Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Non-symmetrical dithiolium salts Mesomorphic properties

M. Veber[a]; C. Jallabert[b]; H. Strzelecka[b]; O. Jullien[b]; P. Davidson[a]
[a] Laboratoire de Physique des Solides LA2, Université Paris XI, Orsay Cédex, France [b] Laboratoire de Chimie et Electrochimie des Matériauz Moléculaires, UA 429, ESPCI, Paris Cédex 05, France

To cite this Article Veber, M. , Jallabert, C. , Strzelecka, H. , Jullien, O. and Davidson, P.(1990) 'Non-symmetrical dithiolium salts Mesomorphic properties', Liquid Crystals, 8: 6, 775 — 785
To link to this Article: DOI: 10.1080/02678299008047388
URL: http://dx.doi.org/10.1080/02678299008047388

LIQUID CRYSTALS, 1990, VOL. 8, NO. 6, 775–785

Non-symmetrical dithiolium salts

Mesomorphic properties

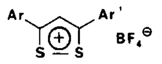
by M. VEBER‡, C. JALLABERT†, H. STRZELECKA†,
O. JULLIEN† and P. DAVIDSON‡
†Laboratoire de Chimie et Electrochimie des Matériauz Moléculaires, UA 429,
ESPCI, 10, rue Vauquelin, 75231 Paris Cédex 05, France
‡Laboratoire de Physique des Solides, LA2, Bâtiment 510, Université Paris XI,
91405 Orsay Cédex, France

(*Received 3 April 1990; accepted 8 July 1990*)

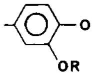
A series of non-symmetrical dithiolium salts has been synthesized. Classical characterization methods (DSC and optical microscopy) show that according to the number and nature of the substituents, these dithiolium salts display crystalline or smectic A phases. These S_A phases have been studied by X-ray diffraction and several models are proposed to describe the molecular organization in the mesophase. In some cases, it was not possible on the basis of X-ray diffraction data alone, to determine which model should apply. In these cases, however, a comparison with similar molecules shows that one of these models is more probable than the others.

1. Introduction

In the course of our work on liquid crystals based on heteroaromatic salts, we present here a series of non-symmetrical 3,5-diaryl 1,2-dithiolium tetrafluoroborates **1**:



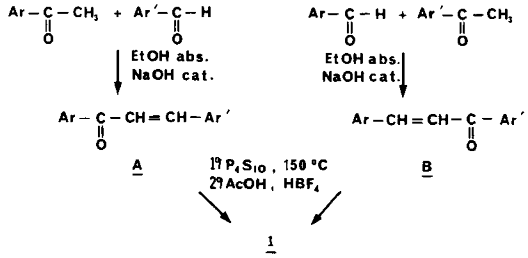
1

We have previously described symmetrical 3,5-diaryl 1,2-dithiolium salts in which Ar = Ar′ [1–3]. In this case, the mesomorphic properties are related to the number of alkyl chains per molecule. Namely, compounds with two chains per cation (i.e. Ar = Ar′ = *p*-alkylphenyl,*p*-(or meta-)alkyloxyphenyl) exhibit S_A phases [1, 2] whereas those with four chains per cation (Ar = Ar′ = ) exhibit columnar mesophases [3]. In order to understand the influence upon the mesomorphic properties of the number and the nature of the substituents grafted onto the aryl groups, we have synthesized the series of salts **1**. In particular, we wanted to know if the salts **1** with three long alkyloxy chains presented S_A, D_h phases, or an intermediate lamello-columnar organization [4].

2. Synthesis and characterization

2.1. *Synthesis*

Tetrafluoroborates **1** were obtained by the same procedure as for symmetrical salts [2] but starting from isomeric chalcones (A or B). These chalcones were prepared by condensation of acetophenones and benzaldehydes bearing different substituents:



The results are summarized in table 1. The yields of isomeric chalcones A and B are approximately the same (between 60 and 90 per cent). On the other hand yields of salts **1** are higher when starting from chalcones B and are then comparable with those obtained for symmetrical dithiolium salts. The experimental part is presented in the Appendix.

2.2. *Microscopic observations and differential scanning calorimetry*

Microscopic observations were performed with a Letiz Orthoplane microscope under polarized light. The variable temperature stage was a Mettler FP 80. DSC results were obtained with a DSC 7 Perkin–Elmer apparatus.

Most of the synthesized salts display fan shaped textures, growing from the isotropic phase as bâtonnets and (or) large homeotropic domains (see figure 1).These textures are characteristic to smectic A phases [5] and have also to be compared with the textures exhibited by the S_A phase of symmetrical dithiolium salts with two alkyloxy chains. In this latter case, the textures presented very few homeotropic domains but large birefringent areas. Therefore, the non-symmetry of the salts

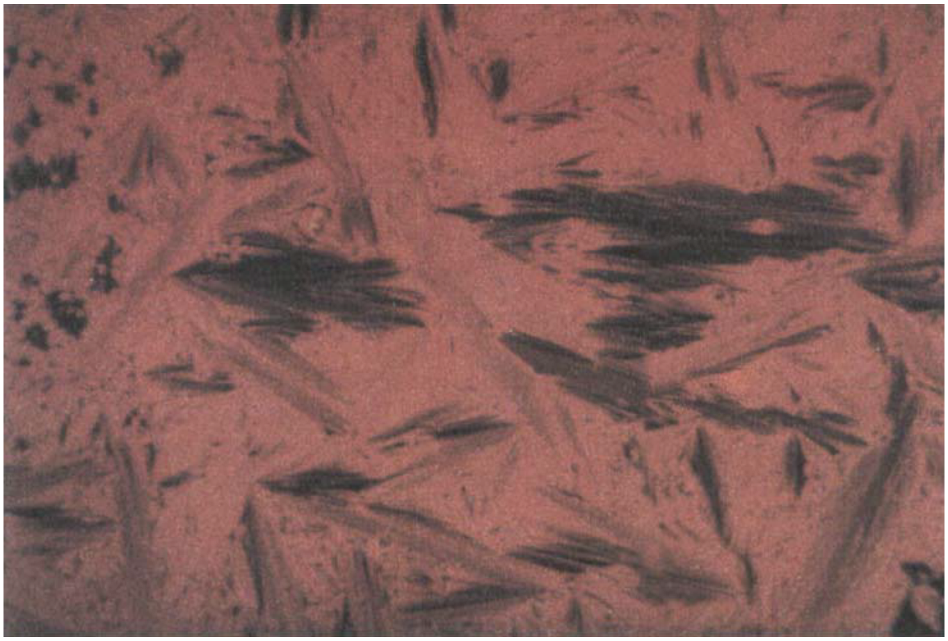
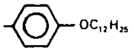
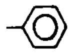
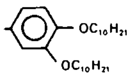
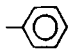
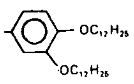
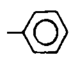
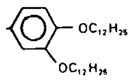
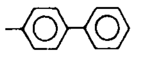
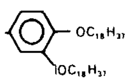
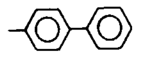
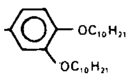
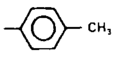
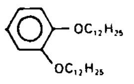
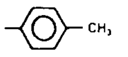
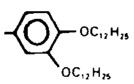
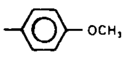
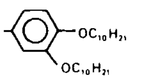
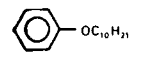
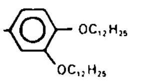
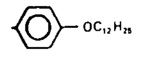


Figure 1. Microscopic texture of salt **1k** in the S_A phase at 144°C, through crossed polarizers.

Table 1. Yields and absorption bands for the different non-symmetrical dithiolium tetrafluoroborates (**1a**–**1l**) obtained from isomeric chalcones A and B (A, Ar–CO–CH=CH–Ar′; B, Ar–CH=CH–CO–Ar′)

Salts **1**	Ar	Ar′	†	Yields‡ of **1** from A	Yields‡ of **1** from B	UV-Vis.§ λ/nm	Yields of chalcones % A	Yields of chalcones % B
a				29		452 369	85	
d			●	6	23	486 365	62	64
e			●		14	489 365		74
f					17	493 427 276		57
g			●		16	494 426 276		54
h				10	17	488 390	86	87
i			●	7.5	15	487 389	91	84
j				27		490 390	65	
k			●	15	21	489 ep. 430	59	78
l			●		21	487 389		74

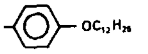
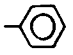
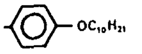
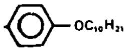
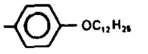
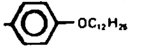
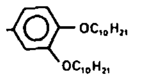
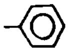
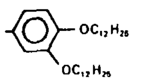
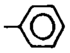
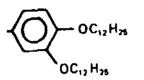
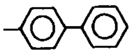
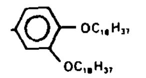
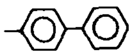
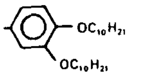
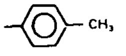
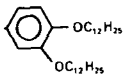
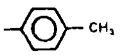
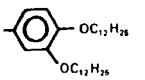
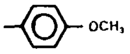
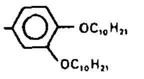
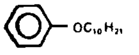
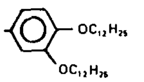
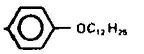
† Mesomorphism is observed.

‡ Data refer to pure recrystallized products.

§ Molecular concentration: 10^{-4} M/CH_2Cl_2.

1 seems to favor homeotropic anchoring. The transition temperatures, summarized in table 2, were determined either by microscopic observations or by DSC measurements see figure 2). Comparison with symmetrical dithiolium salts shows that all of the transition temperatures are lower for the non-symmetrical dithiolium tetrafluroborates

Table 2. Transition temperatures of symmetrical and non-symmetrical dithiolium salts. C, crystal; S_A, smectic A phase; I, isotropic liquid.

Salts	Ar	Ar′	Transition températures °C
a			$$\begin{tikzcd} C_1 \arrow[rr, "113\cdot3"] \arrow[dr, "45\cdot7"'] & & I\dagger \arrow[dl, "84\cdot1"] \\ & C_2 & \end{tikzcd}$$
b		** 	$C \xrightleftharpoons{175} S_A \xrightleftharpoons{190} I$
c		** 	$C \xrightleftharpoons{170} S_A \xrightleftharpoons{213} I$
d			$$\begin{tikzcd} C_1 \arrow[r, "65\cdot4"] & C_2 \arrow[rr, "140"] \arrow[dr, "95\cdot4"'] & & I \arrow[dl, "139\cdot7"] \\ & & S_A & \end{tikzcd}$$
e			$C_x \xrightleftharpoons[88\cdot6]{126\cdot5} S_A \xrightleftharpoons[161]{163\cdot9} I$
f			$C \xrightleftharpoons[156]{172} I$
g			$C \xleftarrow[140]{} S_A \xrightleftharpoons{180} I$
h			$C \xrightleftharpoons[140\cdot7]{145\cdot8} I$
i			$C \xrightleftharpoons[135\cdot3]{134\cdot7} S_A \xrightleftharpoons[140\cdot2]{143\cdot9} I$
j			$C \xrightleftharpoons[162]{180\cdot6} I$
k			$C \xrightleftharpoons[134\cdot5]{142} S_A \xrightleftharpoons[153]{153} I$
l			$C \xleftarrow[132]{} S_A \xrightleftharpoons{146} I$

† From [2]. **$X^- = ClO_4^-$.

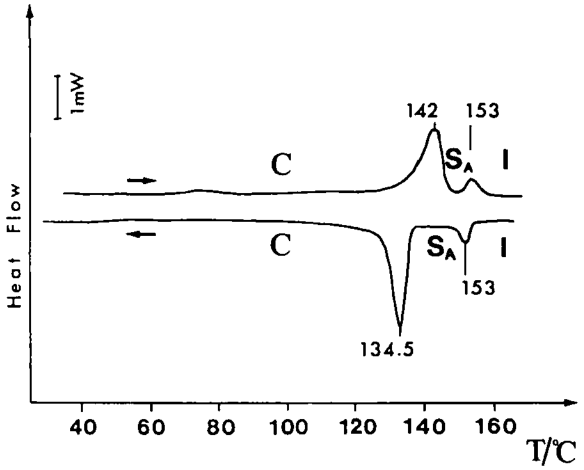


Figure 2. The DSC curve for salt **1k** (heating and cooling rates: 10°C/min).

than for the symmetrical ones. Moreover, if we compare compounds **1i** and **1j**, it can be noted that the presence of the methoxy group leads to a crystalline compound while substitution with a methyl group leads to a mesomorphic salt. Finally, it may be surprising that compound **1g** with a biphenyl shows an enantiotropic S_A phase in spite of the bulkiness of the aromatic substituent. However it should be noted that, in this case, octadecyloxy substituents are necessary to observe the S_A phase.

3. X-ray results

Aligned samples could be obtained by slow cooling from the isotropic into the S_A phase in a magnetic field (1·7 T). The samples were contained in Lindemann glass capillary tubes of 1·5 mm diameter. The samples were examined with an X-ray set up already described [4]: a point focused monochromatic X-ray beam (λCuKα = 1·541 Å) was obtained by reflection with a doubly bent graphite monochromator. The sample, in its capillary tube is set in an oven heated by an air stream (temperature regulation ± 1°C). The oven is placed between the two poles of an electromagnet. The camera is evacuated in order to suppress air scattering. The diffracted X-rays are collected on a cylindrical film 60 mm from the sample.

All the mesomorphic salts show the same type of X-ray diffraction pattern. Let us describe one of them (see figure 3) displayed by the oriented compound **1l**:

> At small angles and along the magnetic field direction (meridian), we can see a series (first and second orders) of equidistant Bragg spots (*a*); they are the reflections on the smectic layers.
>
> At wide angles, along the equator and perpendicular to it, we can see a slightly oriented diffuse ring (*b*) ($\mathbf{s} \approx 1/4{\cdot}6\,\text{Å}^{-1}$ with $|\mathbf{s}| = 2\sin\theta/\lambda$ where $\mathbf{s}$ is the scattering vector). This diffuse ring is due to the lateral interference of the mesogenic cores and to the interference from the molten state of the aliphatic chains. Therefore, this X-ray diffraction pattern is characteristic of a S_A phase.

It can be seen in figure 3 that although the Bragg spots are well defined (the mosaicity of the sample is not very large), the wide angle diffuse ring is not very well

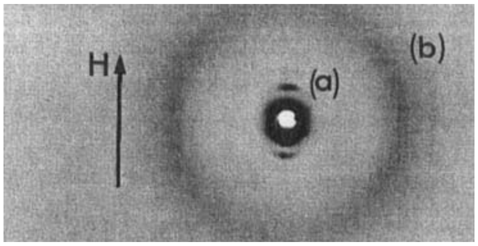


Figure 3. The X-ray diffraction pattern of salt **1l** in its S_A phase. (CuKα = 1·54 Å, sample-film distance: 60 mm).

oriented. This situation usually happens for most hexagonal columnar mesophases [6]. It has also been encountered for the S_A phase of a charge transfer complex [4]. This means that the aliphatic chains are more disordered than in a conventional monolayer S_A phase. By carefully inspecting figure 3, some very weak diffuse intensity can be detected on the equator at a wavevector $\mathbf{q} = 1/3{\cdot}5\,\text{Å}^{-1}$. Such intensity is usually due to the stacking of cores inside columns in columnar phases of discotic systems, [6]. Its observation in figure 3 shows that although the mesophase is clearly of S_A symmetry, locally a very slight short range order due to the cores stacking can be detected. (This short range order in no way affects the global symmetry of the phase which remains of the S_A type.) It should also be noted that no additional X-ray scattering can be detected that would be due to the presence of the anions. This means that the anions should be rather disordered; except that, no more information can be derived from the X-ray diffraction pattern about them. In this respect, the situation is similar to that encountered in a series of hexasubstituted pyrylium salts which have a hexagonal columnar mesophase D_h [7]. The smectic periods for each compound are given in table 3.

Now, let us discuss the molecular packing in this mesophase. We need to distinguish two cases.

(1) *Ar′ does not have any long alkyloxy chain*

In this case, the aliphatic side chains are all grafted on the same phenyl (Ar). (compounds **1d**, **1e**, **1g** and **1i**). Taking into account the length of the cation (measured on Dreiding stereomodels and given in figure 4) compared to the smectic period, it follows that the smectic organization should be partially bilayered (see figure 5 (*a*)). At this point, we assume that a pair of dithiolium cations may be represented by a cylinder and, in the absence of any mesophase density measurements, that the mesophase density is close to 1 which is the case for most usual mesophases. Then,

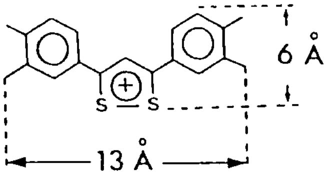


Figure 4. Scheme for the mesogenic dithiolium core.

Table 3. Structural parameters of the S_A phase according to each assumed model (Monolayer, partial bilayer and bilayer models). *M* is the molar mass, *d* is the smectic period, *l* is the molecular length measured in the most extended configuration possible (this value has only been added here for information since it would be difficult to correlate it with the smectic period *d* in a straightforward way), *x* is defined in figure 5, *S* is the mean area per aliphatic chain and V_{CH_2} is the volume per CH_2 group.

					Monolayer model			Partial bilayer model			Bilayer model		
Salts 1	*X*–	*M*/g	*l*/Å	*d*/Å	*x*/Å	*S*/Å^2	*V*/Å^3	*x*/Å	*S*/Å^2	*V*/Å^3	*x*/Å	*S*/Å^2	*V*/Å^3
b	ClO4–	666·5	39	29·5	6·9	37·5	31	—	—	—	9·8	37·5	33
c	ClO4–	722·5	42	31·5	7·0	38·5	30	—	—	—	9·9	38·5	31
d	BF4–	654	26	35·1	—	—	—	8·9	31	34·5	—	—	—
e	BF4–	710	28	37·0	—	—	—	9·0	32	32	—	—	—
g	BF4–	954	39	39·8	—	—	—	10·1	39	30	—	—	—
i	BF4–	724	29	33·1	—	—	—	9·6	36	29	—	—	—
k	BF4–	810	39	29·1	7·7	31	25	—	—	—	10·9	31	26·5
l	BF4–	894	42	30·8	7·8	32	23·5	—	—	—	11·1	32	25·5

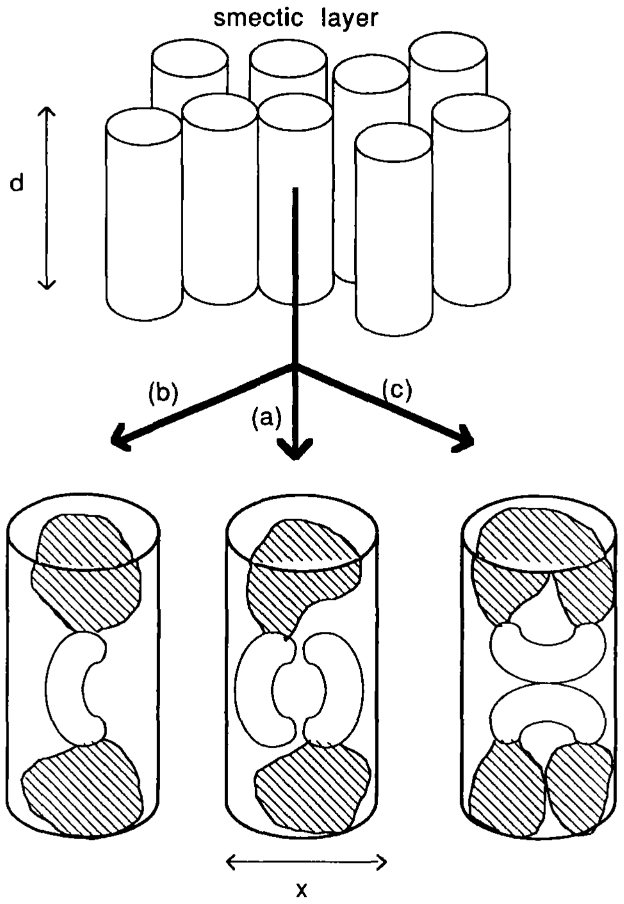


Figure 5. Assumed models for the molecular organization in the S_A phase. (*a*) Partial bilayer model; (*b*) Monolayer model; (*c*) Bilayer model.

the diameter x of this cylinder may be obtained from

$$\rho = \frac{2M}{(\pi x^2/4)\, d N_A}$$

where M stands for the molecular weight of the salt. The value of x for each compound is given in table 3. The mean area per aliphatic chain S can be evaluated from $S = \pi x^2/8$. These values are larger than those found classically in the case of S_A phases [8] and comparable to those of discotic systems [9] and to that of a charge transfer complex [4]. This means that the aliphatic chains are far from being well aligned along the normal to the layers as they usually are in classic S_A phases. On the contrary, they are very disordered which could already be inferred from the already mentioned poor orientation of the wide angle diffuse ring. The mean volume per methylene group may also be calculated: the width of the region of aromatic cores d_{A_r} is $13 \pm 0{\cdot}5$ Å (see figure 4). Therefore the aliphatic volume V_{al} in the cylinder of diameter x and width d is $\pi x^2/4\ (d - d_{A_r})$. (This assumes implicitly that the anions are located in the aromatic region of the cylinder in order to minimize the electrostatic energy.) The volume per CH_2 group V_{CH_2} is $V_{al}/2n$ where $2n$ is the total number of aliphatic carbons in the side chains of a cation. This volume per methylene group is presented in table 3 for each compound **1d**, **1e**, **1g** and **1i**. These results are comparable to those obtained for smectic, hexagonal or lamello-columnar phases [4, 7, 8, 10]. In conclusion, it seems that the partially bilayered model gives reasonable values for S and V_{CH_2} and therefore describes well the case of the compounds which have all of their side chains on the same phenyl ring.

(2) *Both Ar and Ar′ have long alkyloxy chains*

In this second case, each phenyl (Ar) and (Ar′) is substituted by at least one aliphatic chain (compounds **1b**, **1c**, **1k** and **1l**). This case is more complicated because two molecular organizations may account for the observed smectic period. In the first one that we shall call the bilayer packing, the side chains grafted on to the two phenyl rings of a given cation point in the same direction (see figure 5 (*c*)). In the second that we shall call the monolayer packing the side chains grafted on to the two phenyl rings of a given cation point in opposite directions (see figure 5 (*b*)). Since the cationic mesogenic core is approximately twice as long as wide (see figure 4), these two types of organization lead to approximately the same smectic period. Moreover, the assumption that the mesophase density is equal to one implies that the area per aliphatic chain is the same for each model. Therefore the two models may only be distinguished by the volume per methylene group. Unfortunately, these two models give similar values for the volume per methylene group. For compounds **1k** and **1l** these values are somewhat too low compared to what is usually found (28–30 Å^3) [4, 7, 8, 10]; indeed, for crystallized aliphatic chains, i.e. paraffins, $V_{CH_2} \approx 25\,Å^3$ [11]. This difference may be due to the assumption that the mesophase density is equal to one. Actually, the monolayer model leads to values for the volume per methylene group even smaller than those derived from the bilayer model. However, this might be brought about by our assumption that the mesogenic core is strictly aligned along the director. Indeed, if we allow the mesogenic cores to fluctuate in orientation then d_{Ar} will decrease and V_{CH_2} will increase to reach more reasonable values. Such a situation has already been described in the smectic phase of some phasmidic molecules [12]. Therefore, we cannot, on the basis of X-ray diffraction data alone, choose between these two models.

Nevertheless, we have already suggested a bilayer model for the organization in the S_A phase of compounds belonging to a series of pryrilium salts closely related to the present one [13]. This bilayer model is similar to that reported for the lamellar lyotropic phases of amphiphilic molecules [14]. The dithiolium salts **1**, thanks to the ionic character of their mesogenic cores and to the presence of their long alkyloxy chains, possess some kind of amphiphilic properties. Therefore, by analogy, we favour the bilayer model, without being able to rule out the monolayer one.

4. Conclusion

It has been shown that a great number of the non-symmetrical dithiolium salts described in table 1 display S_A phases. It should be noted that salts **1** substituted by three long alkyloxy chains (compounds **1k** and **1l**) do not display either a D_h phase or an intermediate lamello-columnar organization but a S_A phase. This S_A phase, though, has a very weak local order in the stacking of the cores.

The molecular organization in the S_A phase has been discussed for the following cases:

> Where only one end (say Ar) of the mesogenic cores is substituted by aliphatic chains, an unambiguous structural model for the organization of the phase may be proposed. This partial bilayer model is in agreement, as regards the area per aliphatic chain and the volume per methylene, with the values obtained for the usual mesophases.
>
> Where both ends (Ar and Ar′) of the mesogenic core are substituted by aliphatic chains, two models may be proposed: a monolayer and a bilayer model. Though we favour the bilayer model, we cannot rule out the monolayer one only on the basis of structural considerations. Other experiments should be carried out to solve this problem; they could be of two kinds. The first uses the fact that these mesomorphic salts are red. The anisotropic absorption of a characteristic optical transition by an oriented sample may show the orientation of the mesogenic cores with respect to the director. A second would be to study the miscibility between these mesomorphic salts and compounds displaying either a monolayer S_A phase or a bilayer S_A phase. There might also exist a dynamic equilibrium between molecules in a bilayer configuration and molecules in a monolayer configuration.

Finally, let us note that we did not derive from the X-ray diffraction patterns any additional information about the BF_4^- anions except that they should be disordered and located close to the mesogenic cores of the cations where the largest positive electronic charges are to be found.

The authors would like to thank Drs. A.M. Levelut and L. Liébert for valuable discussions.

Appendix

4-alkyloxyacetophenones, 4-alkyloxybenzaldehydes and 3,4-dialkyloxybenzaldehydes were obtained from commercial hydroxy derivatives using a method previously described [15]. 3,4-dialkyloxyacetophenones were prepared by acetylation of 1,2-dialkyloxybenzene (Ac_2O, $AlCl_3$, CH_2Cl_2).

Chalcone A or B were obtained by condensation of acetophenones with appropriate benzaldehydes under basic conditions [16]. The following procedure is representative of the synthesis of the chalcones.

1-(4′-decyloxyphenyl)3-(3,4-didecyloxyphenyl) propenone

To 4-decyloxyacetophenone (5·52 g, 20 mmol) and 3,4-didecyloxybenzaldehyde (8·37 g, 20 mmol) in absolute ethanol was added a catalytic amount of sodium hydroxyde (1 or 2 pellets). The mixture was vigorously stirred for one night at room temperature. The precipitate was filtered off washed with ethanol and recrystallized from ethanol or acetonitrile. Yield: 10·6 g (78 per cent) ^{1}H NMR δ(ppm), (CD Cl_3/TMS): 0·85 (9 H, m, CH_2-CH_3), 1·2–2 (48 h, m, $(CH_2)_8$), 4 (6 H, *t*, OCH_2) and 6·9–8·1 (9 H, m, $CH{=}CH$ and aromatic H). IR KBr: 1650 cm^{-1} ($\nu_{C=O}$), 1600 cm^{-1}, 1590 cm^{-1}, 1500 cm^{-1} (ν aromatics), 1260 cm^{-1} (ν_{OR}).

The dithiolium tetrafluoroborates were prepared by a method already described [2] and detailed here. A mixture of chalcone (2 mmol) and P_4S_{10} (1 mmol) was stirred for 1 hour at 150°C. After cooling 20 ml of acetic acid and 2 ml of HBF_4 (34 per cent) were added and the mixture was refluxed for 1 hour. Dithiolium salt precipitated either directly upon cooling or by addition of ether. The salt was filtered off, washed with ether and recrystallized from ethanol in the presence of HBF_4. The purity of this salt was checked by thin layer chromatography (silica gel, pentane/ethylacetate 90/10). ^{1}H NMR and IR spectra are given here for salt **1k**: ^{1}H NMR δ(ppm), ($CDCl_3$/TMS): 0·9 (9 H, m, CH_2-$C\mathit{H}_3$), 1·2–2·4 (48 H, m, $(CH_2)_8$), 4 (6 H, *t*, $OC\mathit{H}_2$), 6·9–8 (7 H, m, aromatic H) and 8·7 (1 H, s, dithiolyl H). IR KBr: 2950 cm^{-1}, 2900 cm^{-1}, 1605 cm^{-1}, 1490 cm^{-1}, 1360 cm^{-1}, 1300 cm^{-1}, 1280 cm^{-1} (OR), 1200 cm^{-1}, 1160 cm^{-1}, 1100 cm^{-1} (BF_4^-), 840 cm^{-1}, 720 cm^{-1}.

References

[1] Veber, M., Jallabert, C., Strzelecka, H., Gionis, V., and Sigaud, G., 1986, *Molec. Crystals liq. Crystals*, **137**, 373.

[2] Veber, M., Jallabert, C., and Strzelecka, H., 1987, *Synth. Commun.*, **17**, 693.

[3] Strzelecka, H., Jallabert, C., Veber, M., Davidson, P., Levelut, A.M., Malthête, J., Sigaud, G., Skoulios, A., and Weber, P., 1988, *Molec Crystals liq. Crystals*, **161**, 403, and references therein.

[4] Davidson, P., Levelut, A.M., Strzelecka, H., and Gionis, V., 1983, *J. Phys. Lett., Paris*, **44**, L823.

[5] Gray, G. W., and Goodby, J. W. G., 1984, *Smectic Liquid Crystals* (Leonard Hill, and Heydon and Son, Inc).

[6] Levelut, A.M., 1983 *J. Chim. phys.*, **80**, 149.

[7] Davidson, P., Jallabert, C., Levelut, A.M., Strzelecka, H., and Veber, M., 1988, *Liq. Crystals*, **3**, 133.

[8] Guillon, D., and Skoulios, A., 1976, *J. Phys., Paris*, **37**, 797.

[9] Guillon, D., Skoulios, A., Piechoki, C., Simon, J., and Weber, P., 1983, *Molec. Crystals liq. Crystals*, **100**, 275.

[10] Cayuela, R., 1986, Ph.D. Thesis, Bordeaux, p. 91.

[11] Doucet, J., Denicolo, I., and Germain, C., 1984, *J. chem. Phys.*, **80**, 1647.

[12] Levelut, A.M., Fang, Y., and Destrade, C., 1989, *Liq. Crystals*, **4**, 441.

[13] Sigaud, G., Hardouin, G., Gasparoux, H., Gionis, V., Veber, M., and Strzelecka, H., 1983, *Molec. Crystals liq. Crystals*, **92**, 217.

[14] See for instance, Hendrikx, Y., and Levelut, A. M., 1988, *Molec. Crystals liq. Crystals*, **165**, 233.

[15] Strzelecka, H., Jallabert, C., Veber, M., and Malthête, J., 1988, *Molec. Crystals liq. Crystals*, **156**, 347.

[16] Wattanasin, S., and Murphy, W. S., 1980, *Synthesis*, **8**, 647.