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In plane and out of plane anisotropy in Langmuir–Blodgett films of discogenic molecules

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Langmuir–Blodgett films of a discotic mesogenic pyrylium tetrafluoroborate salt (**1**) have been investigated from the point of view of their in-plane anisotropy, i.e. considering the average molecular orientation with respect to the dipping direction. The molecules are found to stand on edge with their flat polycyclic core more or less perpendicular to the dipping direction. Mixing **1** with $N(C_4H_9)_4^+$ $TCNQ^-$ in the spreading solvent leads to a different behaviour of the monolayer at the air–water interface, involving the formation of the Pyrylium-TCNQ salt. In contrast to the films of pure **1**, these films do not exhibit any in-plane anisotropy after deposition on a solid substrate. The temperature dependance of the molecular anisotropy of both films has also been investigated. The results are presented and discussed in the framework of their mesomorphic properties together with the influence of the anion associated with Pyrylium.

1. Introduction

A Langmuir–Blodgett (LB) film is made of a series of superimposed monolayers, yielding a translation symmetry together with a bidimensional structure. Usually, each monolayer is considered as isotropic in the plane, thus belonging to the C_∞ symmetry group. Building an anisotropic monolayer opens the way to in-plane unidimensionality which is a challenge in itself. Moreover, the field of application of unidimensional LB films may become very wide, provided reactive molecules can be used to build them (for example electrically conductive disc-like molecules).

At present, research teams concerned with in-plane unidimensionality in Langmuir films mainly centred their research upon the behaviour of films made at the air–water interface with rod-like polymers and derived very useful theories about the mechanism of flow orientation [1–3]. However, other works proved that anisotropic films can be built up also from monomers like, for example, phthalocyanines [4].

Columnar liquid crystals (LCs) seemed to us a very promising tool since they combine a natural ability for self arrangement with the possibility of being chemically reactive. Some columnar LCs proved to form stable monolayers at the air–water interface [5, 6], in particular, pyrylium salts [7]. The purpose of this work is to give a first inspection of the thermodynamical and orientational properties of two pyrylium salts, $PyBF_4$ and PyTCNQ (see figure 1), both showing a columnar mesophase, but only the former at ambient temperature.

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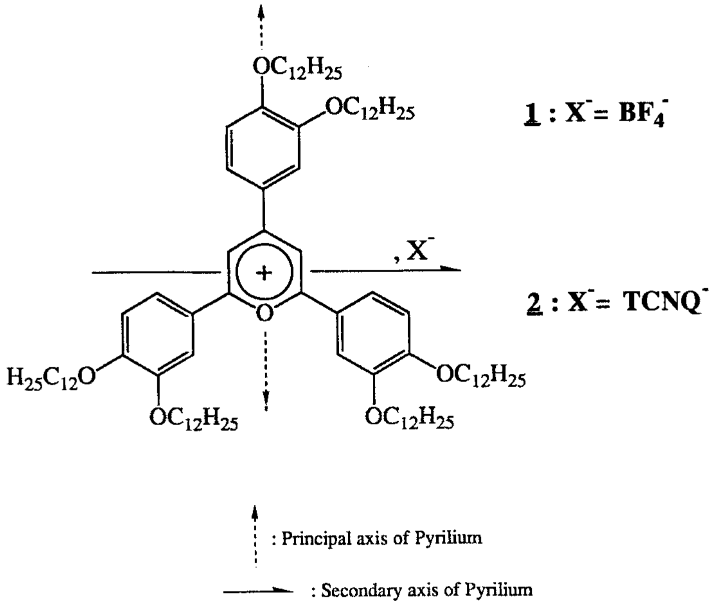

Figure 1. Semi-developed formula of triarylpyrylium cation. The symmetry axes are indicated, together with the two investigated salt counterions.

2. Experimental

The mesophase characteristics of $PyBF_4$ and its synthesis are given elsewhere [8, 9]. A 10^{-4} mol l^{-1} chloroform solution of $PyBF_4$ was used as a spreading solution, the concentration being checked by UV-VIS spectroscopy. The compression isotherms were recorded using an Atemeta-LB 105 trough. The data were recorded automatically once the thermodynamical equilibrium was reached. The deposition of the films was performed at various surface pressures by vertical dipping through the air-water interface onto CaF_2 substrates, precoated with a few layers of behenic acid.

The molecular orientation was measured by infrared linear dichroism performed at normal and 60° incidences. The IR spectra were recorded on a Perkin-Elmer 1720 FTIR. A Perkin-Elmer wire-grid linear polarizer was used for dichroism measurements, and the in-plane dichroic ratio R is defined as: $R = A_{\perp}/A_{//}$, with $A_{\perp}$ and $A_{//}$ being the IR absorptions with the light (at normal incidence) polarized respectively perpendicular and parallel to the dipping direction. Temperature dependent measurements were made using a home-made heater which allows temperatures from 25°C to 100°C. The temperature values were checked by a four-wires platinum resistance. X-ray measurements at low angle were made according to the sample oscillation method [10].

3. Results and discussion

3.1. *PyBF4*

3.1.1 *π/A isotherm*

A typical compression isotherm diagram of PyBF4 measured at 19°C is given in figure 2. As was reported earlier [7], the molecular area values correspond to an

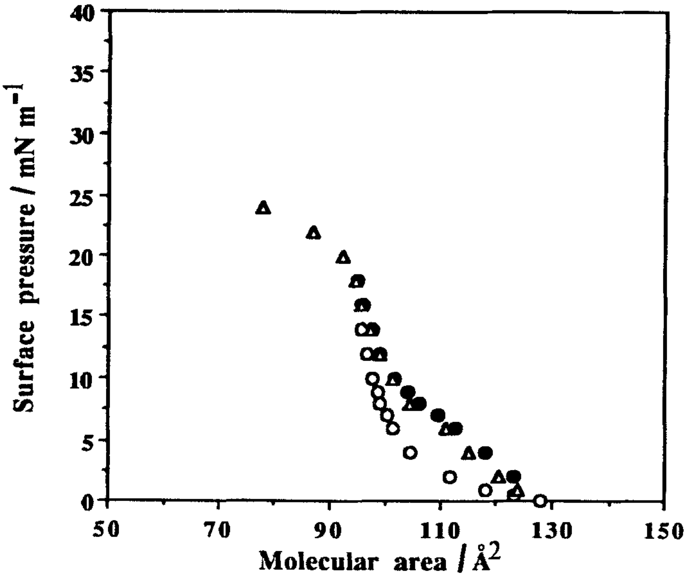

Figure 2. Compression isotherms of the $PyBF_4$ salt, recorded at 19°C. First compression is indicated by black dots: a slightly condensed phase is reached at $7\,mN\,m^{-1}$, then a transition to a more compact phase (stable from $14\,mN\,m^{-1}$ to $18\,mN\,m^{-1}$) occurs. This transition is not reversible on decompression (empty circular dots) and the expanded phase is directly reached. The reappearance of the first condensed phase on recompression (empty triangular dots) suggests no irreversible multilayer formation has occurred before. Above $20\,mN\,m^{-1}$, the film slowly collapses.

edge-on arrangement of the molecules, hence inducing strong interactions between neighbouring aromatic cores and having a weak affinity for water, despite the ionic character of the molecule.

Upon compression, the film undergoes a transition at *c.* $8\,mN\,m^{-1}$, which is not clearly understood yet, but might correspond to some tilting of the molecules, since, from the absence of a well-defined plateau (even at 10°C), the formation of a bilayer is to be excluded. A more condensed state is obtained when raising the pressure up to *c* $19\,mN\,m^{-1}$, then the film slowly collapses. The molecular area at $16\,mN\,m^{-1}$ is about 0·95 nm^2 per molecule, close to the value obtained from a model using van der Waals forces (0·85 nm^2 per molecule) for a vertical edge-on position. The transition is not reversible upon decompression from $16\,mN\,m^{-1}$, but on re-compression from $0\,mN\,m^{-1}$, the cycle is perfectly repeated, suggesting a true monolayer.

3.1.2. *In-plane anisotropy*

Forty monolayers of PyBF4 were sequentially transferred at a constant surface pressure of $16\,mNm^{-1}$ and a dipping speed of $15\,mm\,min^{-1}$, on to a solid plate of CaF_2. The plate was precoated with four layers of behenic acid to ensure a flat and hydrophobic surface. The transfer ratio was about 0·97 and the film obtained was perfectly free of light scattering defects. Low angle X-ray measurements showed an inter-layer periodicity of *c.* 4·2 nm, close to the diameter of the molecule and confirming, therefore, the edge-on settlement of the molecules at the air–water interface.

Infrared linear dichroism recorded at normal incidence with the light polarized parallel and perpendicular to the dipping direction (in-plane dichroism) exhibits a dichroic ratio ($R = A_{\perp}/A_{//}$) of 4·2 for the absorption peak located at 1633 cm^{-1} (see figure 3). At the moment, this is the only peak clearly assigned to a pyrylium symmetrical vibration, polarized along the principal axis of the molecule (see figure 1). Its relatively high absorption tells us that the principal axes must be more or less parallel to the film plane (if they were perpendicular to this plane, there would not be absorption at normal incidence), which will be confirmed by out-of-plane dichroism. Supposing a gaussian distribution of these axes' directions in the monolayer plane, we find that they are more or less perpendicular to the dipping direction with a statistical variation $\Delta\omega$ of $\pm 33°$ around $\omega = \pi/2$ (see figure 4) and an order parameter $P_0 = 2\langle\langle\cos^2\omega\rangle\rangle - 1$ of $-0{\cdot}62$ ($P_0 = 0$ would mean in-plane isotropic distribution of the principal axes, while $P_0 = -1$ would mean all the principal axes at $\omega = \pi/2$). The peaks located at 1583 and 1518 cm^{-1} exhibit the same behaviour and can therefore be attributed to symmetrical vibrations of the aromatic core. In contrast, the peaks at 1598 and 1488 cm^{-1} are polarized parallel to the dipping direction ($R = 0{\cdot}5$). Therefore, they should be attributed to asymmetrical vibrations (i.e. parallel to the secondary axis), and they show that the molecules are tilted with respect to the normal to the substrate.

With the purpose to see the influence of surface pressure on in-plane anisotropy, LB transfers were achieved at 7 mN m^{-1}, with a constant transfer ratio of 0·7, and at

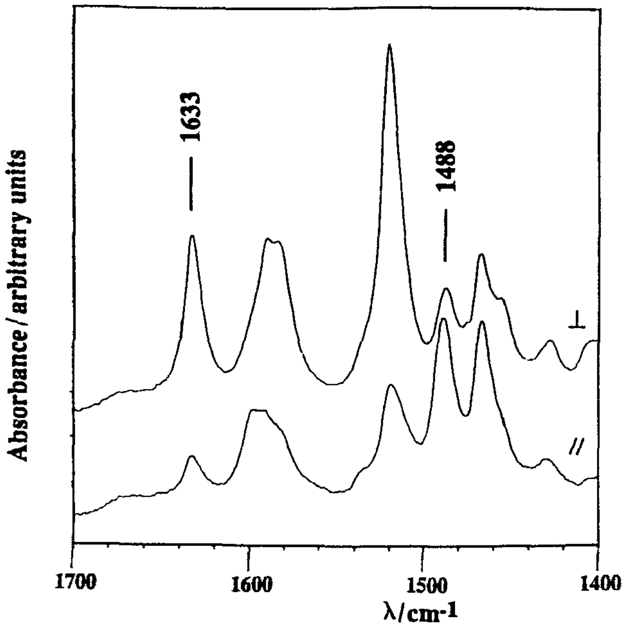

Figure 3. Normal incidence infrared absorbance spectra of a 40 layer thick PyBF$_4$ film. Polarization of the light with respect to the dipping direction is indicated. The 1633 cm^{-1} vibration is polarized along the principal axis of the pyrylium. Its high absorption value suggests that the principal axes are rather parallel to the film plane, and its dichroic behaviour ($R = 4{\cdot}2$) indicates that the molecular planes stand more or less perpendicular to the dipping section.

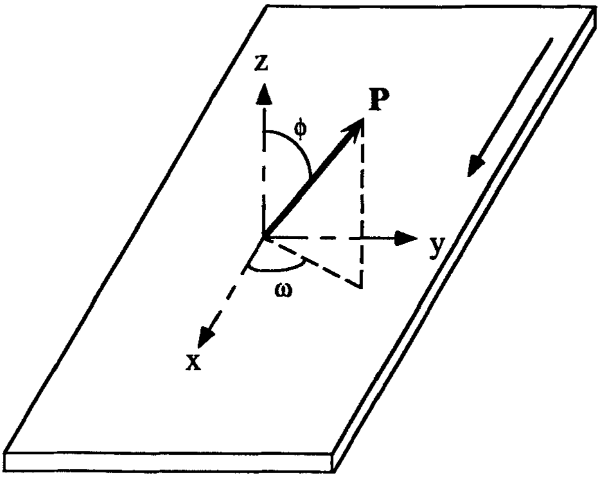

Figure 4. Definition of the parametric angles ω and θ. θ is the angle between the dipole P and the normal z to the film plane. ω is the angle between the projection of P on the film plane and the dipping direction x.

30 mN m^{-1}, with a transfer ratio close to 1, despite the collapse phenomenon: actually, the monolayer density seems to stabilize once the transferring process has begun. The latter films present in-plane dichroic ratios varying from 1·5 to 3·3. This lack of reproducibility is explained by the fact that the collapse at this surface pressure is still very slow so that the anisotropy strongly depends on the molecular area at which the transfer is achieved. Indeed, $R = 3{\cdot}3$ corresponds to a molecular area of 0·82 nm^2, close to the area 16 mN m^{-1}, whereas $R = 1{\cdot}5$ corresponds to a calculated area of 0·52 nm^2 per molecule, i.e. a collapsed film. Surprisingly, the films transferred at 7 mN m^{-1} are quite comparable regarding their in-plane anisotropy to those transferred at 16 mN m^{-1}. So, despite the transition in the π/A isotherm at 8 mN/m^{-1} and different transfer ratios, the surface pressure does not seem to play a noticeable role in the ordering of the molecules. On the contrary, and in complete agreement with [4], a larger width of the substrate, on to which the monolayers are transferred, considerably decreases the in-plane dichroic ratio, corroborating the existence of a flow orientation, even for disc-like molecules.

3.1.3 *Out-of-plane anisotropy*

IR linear dichroism was recorded for PyBF4 films at 16 mN m^{-1} at an incidence of $i = 60°$ with the light electric vector p-polarized (in the incidence plane) perpendicular to the dipping direction (cf. figure 5(*a*)). The out-of-plane dichroic ratio taken from the absorption values at 1633 cm^{-1} is: $R_\perp = (A_{\perp,i=60°})/(A_{\perp,i=0°}) = 0{\cdot}68$. If we suppose a gaussian distribution of the angle ϕ (cf. figure 4) around $\phi_0 = \pi/2$, we find a dispersion $\Delta\phi$ of $\pm 20°$, and an order parameter $P'_0 = 3 \ll\cos^2\phi\gg - 1$ of $-0{\cdot}77$ ($P'_0 = 0$ would mean isotropic distribution of the principal axes with respect to the z axis, while $P'_0 = -1$ would mean all the principal axes in the monolayer plane). Therefore, the principal axes of the pyrylium are more or less parallel to the monolayer plane, which is confirmed by the dichroic behaviour of the peaks located at 1588 and 1518 cm^{-1}. In other words, the way the molecule is represented in figure 1 does not correspond to its orientation within the LB film; indeed, it should be rotated by 90°, with the principal axis horizontal and the secondary axis vertical. Moreover, the low dichroic ratio ($R = 1{\cdot}45$) of the 1489 cm^{-1} peak, attributed to a vibration polarized along the secondary axis, corroborates a tilted position of the molecular planes. Indeed, if the molecule were perfectly perpendicular to the film plane, the absorption at normal incidence should be close to zero.

3.2. *PyTCNQ*

The spreading solution of PyTCNQ is obtained by mixing an equimolar ratio of $PyBF_4$ in chloroform with LiTCNQ in ethyl alcohol. The compression isotherm diagram (see figure 6), recorded under the same conditions as for $PyBF_4$, shows no transition step and the molecular area in the condensed state is about 0·5 nm^2, i.e. half the value shown by $PyBF_4$ films, and may then correspond to an *ab initio* formation of a bilayer.

Transfer onto a solid support is very difficult (t.r. < 0·2) and results in bad quality films. IR in-plane linear dichroism shows no apparent anisotropy of the film on its

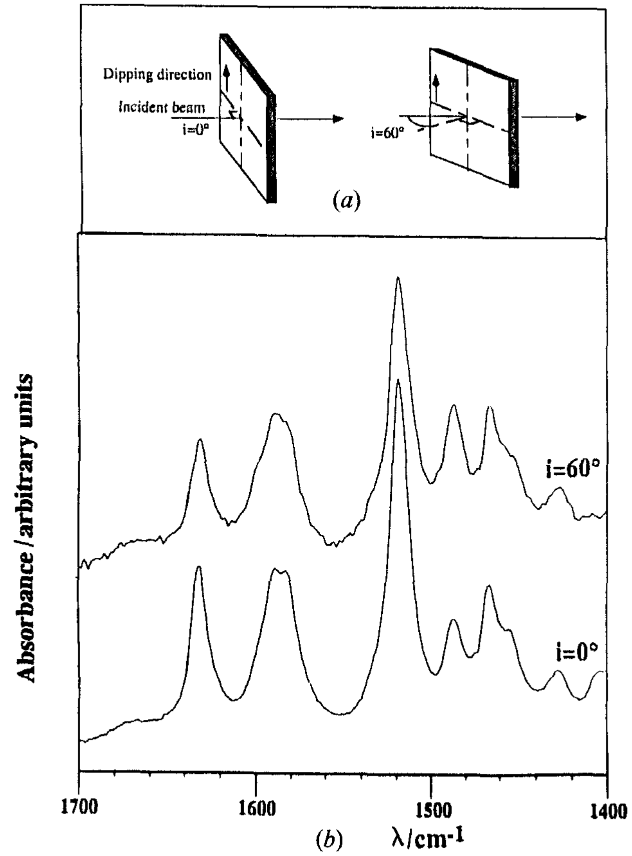

Figure 5. (*a*) Experimental set-up for the out-of-plane linear dichroism measurements: the sample is tilted by 60° around the dipping axis and the light is p-polarized. (*b*) Infrared absorbance spectra of a 40 layer thick $PyBF_4$ film, recorded at normal and 60° incidences. The dichroic ratio ($R_\perp = 0{\cdot}68$) of the 1633 cm^{-1} vibration confirms that the principal axes of the pyrylium are parallel to the film plane.

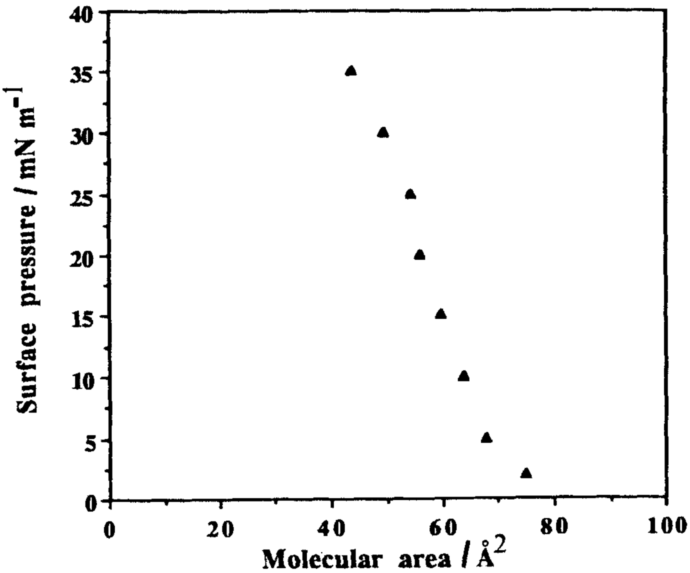

Figure 6. Compression isotherm of the PyTCNQ salt, recorded at 19°C. A compact phase is obtained from 20 mN m^{-1} to 25 mN m^{-1}, then the film slowly collapses. The corresponding molecular area ($\approx 55\,Å^2$) may suggest a bilayer.

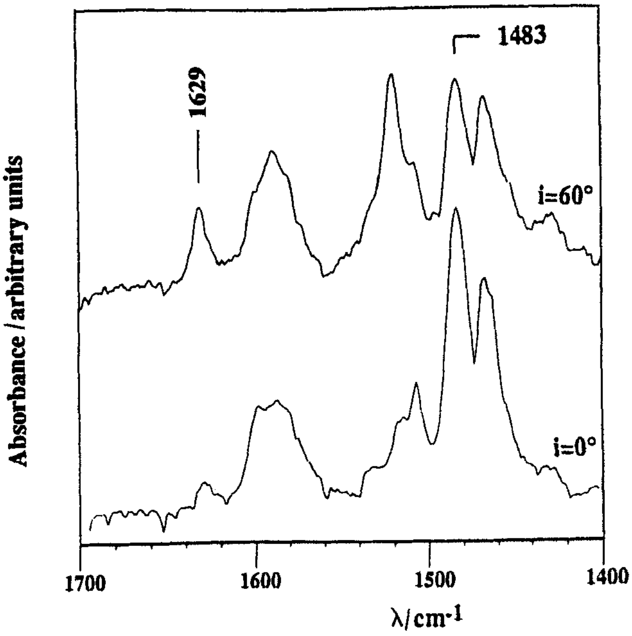

Figure 7. Infrared absorbance spectra of a 40 layer thick PyTCNQ film, recorded at normal and 60° incidences. Contrasting with the BF_4^- salt case, the molecular principal axes stand approximately perpendicular to the film plane.

own plane, but the out-of-plane dichroic ratio recorded at 1629 cm^{-1} is about 2·7 (see figure 6), and that recorded at 1483 cm^{-1} is about 0·65. If our previous attempt to attribute the latter peak to an asymmetrical vibration is correct, these values mean that the secondary axes of the pyrylium (cf. figure 1) lie nearly flat on the substrate, while the principal axes stand more or less perpendicular to it, which is the opposite situation with respect to that of $PyBF_4$.

3.3. *Annealed samples*

Contrasting with the results of [4], no improvement of the in-plane dichroic ratio was observed on annealed $PyBF_4$ films. Actually, the film tends to lose its anisotropy as the temperature is raised. This point is not understood, since it also seems to contradict previous X-ray measurements [11]. Instead, the out-of-plane anisotropy of PyTCNQ films is improved, the dichroic ratio at 1629 cm^{-1} jumping from 2·7 to 5·4. This result means a reinforced verticality of the pyrylium principal axes.

4. Conclusion

In this work, our purpose was to characterize the order induced by the Langmuir–Blodgett technique upon a discotic liquid crystal, the tetrafluoroborate of triarylpyrylium. Comparison with the TCNQ salt suggests that the existence of a bulk columnar behaviour at ambient temperature is implicated in the ordering mechanism. This order was proved to originate in the transfer process and to disappear when the sample is annealed, contrasting with the bulk phase behaviour. A new molecular order has then been evidenced, increasing the interest of the LB technique in the field of liquid crystals.

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