Effect of counterions on the thermotropic and thermochromic properties of ionic liquid crystals

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Novel liquid crystal materials based on 1-alkyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium and bearing bromide, alkyl sulphate or bis(2-ethylhexyl)sulphosuccinate counterions were prepared. Their thermotropic and thermochromic properties were characterized and compared. It was established that the majority of these compounds exhibited SmA mesophases. The observation of thermochromic properties for certain of the compounds is considered to be the consequence of the existence of a charge-transfer complex between the pyridinium cation and its counterion.

1. Introduction

We have recently reported the preparation and characterization of novel liquid crystal materials based on 1-alkyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium bromide (see the scheme) [1]. The materials were designed in such a manner as to combine an oxadiazole and a pyridinium moiety in an ionic compound. This structure could, in principle, enhance their electron transport and conductivity properties, thereby providing new and promising functional materials for optical and electronic applications.

The mesomorphic properties of these compounds, their UV and fluorescence spectra, as well as their thermochromic properties have been investigated. They emit light and give rise to disordered smectic A (SmA) mesophases. They also exhibit thermochromic properties, their colour changing from yellow at room temperature to bright red at the transition to the mesophase. The main limitation of these compounds, as far as their potential applications are concerned, is their low degradation temperature, occurring well below the mesophase to isotropic transition. This makes the orientation of the materials on an appropriate substrate very difficult, as this is usually achieved by slowly cooling the material from the isotropic phase into the mesophase. To overcome this problem, the clearing temperature T_{cl} of the materials must be lowered below their degradation temperatures.

For conventional rod-like liquid crystals, the thermal stability of the mesophase depends mainly on the shape anisotropy of the mesogens and on the amphiphilic character of the core and the side chains. The shape anisotropy can be reduced by shortening the mesogenic groups or by introducing a geometric perturbation [2, 3]. The amphiphilic character can be weakened by diminishing the effects of microsegregation within the phase. This can be accomplished by reducing the difference in polarizability between the core and the side chains, and is usually achieved by replacing the alkyl chains with oligo(oxyethylene) moieties, or by altering the type of the core and/or the number of side chains. For ionic liquid crystals, it is easy to modify the number of side chains using a counterion such as an alkyl sulphate or a bis(2-ethylhexyl)sulphosuccinate as a replacement for a bromide ion. The use of an alkyl sulphate counterion has already been reported in the literature and resulted in the formation of ionic liquid crystals with low phase transition temperatures [4–6].

The replacement of the counterion used could also give an opportunity for investigating the relationship between the pyridinium moiety and its counterion. It is well documented that monomeric compounds bearing pyridinium or bipyridinium units act as electron acceptors, and can form coloured charge-transfer complexes with halide ions acting as electron donors [7–9]. It was interesting therefore to investigate how charge-transfer properties would be affected by the substitution of the bromide ion with a considerably bulkier and less electron-donating counterion such as an alkyl sulphate ion. The mesomorphic properties, UV and fluorescence spectra, and the thermochromic

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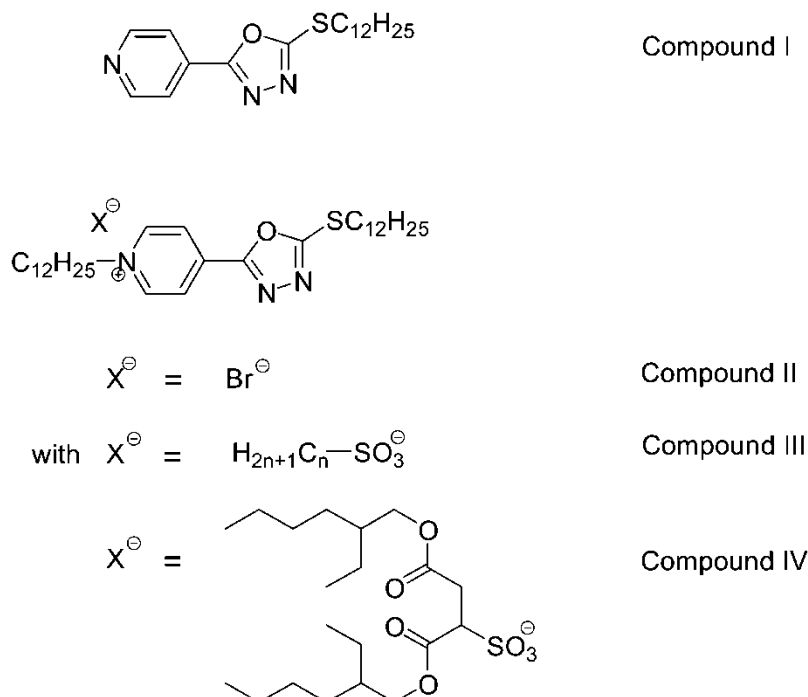
Scheme. Molecular structures of 2-dodecylsulphanyl-5-(4-pyridinyl)-1,3,4-oxadiazole (compound **I**) and of 1-dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium X^- derivatives, with X^- being bromine (compound **II**), alkyl sulphate (compound **IIIa,b**) or bis(2-ethylhexyl)sulphosuccinate (compound **IV**).

properties of the derivatives obtained (see the scheme) were investigated and compared.

2. Experimental
2.1. Materials and synthesis

Pyridinium alkyl sulphate derivatives were prepared by an ion exchange reaction between 1-dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium bromide **II** and the appropriate sodium alkyl sulphate. Compound **II** was synthesized from the corresponding pyridine compound **I** according to a method described elsewhere [1]. The structures of the compounds prepared were established by ^1H and ^{13}C NMR spectroscopy.

2.1.1. Synthesis of 1-dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium alkyl sulphate (III)

1-Dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium bromide and the appropriate alkyl sulphate sodium salt (1.1 equiv.) were dissolved, separately, in minimum quantities of ethanol, at room temperature, and then mixed. The solution obtained was slowly concentrated under reduced pressure until a white precipitate appeared. The precipitate was filtered off, dried under vacuum and recrystallized from ethanol

to give the pure pyridinium alkyl sulphate derivative (50% average yield).

1-Dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium decyl sulphate (IIIa). ^1H NMR (DMSO/250 MHz): 9.2 (d, 6.6 Hz; 2 H); 8.6 (d, 5.9 Hz; 2 H); 4.6 (t, 7.3 Hz; 2 H); 3.7 (t, 6.6 Hz; 2 H); 3.4 (t, 6.6 Hz; 2 H); 1.9 (q, 6.6 Hz; 2 H); 1.8 (q, 7.3 Hz; 2 H); 1.5 (q, 6.6 Hz; 2 H); 1.4 (q, 7.3 Hz; 2 H); 1.2 (m, 48 H); 0.8 (t, 6.6 Hz; 9 H). ^{13}C NMR (DMSO/250 MHz): 167.9; 146.1; 137.1; 124.2; 65.6; 61.1; 32.2; 31.3; 30.7; 29.0 (large); 28.4; 27.8; 25.5; 25.4; 22.1; 13.9. UV (solution in CHCl$_3$, nm): 235 (14.7 × 10^6); 270 (3.7 × 10^6); 280 (4.7 × 10^6); 290 (4.8 × 10^6); 345 (19.2 × 10^6). Elemental analysis for C$_{41}$H$_{75}$N$_3$O$_4$S$_2$: calc. C 66.71, H 10.24, N 5.69, O 8.67, S 8.69; found C 65.49, H 10.40, N 5.56%. This analysis indicates the presence of two molecules of water for three molecules of IIIa: C$_{41}$H$_{75}$N$_3$O$_4$S$_2$.2/3 H$_2$O: calc. C 65.64, H 10.26, N 5.60, O 9.95, S 8.55%. IR (KBr, cm^{-1}): 3127; 3076; 2958; 2872; 2920; 2850; 1648; 1590; 1558; 1511; 1467; 1458; 1379; 1252; 1218; 786; 722; 695; 580.

1-Dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium tetradecyl sulphate (IIIb). ^1H NMR (DMSO/250 MHz): 9.2 (d, 6.2 Hz; 2 H); 8.6 (d, 6.2 Hz; 2 H); 4.6 (t, 6.4 Hz; 2 H); 3.6 (t, 6.2 Hz; 2 H); 1.9 (q; 6.4 Hz, 2 H); 1.8 (q; 6.6 Hz, 2 H); 1.4 (m, 2 H); 1.2 (m; 58 H); 0.8 (t, 6.9 Hz; 9 H). ^{13}C NMR and UV

spectra for compound ***IIIb*** were identical to those obtained for compound ***IIIa***. Elemental analysis for $C_{45}H_{83}N_3O_4S_2$: calc. C 68.05, H 10.53, N 5.29, O 8.06, S 8.07; found C 66.95, H 10.80, N 5.08%. This analysis indicates the presence of three molecules of water for four molecules of ***IIIb***: $C_{45}H_{83}N_3O_4S_2.3/4\ H_2O$: calc. C 66.91, H 10.54, N 5.20, O 9.41, S 7.94%. IR (KBr, cm^{-1}): 3127; 3076; 2958; 2872; 2920; 2850; 1648; 1590; 1558; 1511; 1467; 1458; 1379; 1252; 1218; 786; 722; 695; 580.

2.1.2. *Synthesis of 1-dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium bis(2-ethylhexyl) sulphosuccinate (IV)*

1-Dodecyl-4-[5-(dodecylsulphanyl)-1,3,4-oxadiazol-2-yl]pyridinium bromide and the bis(2-ethylhexyl)sulphosuccinate sodium salt (1.1 equiv.) were dissolved in the minimum quantities of ethanol at room temperature and then mixed. The solution obtained was slowly concentrated to about one third of its original volume and then a few drops of water were added. Phase separation was observed between the ethanol/water mixture and a more dense liquid. This liquid was separated by centrifugation and dried under vacuum affording the pure pyridinium bis(2-ethylhexyl)sulphosuccinate derivative as a very viscous amber coloured liquid (80% yield). ^{1}H NMR (DMSO/250 MHz): 9.2 (d, 6.6 Hz; 2 H); 8.6 (d, 6.6 Hz; 2 H); 4.6 (t, 6.9 Hz; 2 H); 3.9 (t, 5.5 Hz; 4 H); 3.6 (dd, 11.3 + 3.8 Hz; 1 H); 2.8 (m, 2 H); 1.9 (m, 2 H); 1.8 (q, 6.9 Hz; 2 H); 1.2 (m; 54 H); 0.8 (t, 7.6 Hz; 18 H). ^{13}C NMR (DMSO/250 MHz): 171.0; 168.3; 161.8; 146.1; 136.9; 124.2; 66.1; 66.0; 61.4; 61.1; 34.1; 32.1; 31.2; 30.7; 29.7; 29.6; 29.5; 29.0; 28.9; 28.8; 28.7; 28.6; 28.3; 27.8; 25.3; 23.1; 22.9; 22.4; 22.0; 13.9; 13.8; 10.8; 10.7. UV (solution in $CHCl_3$, nm): 235 (13.9×10^6); 270 (3.7×10^6); 280 (4.7×10^6); 290 (5.0×10^6); 345 (18.6×10^6). Elemental analysis for $C_{51}H_{91}N_3O_8S_2$: calc C 65.27, H 9.77, N 4.48, O 13.64, S 6.83; found C 65.35, H 10.34, N 4.45%. IR (KBr, cm^{-1}): 3121; 3060; 2959; 2872; 2926; 2856; 1737; 1645; 1582; 1557; 1506; 1465; 1456; 1379; 1240; 1215; 1036; 726; 699.

Note: the ^{1}H NMR peak corresponding to the methyl group in the α position to the sulphur atom (3.4 ppm) appeared too close to the peak of the water (3.6 ppm) to permit its integration in the case of compounds ***IIIb*** and ***IV***. The ^{13}C NMR peaks of the pyridinium derivatives are in agreement with literature data [6, 10].

2.2. *Characterization*

The thermal stability of the compounds was assessed by thermogravimetric analysis employing a TGA 2050 analyser (TA instruments) at a heating rate of $10°C\,min^{-1}$. UV-visible spectra were recorded on a Perkin Elmer Lambda-16 spectrophotometer and fluorescence spectra on a Perkin-Elmer LS-5B spectrophotometer. Liquid crystal textures were observed using a Leitz-Wetzlar polarizing microscope equipped with a Linkam hot stage. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-10 calorimeter (TA instruments) at a heating/cooling rate of $10°C\,min^{-1}$. Liquid crystalline phases were investigated by X-ray diffraction using $CuK_{\alpha 1}$ radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powdered samples were sealed in Lindemann capillaries and heated using an INSTEC hot-stage.

3. Results and discussion

3.1. *UV-visible absorption and photoluminescence spectroscopy*

The UV absorption spectra for compounds **I**, **II**, **IIIa** and **IV** in dichloromethane are presented in figure 1. Compound **I** exhibits a single intense absorption peak at 280 nm while compounds **II**, **IIIa** and **IV** exhibit similar spectra characterized by the presence of two intense peaks at 235 and 345 nm as well as three small peaks at 270, 280 and 290 nm. The only difference observed between the spectra of compounds **II**, **IIIa** and **IV** was in the intensity of the peaks. Their λ_{max} show a bathochromic shift of 65 nm as the pyridine moiety is changed to pyridinium, i.e. from 280 nm for compound **I** to 345 nm for compound **II**.

The emission fluorescence spectra for the same compounds are given in figure 2. All spectra were recorded from a dilute dichloromethane solution at $\lambda_{exc.} = 340$ nm for **I**, 380 nm for **II**, 330 nm for **IIIa** and
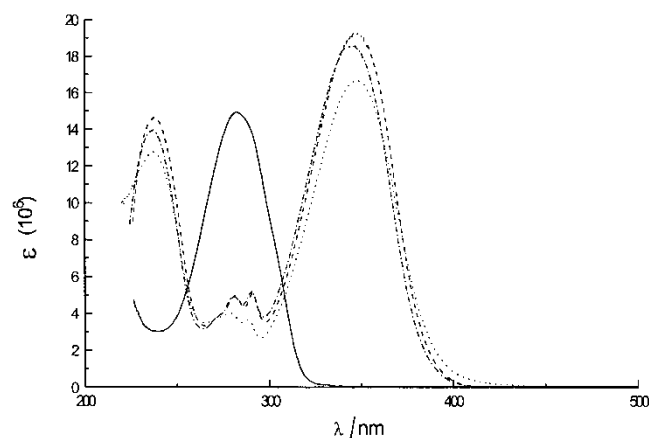

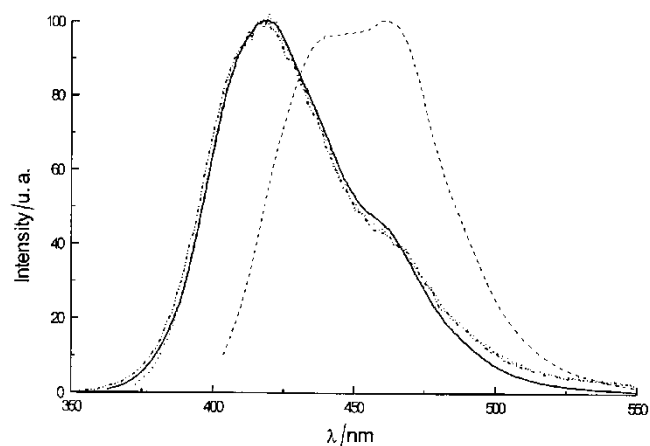Figure 1.   UV-visible spectra of compounds **I**(–), **II** (– –), **IIIa** (·····) and **IV** (–·–).

Figure 2. Fluorescence spectra of compounds **I** (–), **II** (–·–), **IIIa** (·····) and **IV** (–··–).

345 nm for **IV** (all values of $\lambda_{exc.}$ were obtained from their excitation spectra). All the compounds exhibited strong emission fluorescence with two maxima at 420 and 460 nm for **I**, **IIIa** and **IV**; and 440 and 460 nm for **II**.

3.2. Mesomorphic properties

The thermal stability of the compounds was studied by thermogravimetric analysis (TGA) and it was found that they all begin to decompose at temperatures above 145°C. Rapid decomposition becomes evident at temperatures above 170–180°C, i.e. below the T_{cl} of compound **II** but well above that for compounds **IIIa** and **IIIb** (see table). For this reason, X-ray diffraction (XRD) measurements were performed at temperatures lower than 140°C.

Data concerning the transition temperatures and the nature of the mesophase of compound **II** have been presented elsewhere [1]. Summarizing, on heating, compound **II** shows a first transition at 74°C and melts into a disordered mesophase at 119°C. At higher temperatures the compound becomes isotropic and simultaneously degrades, as is usually observed for ionic liquid crystals [11–13]. Thus the possibility of observing well-developed textures on cooling is precluded. The nature of these phases has been investigated

by XRD and it has been established that in all cases lamellar phases were obtained. The crystalline lamellar structure observed at room temperature is transformed, at temperatures above the first transition, into a lamellar crystal phase in which the alkyl chains are in a disordered conformation. At temperatures above the second transition an SmA phase was formed.

The thermal behaviour of compounds IIIa, IIIb and IV was studied by polarizing optical microscopy (POM) and DSC. Compounds IIIa and IIIb melted into birefringent fluid phases at 109 and 116°C and became isotropic at 141 and 144°C, respectively. In contrast to the behaviour of compound II, IIIa and IIIb do not degrade following clearing, and thus well-developed fan-shaped textures were obtained on cooling (figure 3), suggesting the presence of an SmA phase. Their enhanced thermal stability is further illustrated by the fact that successive DSC runs were all identical to the first. The transition temperatures and associated entropy changes of the compounds are shown in the table. For compound **IV** no transitions were observed from −50 up to 150°C by POM or DSC. Its fluidity and the absence of birefringence indicate that it exhibits only an isotropic phase in the temperature range examined. This was confirmed by XRD, its pattern being characteristic of an isotropic fluid.

At room temperature the X-ray patterns of compounds **IIIa** and **IIIb** were analogous to the crystal phase observed for compound **II**. In the small angle region, they contained up to five equidistant reflections suggesting the presence of a lamellar structure. A large number of sharp reflections in the wide angle region indicate the presence of a well-developed crystal phase. The lamellar periods d measured for compounds **IIIa** and **IIIb** were higher than that for **II**. Thus d was 28.5 Å for **II**, while for compounds **IIIa** and **IIIb** was 38.2 and 42.3 Å, respectively. This can be attributed to the presence of the bulkier sulphate group with its long aliphatic chain.

Table. Transition temperatures T (°C) and entropies ΔS (J mol^{-1} K^{-1}) observed by DSC.

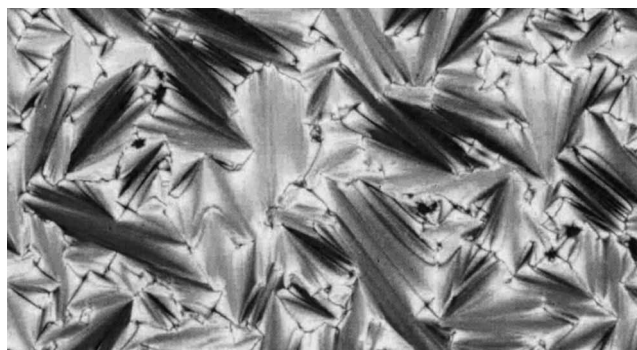| Compound	T [ΔS] Cr$_1$→Cr$_2$	T_f [ΔS] Cr$_2$→SmA	T_f [ΔS] Cr→SmA	T_{cl} [ΔS] SmA→I
II	73.8 [102.6]	118.6 [58.3]	—	184.6 [4.7]
IIIa	—	—	116.0 [156.9]	141.4 [6.2]
IIIb	—	—	108.9 [154.8]	143.9 [4.9]
IV	—	—	—	—

Figure 3. Textures observed by POM at 130°C for compound **IIIb** in the SmA phase.

The XRD patterns obtained at temperatures above the crystal–smectic transition temperatures exhibited characteristic features for smectic disordered mesophases, i.e. two sharp equidistant small angle reflections related to the smectic period and a diffuse wide angle reflection centred at about 4.5 Å, attributed to the correlation distances between adjacent melted chains (figure 4). The evolution of the smectic periods was studied in order to assess the exact nature of the disordered smectic phase; as commonly observed for SmA mesophases, their periodicity decreases with increasing temperature with a relative thermal expansion coefficient $(\partial d/\partial T)/d$ of 4×10^{-2} and $6 \times 10^{-2}\,\mathrm{K}^{-1}$ for **IIIa** and **IIIb**, respectively. The smectic periods were 27.6 Å for **IIIa** and 29.3 Å for **IIIb** at 125°C, being smaller therefore than that obtained for **II** at the same temperature (29.6 Å). This can be explained by the larger size of the sulphate counterion compared with bromide (2.58 Å for the sulphate as compared with the 1.88 Å of the bromide [14]), which increases the lateral molecular area occupied by the polar part of the compounds. Thus the side chains have more space to fill laterally, and the smectic period is decreased. This explanation is in good agreement with the observed increase of the average correlation distance between adjacent chains in the disordered conformation, i.e. from 4.2 Å for compound **II** to 4.5 Å for compounds **IIIa** and **IIIb**.

The main objective of this work was to lower the mesomorphic range of the compounds in order to avoid the problem of thermal degradation observed for **II**. The approach followed proved successful for compounds **IIIa** and **IIIb**, while compound **IV** exhibited an isotropic liquid phase. The reduction of the clearing temperature T_{cl} was about 42°C for compounds **IIIa**

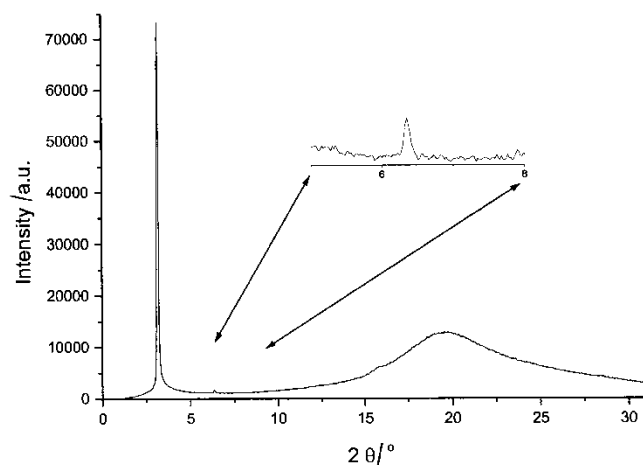and **IIIb**. The melting temperatures T_{f} were decreased by about 2 and 10°C for **IIIa** and **IIIb**, respectively. The decreases in T_{f} and T_{cl} also had an influence on the mesomorphic range which reduced from 66°C for **II** to 25 and 35°C for **IIIa** and **IIIb**, respectively. Finally the change of the counterion also resulted in the complete disappearance of the second crystal phase observed for compound **II**.

The effects on T_{cl}, as noted before, mainly depend on the amphiphilic character and on the effects of phase microsegregation resulting in the spatial separation of the side chains from the polar groups. By increasing the number of side chains, the thermal stability of the mesophase was decreased and thus it appeared at lower temperatures. On the other hand the length of the alkyl sulphate chain has little effect on T_{cl}, as the decrease observed was similar for compounds **IIIa** and **IIIb**.

For T_{f}, the effects observed can be explained by the decrease of the thermal stability of the crystal structure due to the weakening of the cohesion forces. To reduce these forces, it is possible to either reduce the size of the polar part or introduce a steric hindrance in the molecule, such as the bulky alkyl sulphate moiety. Indeed the sulphate head has the expected effect on the cohesion forces of the crystal phase, since the T_{f} was depressed weakly for both compounds.

3.3. *Thermochromic properties*

The crystal to SmA transition of compound **II** is associated with a colour change from pale yellow to bright red. This thermochromic effect occurred rapidly following the transition to the SmA phase, and was almost fully reversible upon cooling [1]. This type of effect has been described already for other compounds with similar structures, such as poly(oxadiazole) [15] or *N*-alkylcyanopyridinium iodide [16]. In the case of poly(oxadiazole) this property was attributed to a change in the average conjugation distances due to a change in the conformation of the main chain. For the cyanopyridinium derivative the formation/destruction of a coloured charge-transfer complex between the pyridinium moiety and its halide counterion has been suggested. In the case of small molecules such as compound **II**, it is reasonable to assume that the origin of this phenomenon may be attributed to charge-transfer rather than to a change in conformation of the main chain.

The replacement of the counterion used also provides an opportunity to investigate the relationship between the pyridinium core and its counterion. It is well documented that monomeric compounds bearing pyridinium or bipyridinium units, acting as electron acceptors, can form coloured charge-transfer complexes

Figure 4. X-ray diffraction pattern of compound **IIIa** in the SmA phase at 125°C.

with halide ions acting as electron donors [7–9]. It is anticipated however that charge-transfer complex formation will not be possible with the sulphate group, which has considerably weaker electron donor properties. Thus, if it were possible to establish that neither compound **IIIa** nor **IIIb** exhibits thermochromic properties, and that they have been unaffected by the change of counterion, this would support the charge-transfer explanation.

The first indication was obtained easily by studying compounds **IIIa** and **IIIb** under the same conditions as used for **II**. Thus no colour change was observed upon heating above the melting temperature. To establish that the compounds were unaffected by the change of counterion, it is necessary to comment on the differences observed between both the UV and fluorescence spectra of compounds **I–IV**. The UV spectra showed that all pyridinium derivatives exhibited the same characteristics, with only minor differences in the values of ε, particularly for the three small peaks between 270 and 290 nm; however they differ drastically in comparison with the spectra of the pyridine derivative **I** (see figure 1). This indicates that the type of the counterion does not affect the properties of the pyridinium core. Furthermore, this interpretation is in good agreement with the results of ^{1}H and ^{13}C NMR spectroscopy, where all pyridinium moieties have identical chemical shifts. Thus, the presence or absence of thermochromism cannot be related to the property of the aromatic core alone.

On the other hand, the fluorescence measurements are even more remarkable, as the spectra of the different pyridinium derivatives differ according to the type of counterion employed (bromide or sulphate). Furthermore, the spectra of pyridinium sulphate derivatives (compounds **IIIa** and **IV**) are almost identical to that of the pyridine derivative (compound **I**) (see figure 2).

These results indicate that the pyridinium-oxadiazole ring does not seem to be affected by the change of counterion (according to the UV spectra and the NMR measurements). Therefore the absence of thermochromism for compounds **III** and **IV** cannot be explained just by a change of the property of the rigid core. It has been shown also that the thermochromic compound **II** shows a fluorescence spectrum differing from the other compounds studied, in particular regarding the peak at 460 nm. This peak could therefore be the evidence supporting the presence of a strong charge-transfer between the pyridinium ring and its bromide counterion. This is, to the best of our knowledge, the first experimental evidence tending to confirm the generally accepted explanation for the observation of thermochromism in pyridinium halide derivatives. However, since this charge-transfer complex formation has also been observed in solution, this is an indication that although it could exist in all physical states of the compound, it may only express itself fully when found in a disordered state, such as in the disordered smectic mesophase. This has already been reported [17] for some poly(xylylviologens), for which it has been suggested that strong interactions occur in amorphous regions.

4. Conclusions

Ionic liquid crystalline compounds bearing an oxadiazole and a pyridinium group were synthesized, having bromide, alkyl sulphate or bis(2-ethylhexyl)sulphosuccinate counterions. The latter two types of counterion were synthesized in order to overcome some of the limitations of the bromide derivative, especially its rapid degradation occurring well before its transition from the mesophase to isotropic phase. This was achieved by employing alkyl sulphate derivatives, since their clearing points are sufficiently depressed but a stable SmA mesophase is retained. On the other hand total suppression of both the crystalline and liquid crystalline phase was realized when the bis(2-ethylhexyl)sulphosuccinate ion was employed. The enhanced thermal stability of these compounds could be beneficial for potential optoelectronic applications.

The second consequence of the change of counterion was the loss of the thermochromic properties of the bromide derivative. The origin of this thermochromism was believed to be due to a charge-transfer couple formation between the bromide and the pyridinium ring, although this was not established unambiguously. This hypothesis is strengthened by the comparison of the fluorescence spectra of the different pyridinium derivatives indicating that no charge-transfer complexes were formed when alkyl sulphate derivatives were used.

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