 is shown in Figure 2b. The (001) reflection is now the most intense and the highest order reflection is the (007) at $2\theta = 16.7°$. The periodic distance for pH 6.0 films is 37.1 Å. As with previous X-ray diffraction studies of L–B films the odd order diffraction peaks were generally stronger than the adjacent even order peaks.[25,26]

3. Absorption Spectra. a. I and II in $CHCl_3$. The absorption spectra of I, II, and unsubstituted anthracene in $CHCl_3$ are shown in Figure 4. For the first singlet vibronic transition of I the 0–0, 0–1, and 0–2 components are seen at 26 380 cm^{-1} ($\epsilon = 3850$ M^{-1} cm^{-1}), 27 850 cm^{-1} (4500), and 29 240 cm^{-1} (3200), respectively, while the 0–3 and 0–4 occur as shoulders. A second singlet transition is seen as an intense maximum at 38 900 cm^{-1} ($\epsilon = 200\,000$ M^{-1} cm^{-1}). The peak positions are very similar for I and unsubstituted anthracene although the increased widths of the peaks in the first singlet vibronic progression of I result in smaller peak-to-valley ratios. An approximately 1400 cm^{-1} red shift is observed for the spectrum of II where the first singlet 0–0, 0–1, 0–2, and 0–3 transitions are found at 24 940 cm^{-1} ($\epsilon = 9800$ M^{-1} cm^{-1}), 26 310 cm^{-1} (10 300), 27 780 cm^{-1} (6000), and 29 150 cm^{-1} (2700), respectively, and the second singlet is found at 37 880 cm^{-1} (107 000). Except for this red shift the spectrum of II is quite similar to that of unsubstituted anthracene.

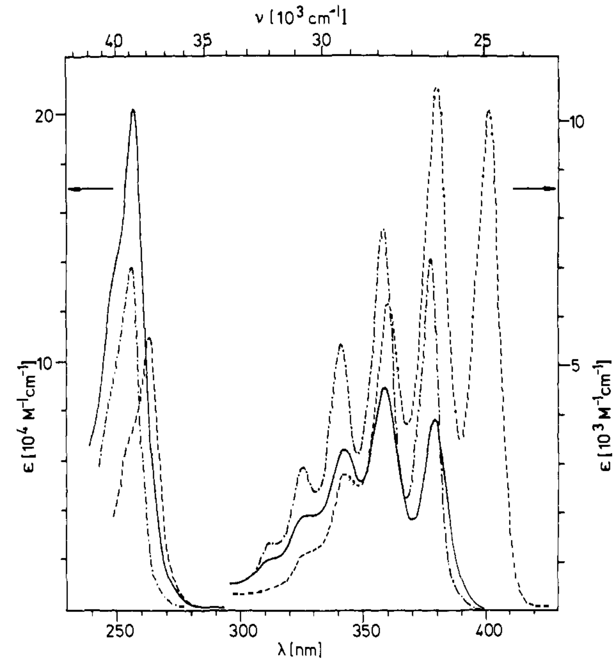

Figure 4. UV–visible absorption spectra in $CHCl_3$ of I (—), II (- - -), and anthracene (- · -).

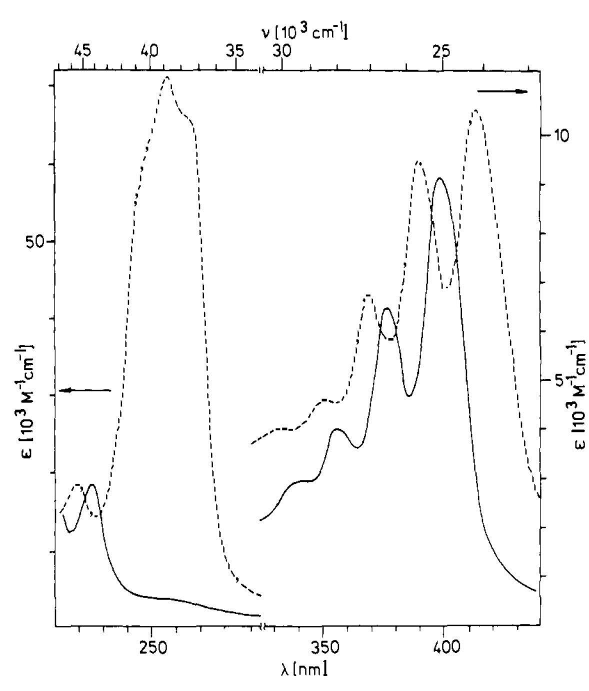

Figure 5. UV–visible absorption spectrum of 40 monolayers of I (—) and II (- - -) (pH 6.0, $[Cd^{2+}] = 5.5 \times 10^{-4}$ M, $\Pi = 21$ mN/m and transfer speed = 7.7 mm/min).

b. L–B Films of I and II. Spectra recorded with unpolarized light of multilayers of I and II deposited on hydrophobic quartz are shown in Figure 5. For multilayers of I transferred at pH 6.0 and a film pressure of 21 mN/m the first singlet vibronic transition has undergone an approximately 1300 cm^{-1} red shift and a slight increase in intensity relative to the $CHCl_3$ solution spectrum. The 0–0, 0–1, and 0–2 transitions are found at 25 060 cm^{-1} ($\epsilon = 9150$ M^{-1} cm^{-1}), 26 520 cm^{-1} (6440), and 28 050 cm^{-1} (3950), respectively, and are broader than in solution, the 0–0 transition showing a fwhm of ~1350 cm^{-1} vs. ~900 cm^{-1} in $CHCl_3$. A striking similarity of the multilayer absorption spectrum of I to the spectrum of the *ab* face of single-crystal anthracene can be seen in the almost complete disappearance of the second singlet transition that was seen in the solution spectrum with

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(25) Matsuda, A.; Sugi, M.; Fukui, M.; Iizima, S.; Miyahara, M.; Otsubo, Y. *J. Appl. Phys.* **1977**, *48*, 771.

(26) McIntosh, T. J.; Waldbillig, R. C.; Robertson, J. D. *Biochim. Biophys. Acta* **1976**, *448*, 15.

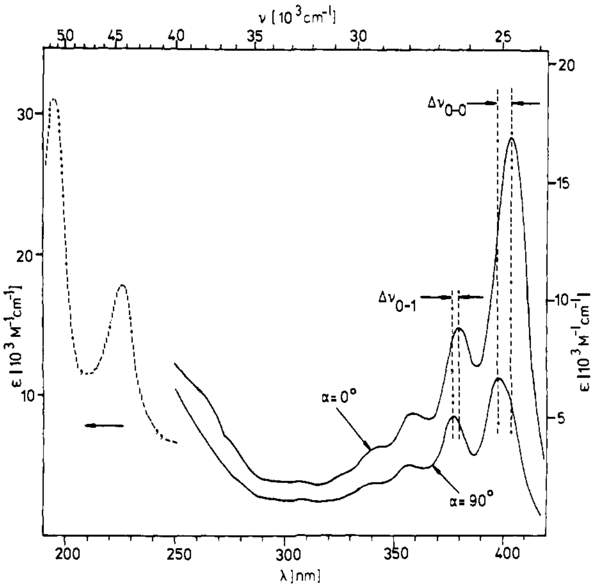

Figure 6. Polarized UV–visible absorption spectrum of 40 monolayers of I (same transfer conditions as in Figure 5). α is the angle between the electric vector and the transfer direction. Dashed portion of the spectrum was recorded with unpolarized light.

considerable intensity at 38 900 $\mathrm{cm^{-1}}$. Two weak shoulders are now found in this region at ~36 000 and ~38 500 $\mathrm{cm^{-1}}$ on the low-energy side of a peak of moderate intensity at 44 000 $\mathrm{cm^{-1}}$ (ϵ = 18 000 $\mathrm{M^{-1}\ cm^{-1}}$).

Multilayers of II deposited under identical conditions show a smaller red shift of ~150 $\mathrm{cm^{-1}}$ relative to the $CHCl_3$ solution spectrum and show little change in the intensity of the first singlet transition. The 0–0, 0–1, 0–2, and 0–3 transitions are found at 29 330 $\mathrm{cm^{-1}}$ (ϵ = 11 700 $\mathrm{M^{-1}\ cm^{-1}}$), 25 710 $\mathrm{cm^{-1}}$ (11 000), 27 170 $\mathrm{cm^{-1}}$ (7800), and 28 730 $\mathrm{cm^{-1}}$ (5080), respectively, and have line widths comparable to those of I multilayers. The 37 880-$\mathrm{cm^{-1}}$ transition undergoes a blue shift to 39 220 $\mathrm{cm^{-1}}$ and is seen with considerable intensity (ϵ = 64 000 $\mathrm{M^{-1}\ cm^{-1}}$) and with a pronounced shoulder at 38 500 $\mathrm{cm^{-1}}$ and a weaker shoulder at 36 000 $\mathrm{cm^{-1}}$.

It should be pointed out that in the solution spectra of both I and II the first singlet transition has most of its intensity in the 0–1 transition and slightly less in the 0–0 while in the multilayer spectrum the 0–0 transition is more intense than the 0–1 transition, as in the anthracene crystal.

c. Polarized Absorption Spectrum of L–B Films of I. The polarized absorption spectrum of multilayers of I deposited at pH 6.0 and 21 mN/m is shown in Figure 6. This spectrum was recorded with the incident light normal to the substrate surface and the electric vector either parallel to ($\alpha = 0°$) or perpendicular to ($\alpha = 90°$) the transfer direction T, i.e., the direction in which the substrate moved through the compressed monolayer during the transfer process. Transfer to the hydrophobic quartz substrate clearly results in a large polarization effect. The spectrum in Figure 6 shows an energy splitting for the two polarizer orientations ($|\nu(\alpha = 0°) - \nu(\alpha = 90°)|$) of 360 $\mathrm{cm^{-1}}$ for the 0–0 transition, 250 $\mathrm{cm^{-1}}$ for the 0–1 and a polarization ratio ($f(\alpha = 0°)/f(\alpha = 90°)$) of 2.5 for the entire vibronic progression. For all multilayers of I prepared in this study the maximum (minimum) energy and minimum (maximum) extinction coefficient are always found at $\alpha = 90°$ ($\alpha = 0°$), i.e., the polarization directions are independent of substrate orientation during the transfer procedure and are determined by the transfer direction only. It should be noted that films prepared at pH 6.0 show larger energy splittings and polarization ratios than those prepared at pH 4.9. In the latter case the 0–0 transition is split by 150 $\mathrm{cm^{-1}}$, the 0–1 by 100 $\mathrm{cm^{-1}}$, and the polarization ratio for the entire transition is 1.4. Between 35 000 and 40 000 $\mathrm{cm^{-1}}$ in the region of the second singlet transition the two shoulders at ~36 000 and 38 500 $\mathrm{cm^{-1}}$ are seen with $\alpha = 0°$ polarization.

Discussion

In both the crystalline state[27,28] and as L–B films[9] most straight-chain fatty acids occupy an area of ~18.3–18.6 Å²/molecule in the plane perpendicular to the alkyl chain. Anthracene, on the other hand, requires ~21.3 Å²/molecule in the plane perpendicular to the unit cell c axis, i.e., the plane which is approximately perpendicular to the L molecular axis (see Figure 1).[29] The Π–A curve of I (Figure 1), however, shows a zero-pressure area of 26 ± 0.5 Å²/molecule, a value which is quite close to the 25.85 Å²/molecule for the ab face of single-crystal anthracene in which the L molecular axis makes an angle of ~31° with the ab normal. Assuming the fatty acid chain and the anthracene L axis are approximately colinear in I the anthracene moiety then requires an additional 3 Å²/molecule in the solid state. The value of 26 Å²/molecule thus seems reasonable for a structure in which the anthracenes are close-packed and the L axis is tipped at an angle of ~30° to the water surface. Evidence that this orientation is maintained following transfer to either hydrophobic glass or quartz substrates is provided by the low-angle X-ray diffraction results. The 36.0- (pH 4.9) and 37.1-Å (pH 6.0) distances across the bilayer are both compatible with a structure in which the anthracene portion of I forms a close-packed array with the L axis at 30°–35° to the surface normal. The fatty acid chains, however, probably retain a fair degree of disorder since they occupy a smaller area and cannot close-pack. This disorder manifests itself in the low-angle X-ray diffraction results where the highest order of diffraction seen is much lower than for multilayers of straight-chain fatty acids.[22,30]

The 1300-$\mathrm{cm^{-1}}$ red shift relative to the solution spectrum and the polarization effects shown by multilayers of I are quite analogous to those observed for the ab (or (001)) face of single-crystal anthracene.[31-33] Theory explains the anthracene spectrum in terms of Frenkel excitons[16,34] and attributes the energy splitting and polarization ratio to a dipole–dipole interaction between the transition dipoles of the two translationally nonequivalent molecules in the unit cell. This interaction splits the first singlet vibronic transition into two components that are polarized at 90° to each other and have different oscillator strengths. Spectroscopic studies of the anthracene (001) face using polarized absorption[33,35-37] and polarized reflection[31,32,38] spectroscopy report room temperature energy (Davydov) splittings for the first singlet transition from 170 $\mathrm{cm^{-1}}$ [25] to 380 $\mathrm{cm^{-1}}$ [37] and polarization ratios from 2.5[33] to 3.4.[38] Although the splitting measured for the 0–0 transition of multilayers of I prepared at pH 6.0 is significantly higher than most of the values obtained for the crystal, the polarization ratio is much lower. The relative magnitude of the splittings for the 0–0 and 0–1 components are, however, consistent with the experimental results of Clark and Philpott for anthracene (001)[32] and with several different theoretical studies.[39-41] Additional similarity between the absorption spectrum of the ab face of anthracene and multilayers of I can be seen in the region of the L-axis-polarized second singlet transition.

The prediction by Fox and Yatsiv[42] that the energies of excitons in molecular crystals are strongly dependent on the direction of

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(27) Vand, V.; Morley, W. M.; Lomer, T. R. *Acta Crystallogr.* **1951**, *4*, 324.

(28) Sydow, E. v. *Acta Crystallogr.* **1955**, *8*, 557.

(29) Mason, R. *Acta Crystallogr.* **1964**, *17*, 547.

(30) Frieling, M. v., unpublished results.

(31) Clark, L. B. *J. Chem. Phys.* **1970**, *53*, 4092.

(32) Clark, L. B.; Philpott, M. R. *J. Chem. Phys.* **1970**, *53*, 3790.

(33) Bree, A.; Lyons, L. E. *J. Chem. Soc.* **1956**, 2658.

(34) Davydov, A. S. *Theory of Molecular Excitons*; McGraw-Hill: New York, 1962.

(35) Jetter, H. L.; Wolf, H. C. *Phys. Status Solidi* **1967**, *22*, K39.

(36) Lacy, A. R.; Lyons, L. E. *J. Chem. Soc.* **1964**, 5393.

(37) McRea, E. G. *Aust. J. Chem.* **1963**, *16*, 315.

(38) Morris, G. C.; Sceats, M. G. *Chem. Phys.* **1974**, *3*, 164.

(39) Schlosser, D. W.; Philpott, M. R. *Chem. Phys.* **1980**, *49*, 181.

(40) Mahan, G. D. *J. Chem. Phys.* **1964**, *41*, 2930.

(41) Silbey, R. J.; Jortner, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *42*, 1515.

(42) Fox, D.; Yatsiv, S. *Phys. Rev.* **1957**, *108*, 938.

propagation of the adsorbed radiation was first verified in the experimental work of Clark and Philpott.[32,43] The latter workers examined the (001), (20$\bar{1}$), and ($\bar{1}$10) faces of anthracene using reflection spectroscopy and found that the energies, Davydov splittings, and intensities of the first and second singlet transitions were in qualitative agreement with calculations based on Fox and Yatsiv's work. The second singlet, in particular, showed the greatest angular dependence. When the (001) face was examined with polarized light an absorption showing some vibrational structure was seen at ~37 300 cm^{-1} with $\|b$ polarization. This absorption is generally thought to be the *b* Davydov component of the second singlet transition. Although the assignment of the $\perp b$ is uncertain it is predicted to be at least 12 000 cm^{-1} higher in energy and ~4 times more intense than the $\|b$ component.[39] The spectrum of I multilayers in the region of the second singlet transition shows shoulders at ~36 000 and 38 500 cm^{-1} with $\alpha = 0°$ polarization which we tentatively assign as the $\|b$ transition. The fact that these transitions are not seen as clear maxima as in the anthracene (001) spectrum is probably due to the greater inhomogeneous line widths, as seen in the first singlet vibronic transition, and to overlap with the neighboring high-energy transition at 44 000 cm^{-1}. This latter transition has an extinction coefficient of 18 000 M^{-1} cm^{-1} and is apparently related to the peak at 45 000 cm^{-1} seen with both $\|b$ and $\perp b$ polarization in the spectrum by Clark[31] and also found in the multilayer spectrum of II. It was not possible to determine the polarization of this transition in the multilayers because of the wavelength cut-off of the Glan polarizers. An absorption maximum with $\alpha = 90°$ polarization, corresponding to $\perp b$ for anthracene (001), could not be found between 36 000 and ~43 500 cm^{-1} though spectra recorded to 52 500 cm^{-1} with unpolarized light do show a maximum at 51 300 cm^{-1} ($\epsilon \sim$ 31 000 M^{-1} cm^{-1}).

That the nearly total loss of the second singlet transition in I is due to Davydov splitting is confirmed by a comparison of the spectra of multilayers of I and II in the region of this intense transition. Multilayers of II have been previously characterized by Vincett and Barlow.[23] As a result of L–B Π–A measurements along with results from UV–visible spectroscopy and X-ray diffraction they proposed a multilayer structure in which (i) the alkyl chains interpenetrate and (ii) the anthracene L and M axis are at ~20–25° and 55°, respectively, to the substrate surface. These workers failed, however, to examine the spectral region of the second singlet transition.

This intense electronic transition, which is polarized along the L axis and has a gas-phase oscillator strength of ~4.8 in unsubstituted anthracene shows up strongly in the multilayer absorption spectrum of II (Figure 5), though with diminished intensity relative to the single-crystal studies. This confirms that the L molecular axis of the anthracene moiety has a substantial component parallel to the substrate surface in multilayers of II. The near total absence of this transition of I cannot, however, be accounted for by an orientation in which the anthracene L axis is perpendicular to the surface (i.e., where the light electric vector and the transition dipole are orthogonal) because (1) the distances of 36.0 Å (pH 4.9) and 37.1 Å (pH 6.0) across the bilayer seem to rule out such a configuration and (2) we could not see this transition using non-normally incident p-polarized light (45° from the perpendicular) between 35 000 and 45 000 cm^{-1}. Assuming (1) the previously discussed value of 30–35° for the angle between L and the surface normal but (2) the absence of Davydov splitting, we would expect to see the second singlet transition with only slightly diminished intensity relative to II. This implies a Davydov splitting of at least 15 000 cm^{-1} for the second singlet transition in I multilayers, a value entirely in agreement with theoretical predictions[32,39] and in contrast to the much smaller splittings predicted and measured for anthracene (20$\bar{1}$) and ($\bar{1}$10) where the $\perp b$ component appears with much greater intensity.

The fact that we can observe in multilayers of I a dependence of the absorption spectrum on the polarization of the light with respect to the macroscopic transfer direction implies that these films possess either crystallinity or, more likely, polycrystallinity with a preferred orientation for the crystallites. We examine these possibilities below.

In an early electron diffraction study Germer and Storks[6] reported that stearic acid L–B multilayers formed monoclinic crystalites on various metal and organic surfaces with the *a* and *b* axes lying in the surface plane and showing a preferred orientation relative to the transfer direction *T*. In more recent studies Peterson and co-workers[10,11] used both transmission and reflection electron diffraction to demonstrate that under certain circumstances multilayers of ω-tricosenoic acid also deposit anisotropically. This was further confirmed with use of polarized optical microscopy.[44] Similar behavior was observed by Koyama et al.[45] in a polarized IR study of stearic acid on single-crystal silicon. They showed that the stearic acid unit cell orientation was independent of the silicon crystal orientation and was entirely due to the transfer process. It was proposed that "dynamical strain" during film transfer induced a preferred orientation for the stearic acid unit cell. Similar proposals have since been made for other L–B films.[46] Given these results and the fact that the anthracene moiety of I is highly anisotropic it does not seem unreasonable that L–B multilayers of I should deposit with the unit cell, probably monoclinic, showing a preferred orientation.

The pH dependence of the Davydov splitting and polarization ratios is doubtless due to the structural changes indicated by the low-angle X-ray diffraction results. The 1.1-Å increase in the bilayer thickness upon changing the subphase pH from 4.9 to 6.0 probably results in a slightly different orientation of the anthracene moiety in the unit cell and thus produces a corresponding change in the interaction energy. Raising the pH and incorporating more Cd^{2+} ions into the film might also result in improved long-range order since the divalent metal ions can bridge neighboring carboxylate groups.

The analogy between the (001) face of anthracene and multilayers of I is only approximate, however. The Davydov splitting obtained for the multilayer first singlet 0–0 transition is certainly at the high end of those values measured for the crystal and quite surprising for a system that contains more disorder than the crystal. This disorder certainly contributes to the much greater line widths in the multilayer spectrum. The multilayer 0–0 transition at ~25 000 cm^{-1}, for example, is ~2.5 greater than that reported by Morris and Sceats for the single crystal at 286 K.[38] Rather poor correspondence is also seen in the region of the $\alpha = 0°/\perp b$ transition between 35 000 and 40 000 cm^{-1}. Nevertheless, the gross features of the multilayer spectrum do agree with those of anthracene (001) and the slightly high splitting measured in the first singlet as well as other differences are probably due to the alkyl substituent imposing a slightly different unit cell on I relative to the anthracene molecular crystal.

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[43] Clark, L. B. *J. Chem. Phys.* **1969**, *51*, 5719.

[44] Peterson, I. R. *Thin Solid Films* **1984**, *116*, 357.

[45] Koyama, Y.; Yanagishita, M.; Toda, S.; Matsuo, T. *J. Colloid Interface Sci.* **1977**, *61*, 438.

[46] Chollet, P.-A.; Messier, J. *Thin Solid Films* **1983**, *99*, 197.