

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Ionic liquid crystals: synthesis and mesomorphic properties of dimeric 2,4,6-triarylpyrylium tetrafluoroborates

M. Veber; G. Berruyer

Online publication date: 06 August 2010

To cite this Article Veber, M. and Berruyer, G.(2000) 'Ionic liquid crystals: synthesis and mesomorphic properties of dimeric 2,4,6-triarylpyrylium tetrafluoroborates', *Liquid Crystals*, 27: 5, 671 – 676

To link to this Article: DOI: 10.1080/026782900202534

URL: <http://dx.doi.org/10.1080/026782900202534>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ionic liquid crystals: synthesis and mesomorphic properties of dimeric 2,4,6-triarylpyrylium tetrafluoroborates

M. VEBER* and G. BERRUYER

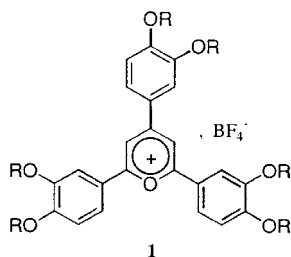
Laboratoire de Physique des Solides, Bât 510, Université Paris Sud,
91405 Orsay Cedex, France

(Received 30 September 1999; accepted 19 November 1999)

The synthesis of some dimeric pyrylium salts is described. The link between the two cationic parts of the molecule can be flexible or rigid. Surprisingly, the starting dimeric chalcones with a rigid link exhibit monotropic columnar hexagonal phases. Results concerning the spectroscopic and mesomorphic properties of the pyrylium salts and the chalcones are given.

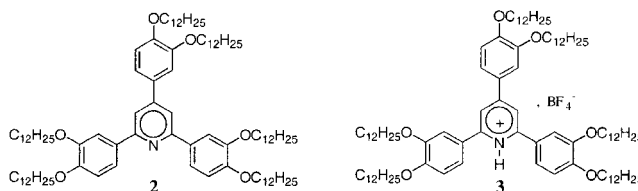
1. Introduction

Most thermotropic liquid crystal materials are neutral compounds. Recently, however, some interest has grown concerning non-conventional liquid crystals [1] and the influence of the ionic character upon mesomorphic properties [2]. Some years ago results appeared concerning the mesomorphic behaviour of 2,4,6-triarylpyrylium salts **1** [3, 4].



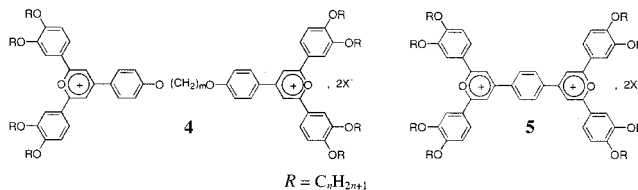
Such ionic compounds exhibited columnar hexagonal phases, even in the case of very short alkyl chains *R* (from $n = 2$ to $n = 12$), over a wide range of temperature (from room temperature to almost 300°C for the higher homologues). Some X-ray and solid state NMR experiments showed that the behaviour of the short chain systems was due to high temperature motions of the anions. Indeed, the tetrafluoroborate anions behave like ‘ball bearings’ and therefore decorrelate the columns [3]. It seems therefore that the ionic character of such systems can be responsible for the mesomorphic properties. Indeed the pyridine compound **2** is purely crystalline, but the corresponding pyridinium salt **3** is mesomorphic and exhibits a Col_h columnar phase [5]. Such behaviour

has also been observed in the case of vinamidinium salts and their conjugated bases, the vinamidines [6].



Moreover, the pyrylium salts **1** exhibit interesting photophysical properties [7]. The presence of the long paraffinic chains allowed studies to be made using non-polar solvents such as heptane or toluene. In such solvents, some aggregation can take place resulting in a blue shift in the absorption spectra and a red shift of the fluorescence spectra. Finally, they behave as amphiphilic materials and lead to Langmuir monolayers and Langmuir–Blodgett films, oriented during the dipping process [8].

In order to increase our understanding of the mesomorphic properties of such ionic systems, as well as their photophysical properties, we synthesized the dimeric pyrylium salts **4** and **5**, with flexible and rigid links, respectively, between the two cationic parts of the molecule.

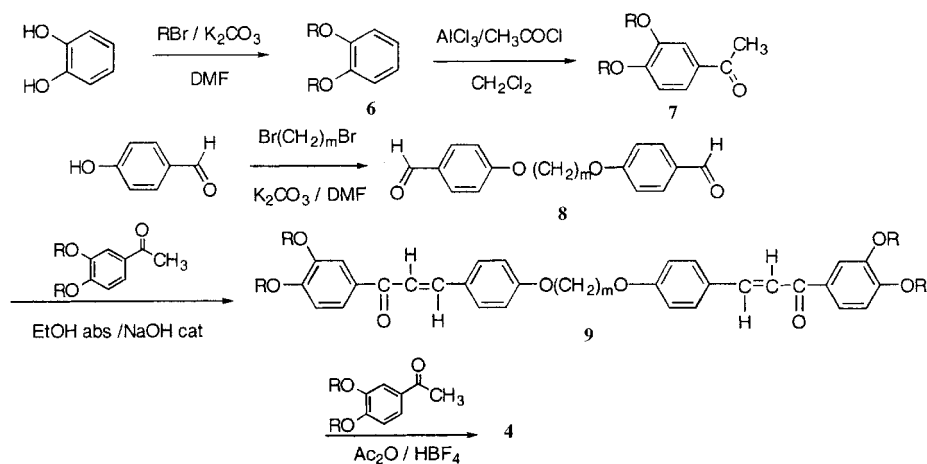
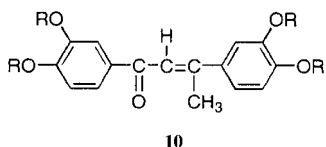


* Author for correspondence; e-mail: veber@lps.u-psud.fr

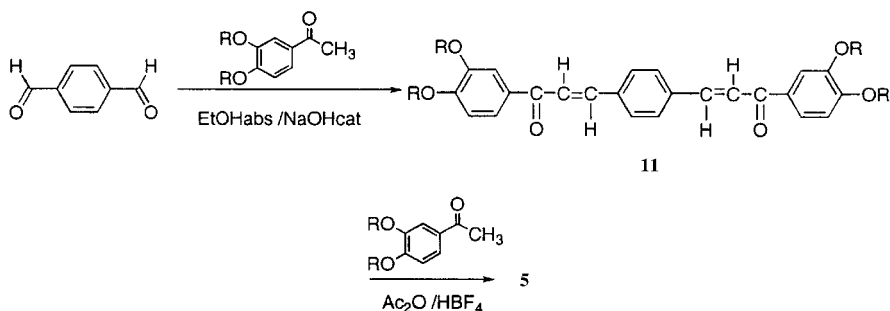
2. Synthesis

The dimers **4** were obtained (scheme 1) following the same reaction pathway as in the case of the monomers [1].

A Williamson etherification reaction in dimethylformamide, using potassium carbonate as the base, leads to the pyrocatechol ethers **6** [9]. A Friedel–Crafts acylation reaction, in dry dichloromethane, leads then to the 3,4-dialkoxyacetophenone **7**. The dialdehydes **8** were prepared starting from two equivalents of 4-hydroxybenzaldehyde and one equivalent of the required α,ω -dibromide, under the reaction conditions described above in the case of the pyrocatechol ethers. An aldolization reaction, using a catalytic amount of sodium hydroxide, between the acetophenones **7** and the dibenzaldehydes **8** leads to the dichalcones **9**. Finally, a double heterocyclization reaction in acetic anhydride, in the presence of anhydrous tetrafluoroboric acid, gives the dimeric pyrylium salts **4**. To obtain the best yields, a large excess of the acetophenones has to be used: indeed in such acidic conditions, another by-product can be produced, namely the dypnone **10**.



Scheme 1.



Scheme 2.

The dimer **5** ($R = C_{12}H_{25}$) was obtained in the same way (scheme 2), starting from terephthalic aldehyde. In that case also, a large excess of the substituted acetophenone had to be employed to obtain the best yield of the heterocyclized compound.

Yields and transition temperatures of the different products synthesized are given in the table.

3. Results

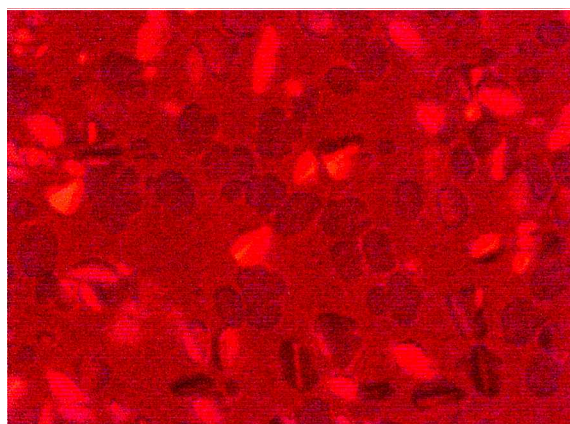
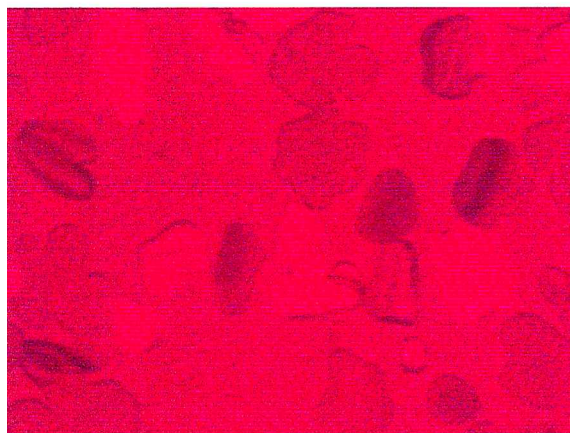
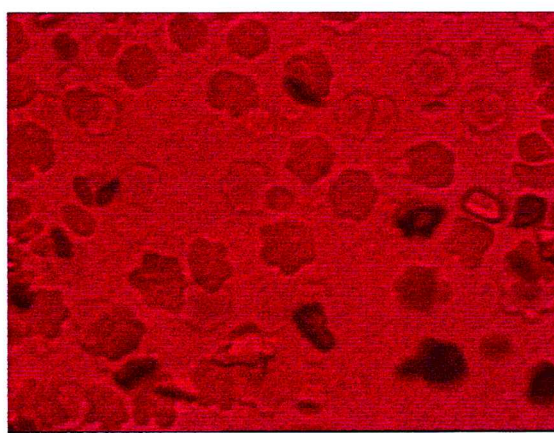
3.1. Dimers **4**

UV-Vis spectra were recorded using dry dichloromethane as solvent for the dimers **4** with eight dodecyloxy chains and two spacer lengths: $m = 11$ and 12 . In both cases, two strong absorption bands were detected at $\lambda = 505$ and 447 nm. Two others, less intense, appeared at $\lambda = 388$ and 317 nm. The positions and intensities of such absorption peaks are in agreement with results obtained in the case of monomeric five chain substituted pyrylium salts. So it seems that the dimerization process has no influence upon the absorption properties of the salts.

Microscopic observations on all the dimers gave results consistent with columnar hexagonal phases. On the isotropic liquid cooling, dendritic domains with hexagonal symmetry and linear defects could be obtained, see figure 1 (*a-c*).

Table. Yields and transition temperatures for chalcones **9** and **11** and dimers **4** and **5**.

Salts	<i>n</i>	<i>m</i>	Dibenzaldehydes		Dichalcones		Dimers	
			Yields/%	mp/°C	Yields/%	Transition temp/°C	Yields/%	Clearing temp/°C
4	12	6	74	78.0	60	Cr → I (115.5)	63	114 ^a
	12	10	71	81.1	54	Cr → I (96.4)	4	145 ^a
	12	11	86	82.4	61	Cr → I (93.1)	13	156 ^a
	12	12	80	75.0	57	Cr → I (99.1)	6	204
	10	12	82	74.0	40	Cr → I (102.0)	27	236 ^a
	8	12	80	75.0	43	Cr → I (99.1)	7.5	240 ^a
5	12	—	—	—	63	Cr → I (118.2) ^b I → Col _h (104.0) → Cr(92.5)	11.5	168 ^a
	10	—	—	—	77	Cr → I (116.6) I → Col _h (101.2) → Cr(101.0)	—	—

^a Melting points not defined.^b DSC results.**a****b****c****d**Figure 1. Characteristic textures of 2,4,6-triarylpyrylium dimers. (a) Salt **4**: *n* = 10, *m* = 12, 164°C; (b) salt **4**: *n* = 8, *m* = 12, 182°C; (c) salt **4**: *n* = 8, *m* = 12, 220°C; (d) salt **5**: 160°C.

DSC measurements were performed in the case of the dimer **4** with $n = 12$ and $m = 12$, without reaching the clearing temperature (in order to avoid some decomposition of the sample). On heating, three transitions were detected at 74, 88 and 125°C. All these transitions were very broad and only the overall enthalpy value was obtained: 7.1 J g⁻¹. On cooling, only two transitions were observed, at 117.8 and 61.1°C. Their respective enthalpies were 1.3 and 1.7 J g⁻¹. The clearing temperature of this compound, given by microscopic observations, was 204°C. As only very broad and poorly defined DSC peaks were observed on heating, the polymorphism exhibited by the dimer was studied by X-rays. Two X-ray diffraction patterns were measured in the mesomorphic range, at 139 and 99°C. In both cases, two peaks were observed, in a spacing ratio 1:√3, which is characteristic of a hexagonal lattice with hexagonal parameters of $a = 28.3 \pm 0.5 \text{ \AA}$ and $29.7 \pm 0.5 \text{ \AA}$, respectively. The intensity of the profile obtained at 139°C is given in figure 2. Such hexagonal lattice parameters are slightly smaller than in the case of the monomeric pyrylium salt bearing six dodecyloxy chains ($a = 31.2 \text{ \AA}$). Moreover, no sign of core-to-core interactions could be detected. Taking into account such results, it seems that the transition indicated at 125°C (heating cycle) and 117.8°C (cooling cycle) is a reversible transition between two columnar hexagonal phases with slightly different hexagonal parameters.

3.2. Dimer 5

Two chalcones bearing different chain lengths ($n = 10$ and 12) have been obtained (see the table); the heterocyclization reaction was only successful in the case of

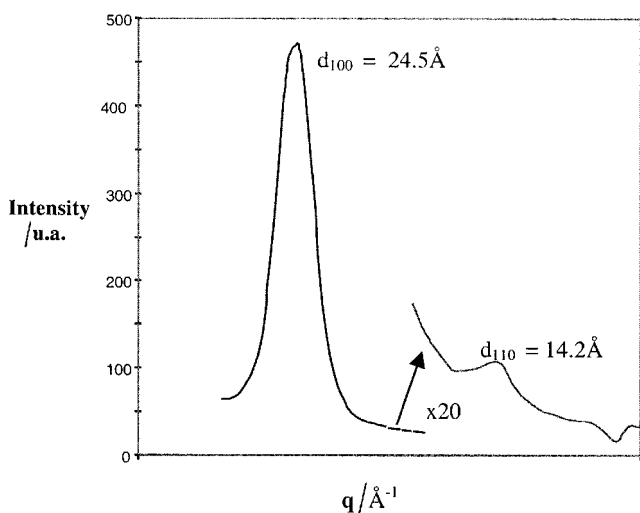


Figure 2. Intensity profile of the X-ray diffraction pattern of the salt **4** ($n = 12$; $m = 12$), taken at 139°C.

the dodecyloxy substituted compound. Once more, the dimeric salt obtained shows, from microscopic observations, mesomorphic behaviour. In figure 1(d), homeotropic domains are growing, first as circular germs which then become hexagonal in shape. Finally, dendritic domains appear with six-fold symmetry, which is once more characteristic of columnar hexagonal phases [10, 11].

3.3. Chalcones

As described in scheme 2, the chalcones **9** and **11** are intermediates in the synthesis of the salts **4** with a flexible spacer and **5** with a rigid spacer. Microscopic observations performed on the chalcones **9** showed that they were crystalline; surprisingly, similar observations made upon the chalcones **11** with a rigid spacer, showed short range monotropic mesophases—very short in the case of the decyloxy derivative, see the table. Indeed, during our studies concerning either monomeric pyrylium salts [3, 4] or some symmetrical or non-symmetrical dithiolium salts [12], we have synthesized more than fifty chalcones, all bearing long paraffinic chains: none of them were liquid crystalline. They exhibited large degrees of supercooling, and therefore it seems that the dimerization has an influence upon the mesomorphic properties of these compounds by lengthening the rigid parts of the molecules.

Characteristic defects of such phases can be seen in figure 3(a) (compound **11**; $n = 10$) and figure 3(b) (compound **11**; $n = 12$). Both textures, with fan-shaped domains and large homeotropic domains (in the case of the dodecyloxy derivative) are consistent with columnar hexagonal phases. Attempts to study these dimeric chalcones by X-ray diffraction techniques were unsuccessful due to the monotropic character of the phases. The transition temperatures of both compounds are given in the table.

Work is in progress to characterize fully all the columnar phases exhibited by the dimers synthesized (especially by studying oriented samples by X-ray diffraction) and to obtain a more accurate understanding of their photophysical properties. Concerning the dimeric chalcones, higher homologues will be synthesized in order to obtain enantiotropic phases.

4. Experimental

4.1. Characterization

¹H NMR spectra were recorded, in CDCl₃, on a Bruker AC300 spectrometer. Microscopic observations were made on a Leitz Orthoplan polarizing microscope equipped with a Mettler FP52 hot stage and a FP5 central processor. All the synthesized products gave satisfactory analyses.

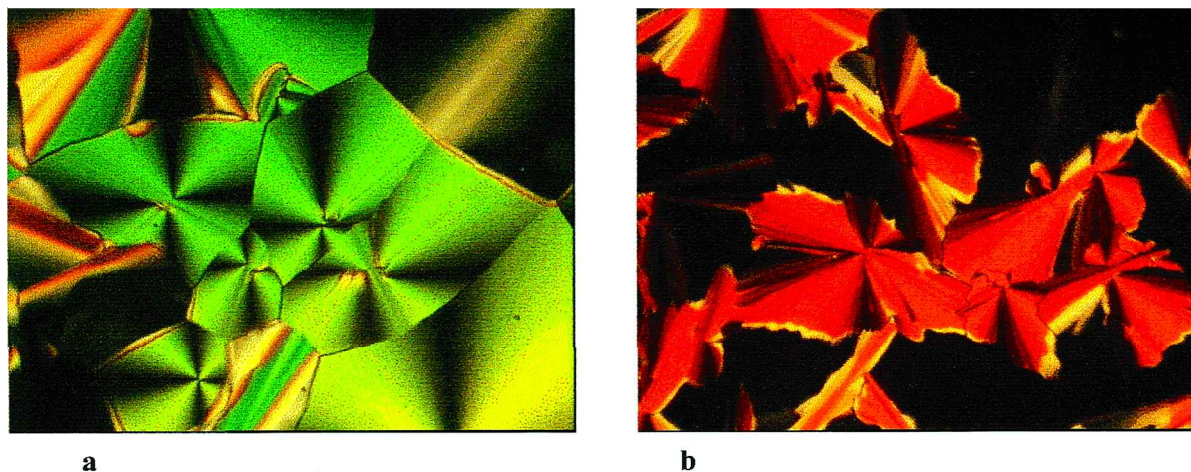


Figure 3. Characteristic textures of the chalcones **11**. (a) Compound **11**: $n = 10$, 101°C; (b) compound **11**: $n = 12$, 103°C.

4.2. Chalcones **9**

In a typical experiment, the dibenzaldehyde (4.61 mmol) and the 3,4-disubstituted acetophenone (9.22 mmol) were dissolved in absolute ethanol at 40°C. When the reaction mixture was homogeneous, a small pellet of sodium hydroxide was added and the temperature raised to 80°C for 24–36 h. The disappearance of the acetophenone was followed by TLC on silica gel (eluent: dichloromethane). After cooling to room temperature, the precipitate was filtered off and washed with ethanol. Several recrystallizations from ethanol/butanol (60/40) mixture, acetone, absolute ethanol or ethyl acetate (depending on the chain length) gave the pure chalcones.

Typical NMR data are given for $n = 12$; $m = 6$. ^1H NMR: δ (ppm) = 7.75 (d, 2H, $J_{\text{trans}} = 15$ Hz, ethylenic H); 7.60 (m, 8H); 7.41 (d, 2H, $J_{\text{trans}} = 15.5$ Hz, ethylenic H); 6.90 (2d, 6H, $J_{\text{ortho}} = 6.5$ Hz, aromatic H); 4.00 (2t, 12H, $J = 7$ Hz, OCH_2CH_2); 1.80 (m, 12H, OCH_2CH_2); 1.40 (m, 76H, $(\text{CH}_2)_9$); 0.90 (t, 12H, $J = 7$ Hz, CH_3).

4.3. Chalcones **11**

In a typical experiment, terephthalic aldehyde (5.5 mmol) and the substituted acetophenone (10 mmol) were dissolved in absolute ethanol at 60°C. To the homogeneous mixture was added a small pellet of sodium hydroxide. An abundant precipitate appeared and the mixture was vigorously stirred at 60°C for 20 h. After cooling to room temperature, the yellow precipitate was filtered off and washed with ethanol until the washings were no longer coloured. The dichalcones were recrystallized from absolute ethanol, ethyl acetate/dichloromethane mixture or ethanol/dichloromethane mixture, depending on the length of the paraffinic chains.

Typical NMR data are given for $n = 12$. ^1H NMR: δ (ppm) = 7.75 (d, 2H, $J_{\text{trans}} = 15$ Hz, ethylenic H); 7.60

(m, 10H); 6.85 (d, 2H, $J_{\text{ortho}} = 6.25$ Hz, aromatic H); 4.00 (2t, 8H, OCH_2CH_2); 1.85 (m, 8H, OCH_2CH_2); 1.40 (m, 72H, $(\text{CH}_2)_9$); 0.90 (t, 12H, CH_3).

4.4. Heterocyclization reactions

In a typical experiment the finely crushed chalcone (0.16 mmol) and the acetophenone (1.6 mmol) were poured into 10 ml of acetic anhydride. To this mixture was added over 30 min 0.67 ml of anhydrous tetrafluoroboric acid in 0.3 ml of acetic anhydride (the anhydrous tetrafluoroboric acid was prepared by adding dropwise 0.67 ml of commercial aqueous tetrafluoroboric acid (37%) to 0.3 ml of acetic acid). The yellow solution turned rapidly to black-red. The reaction mixture was then heated at 50°C for 12–18 h. The disappearance of the chalcone was followed by TLC (eluent: dichloromethane). After cooling to room temperature, the precipitate was filtered off and washed with ethyl acetate. Several recrystallizations from ethyl acetate, acetic acid, ethyl acetate/acetone (50/50) and ethyl acetate/acetone in the presence of a drop of tetrafluoroboric acid, led to the desired pyrylium salt.

Typical NMR data are given in the case of salt **4** ($n = 12$; $m = 12$). ^1H NMR: δ (ppm) = 8.21 (d, 4H, $J = 2$ Hz); 8.06 (s, 4H); 7.89 (d, 4H, $J = 2$ Hz); 7.40 (s, 4H); 6.97 (d, 4H, $J = 2$ Hz); 6.90 (d, 4H, $J = 2$ Hz); 4.04 (t, 8H, $J = 7$ Hz); 3.95 (t, 8H, $J = 7$ Hz); 3.84 (t, 4H, $J = 7$ Hz); 1.89 (q, 10H, $J \sim 7$ Hz); 1.74 (q, 10H, $J \sim 7$ Hz); 1.36 (m, $J = 160$ Hz); 0.85 (t, 24H, $J = 7$ Hz).

References

- [1] TSCHERSKE, C., 1998, *J. Mater. Chem.*, **8**, 1485.
- [2] NEVE, F., 1996, *Adv. Mater.*, **8**, 277.
- [3] DAVIDSON, P., JALLABERT, C., LEVELUT, A. M., STRZELECKA, H., and VEBER, M., 1988, *Liq. Cryst.*, **3**, 133.

- [4] VEBER, M., SOTTA, P., DAVIDSON, P., LEVELUT, A. M., JALLABERT, C., and STRZELECKA, H., 1990, *J. Phys. Fr.*, **51**, 1283.
- [5] VEBER, M., unpublished results. The pyridinium salt is very unstable leading by hydrolysis to the starting pyridine; the mesophase was characterized only by microscopic observation.
- [6] ZINSOU, A., VEBER, M., STRZELECKA, H., JALLABERT, C., and LEVELUT, A. M., 1994, *Liq. Cryst.*, **17**, 513.
- [7] ECOFFET, C., MARKOVITSI, D., JALLABERT, C., STRZELECKA, H., and VEBER, M., 1992, *J. Chem. Soc. Faraday Trans.*, **88**, 3007.
- [8] ALBOUY, P. A., VANDEVYVER, M., PEREZ, X., ECOFFET, C., MARKOVITSI, D., VEBER, M., JALLABERT, C., and STRZELECKA, H., 1992, *Langmuir*, **8**, 2262.
- [9] STRZELECKA, H., JALLABERT, C., VEBER, M., and MALTHETE, J., 1988, *Mol. Cryst. Liq. Cryst.*, **156**, 347.
- [10] BOULIGAND, Y., 1980, *J. Phys.*, **41**, 1307.
- [11] OSWALD, P., 1988, *J. Phys. Fr.*, **49**, 1083; OSWALD, P., 1988, *J. Phys. Fr.*, **49**, 2119.
- [12] VEBER, M., JALLABERT, C., STRZELECKA, H., JULLIEN, O., and DAVIDSON, P., 1990, *Liq. Cryst.*, **8**, 775 and references therein.