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New ionic liquid crystals based on azobenzene moiety with two symmetric imidazolium ion group substituents

Qixian Zhang[ab], Changsheng Shan[b], Xiaodan Wang[b], Lili Chen[b], Li Niu[b] and Bin Chen[a]*

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Imidazolium-substituted azobenzene liquid crystal derivatives were synthesised and their chemical structures were determined by ^{1}H NMR, ^{13}C NMR and UV spectroscopy and elemental analysis. The liquid crystalline properties pf the new compounds were investigated by differential scanning calorimetry, polarising optical microscopy and powder X-ray diffraction. The monomer **DC$_{10}$** was found to exhibit a monolayer smectic C (SmC) phase with schlieren texture on both heating and cooling. The effects of ionic interactions as well as the length of the alkyl chains on the mesophase are discussed. The results indicate that ionic interactions between imidazolium groups are the driving force for the formation of the monolayer SmC phase, the thermal stability of which is enhanced.

Keywords: ionic liquid crystal; synthesis; azobenzene derivative; imidazolium substituent; smectic phase; schlieren texture

1. Introduction

In recent years, considerable scientific and technological effort has been devoted to liquid crystals owing to their extensive applications in several fields, such as organic electronics (*1*), optoelectronic devices (*2*), biomedical applications, and as a templating medium (*3*), etc. Ionic liquid crystals are a class of liquid-crystalline compounds that contain anions and cations (*4*). Ionic metallomesogens are one type of metal complexes with liquid crystal mesophases. Different types of ionic metallomesogens have been synthesised and studied, such as metal complexes of the porphyrins, metal complexes of the phthalocyanines, lanthanide complexes, metal carboxylates, lyotropic metallomesogens, etc. These ionic metal-containing liquid crystals are particularly promising for the development of novel sensor devices, templates materials and electroactive materials (*5*). Ionic liquids, which exhibit many useful properties such as a very low vapour pressure, high thermal stability, non-flammability, high chemical stability, high ionic conductivity and a wide electrochemical window (*6, 7*), may serve widely as a new generation of solvents in synthesis, catalysis, separation and electrochemistry (*8–10*). Full conjunction of the two fields of ionic liquid chemistry and liquid crystal chemistry could lead to a vast new range of materials for research and industry. Ionic liquid crystals (ILCs) are a class of liquid-crystalline compounds combining the properties both of ionic liquids and liquid crystals (*11*).

Beginning in the late 1980s, an increasing number of reports on ILCs have appeared in the literature. Among the known ILCs, imidazolium salts are the most frequently studied; imidazoles can form ionic liquids and ILCs by quaternisation (*12*). They exhibit interesting potential applications in dye-sensitised solar cells (*13*), ordered reaction media (*14*) and ion transport systems (*15*). Liquid crystalline materials based on imidazolium reported to date can be classified into two types in terms of their molecular construction. One is the imidazolium group as a mesogenic core, which is substituted by one or multiple long aliphatic tails. Most studies have focused on varying the length of the alkyl chain or introduction of other substitution patterns (*16–20*) (e.g. pendant hydroxyl group on the alkyl chain, functionalised aryl groups, amide groups and pendant mesogenic groups). In most cases smectic mesophases are observed. The mesophases arise from a combination of electrostatic interactions in the head group region and weaker van der Waals forces in the hydrophobic tails (*11*). The other molecular construction is when the imidazolium group is linked via a flexible linkage to a conventional liquid crystal mesogen on the tail ends. In these types of imidazolium-based materials, the liquid crystalline properties originate from their strong amphiphilic character. The ionic interaction of the imidazolium groups tends to stabilise both smectic A (SmA) and smectic E (SmE) phases. When multiple imidazolium groups were attached on the tail ends of discotic

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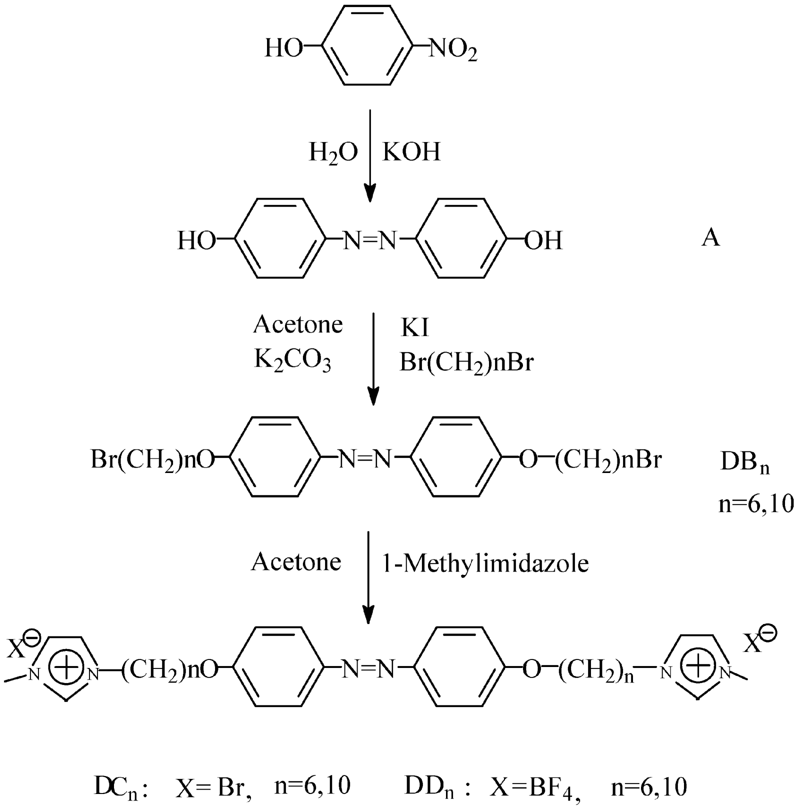


Scheme 1. Synthesis of azobenzene derivatives with two symmetric substitution imidazolium ion groups.

liquid crystals, stabilised columnar phases were observed (*21*). Azobenzene units have been widely used as a mesogenic group in liquid crystals. Liquid crystalline materials containing azobenzene chromophores are easily induced through trans–cis–trans isomerisation cycles by irradiation with linearly polarised light (*22*). Incorporation of imidazolium ion functionalities into the paraffin side-chain terminated azobenzene derivatives could lead to a new series of liquid crystalline materials for research and industrial applications, such as azobenzene derivatives with a broad mesophase range that are promising in high-density optical data storage and photochemical devices (*23*). Previously, we reported the synthesis and characterisation of a novel series of azobenzene derivatives with one imidazolium ion group substituent (*24*). We found that ionic interactions between imidazolium salts can enhance the stability of smectic phases. In order to further investigate the effects of ionic interactions on the mesophase of azobenzene liquid crystals, we incorporated two imidazolium groups into a azobenzene moiety via different length alkyl chains. In this paper, the synthesis and thermotropic liquid crystalline properties of these azobenzene derivatives are described. Moreover, the influence of the anion on the mesomorphic properties was also explored.

2. Experimental

Materials and characterisation

All reagents used in this work were commercial products of high grade employed as received unless otherwise indicated. All solvents were distilled before use by standard procedures. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with a Varian Unity 400 spectrometer (400 MHz), using tetramethylsilane (TMS) as an internal chemical shift reference. Elemental analyses were carried out on a Thermo Quest Italia S.P.A. FlashEA1112 apparatus. UV–visible spectra were measured with a Cary 500 UV–visible–NIR spectrophotometer. Morphologies as well as changes in birefringence were observed by polarising optical microscopy (POM) using a Leica DMLP microscope equipped with a Leitz 350 heating stage. Differential scanning calorimetry (DSC) was carried out on Perkin-Elmer DSC-7 and a scan rate of 10°C min^{-1} for both heating and cooling. Powder X-ray diffraction (XRD) experiments were performed on a Philips X-ray generator (PW 1700), and a flat plate camera using nickel-filtered Cu K_a radiation.

Synthesis

The synthetic strategy for the azobenzene derivatives is shown in Scheme 1. The following are typical synthetic processes. The intermediate 4,4′-dihydroxyazobenzene (**A**) was first prepared through a similar method to that described previously (*25*). A mixture of potassium hydrate (50 g, 760 mmol), 4-nitrophenol (10 g, 72 mmol), and water (10 ml) was vigorously stirred for about 2 h at 150°C. The temperature slowly rose to 220°C and the reaction mixture was left to stand for 2.5 h. After the reaction was completed, the reaction mixture was dissolved in water and neutralised with hydrochloric acid to pH 6. The crude product was filtered on a Buchner funnel, and then recrystallised from 50% (v/v) aqueous ethanol solution to give yellow crystals of compound **A**. Yield: 41%. ^{1}H NMR (400 MHz, DMSO): 10.13 (s, 2H, OH), 7.74 (d, J=8.9 Hz, 4H, Ar–H), 6.92 (d, J=8.9 Hz, 4H, Ar–H).

Compounds $\mathbf{DB_n}$ *(n=6, 10).*

4,4′-Bis(6-bromohexyloxy)azobenzene ($\mathbf{DB_6}$) was prepared from 1,6-dibromohexane and 4,4′-dihydroxyazobenzene (**A**). A mixture of compound **A** (2.40 g, 9.87 mmol), a 10-fold excess of 1,6-dibromohexane (24 g, 98.7 mmol), potassium carbonate (10 g, 74 mmol), potassium iodide (50 mg) and dry acetone (130 ml) was vigorously stirred and refluxed for 24 h under a flow of dry nitrogen. After cooling to room temperature, the reaction mixture was filtered hot to remove salts and the excess acetone was evaporated in vacuum. Then, ethanol was added to remove excess 1,6-dibromohexane; the product was insoluble in ethanol. The crude product was purified on silica gel 100–200 using a mixture of dichloromethane and hexane (1:1) as an eluent to give $\mathbf{DB_6}$ as a yellow solid. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.88 (d, 4H, J=8.7 Hz, Ar–H), 6.99 (d, 4H, J=8.7 Hz, Ar–H), 4.04 (t, 4H, J=12.6 Hz, OCH_2), 3.44 (t, 4H, J=13.2 Hz, CH_2Br), 1.82–1.93 (m, 8H, CH_2), 1.52–1.54 (m, 8H, CH_2).

4,4′-Bis(10-bromodecyloxy)azobenzene ($\mathbf{DB_{10}}$) was synthesised according to the procedure used for $\mathbf{DB_6}$. The target material was obtained as light yellow solid with a yield of 74%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.95 (d, 4H, J=8.7 Hz, Ar–H), 6.99 (d, 4H, J=8.7 Hz, Ar–H), 4.04 (d, 4H, J=12.9 Hz, OCH_2), 3.41 (d, 4H, J=13.8 Hz, CH_2Br), 1.77–1.90 (m, 4H, CH_2), 1.39–1.45 (m, 4H, CH_2).

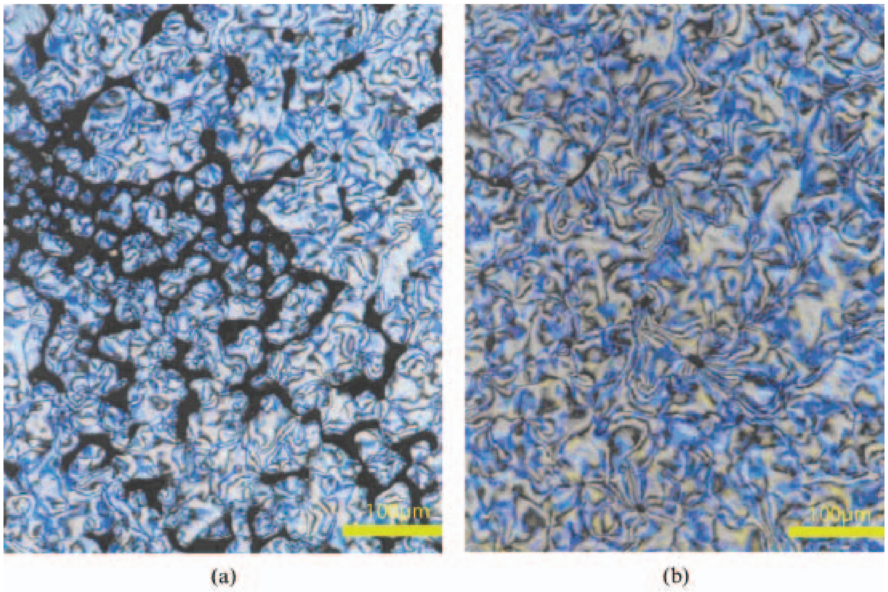
Compounds $\mathbf{DC_n}$ *(n=6, 10).*

4,4′-Bis(1-hexyloxy-3-methylimidazolium bromide) azobenzene ($\mathbf{DC_6}$) was prepared from $\mathbf{DB_6}$ and 1-methylimidazole. $\mathbf{DB_6}$ (2.54 g, 0.02 mol) and 1-methylimidazole (1.64 g, 0.02 mol) were dissolved in 30 ml of dry acetone, the mixture was vigorously stirred and refluxed for 24 h under a flow of dry nitrogen. After cooling to room temperature, the excess acetone was evaporated in vacuum. The crude product was precipitated by addition of excess hexane, then recrystallised from ethanol and finally dried under vacuum giving pure $\mathbf{DC_6}$ as a yellow solid. Yield: 76%, ^{1}H NMR (400 MHz, DMSO): 9.13 (s, 2H, imidazolium ring), 7.82 (d, 4H, J=8.8 Hz, Ar–H), 7.78 (s, 2H, imidazolium ring), 7.70 (s, 2H, imidazolium ring), 7.09 (d, 4H, m, J=8.8 Hz, Ar–H), 4.17 (t, 4H, J=14.4 Hz, N–CH_2), 4.06 (t, 4H, J=12.4 Hz, OCH_2), 3.85 (s, 6H, N–CH_3), 1.72–1.86 (m, 8H, CH_2), 1.43–1.51(m, 4H, CH_2), 1.30–1.36 (m, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO): 24.88, 25.23, 28.34, 29.31, 35.76, 48.70, 67.77, 114.93, 122.27, 123.60, 124.12, 136.50, 146.06, 160.85. Elemental analysis: calculated for $C_{32}H_{44}Br_2N_6O_2$, C 54.55, N 11.93, H 6.29; found, C 54.23, N 11.78, H 6.42%.

4,4′-Bis(1-decyloxy-3-methylimidazolium bromide)azobenzene ($\mathbf{DC_{10}}$) was obtained from $\mathbf{DB_{10}}$ and 1-methylimidazole using the same synthetic procedure as for $\mathbf{DC_6}$. Yield: 74%. ^{1}H NMR (400 MHz, DMSO): 9.12 (s, 2H, imidazolium ring), 7.81 (d, 4H, J=8.8 Hz, Ar–H), 7.77 (s, 2H, imidazolium ring), 7.76 (s, 2H, imidazolium ring), 7.09 (d, 4H, m, J=8.8 Hz, Ar–H), 4.15 (t, 4H, J=14.4 Hz, N-CH_2), 4.06 (t, 4H, J=12.8 Hz, OCH_2), 3.85 (s, 6H, N–CH_3), 1.72–1.79 (m, 8H, CH_2), 1.39–1.42 (m, 24H, CH_2). ^{13}C NMR (100 MHz, DMSO): 25.43, 28.30, 28.55, 28.70, 28.83, 29.34, 35.71, 48.70, 67.88, 114.89, 122.21, 123.53, 124.05, 136.45, 146.02, 160.85. Elemental analysis: calculated for $C_{40}H_{60}Br_2N_6O_2$, C 58.82, N 10.29, H 7.40; found, C 58.96, N 10.08, H 7.51%.

Compounds $\mathbf{DD_n}$ *(n=6, 10).*

4,4′-Bis(1-hexyloxy-3-methylimidazolium tetrafluoroborate)azobenzene ($\mathbf{DD_6}$) was prepared from $\mathbf{DC_6}$ and $NaBF_4$. $\mathbf{DC_6}$ (24mmol) was dissolved in 30 ml of H_2O, and then a solution of 6 mmol of $NaBF_4$ in 20 ml of H_2O was added dropwise. The mixture was stirred for 1 h at 80°C under nitrogen; the precipitate that came out from the water solution in the procedure was filtered and washed with water several times. The crude product was recrystallised from ethanol and dried in vacuum for 24 h giving pure $\mathbf{DD_6}$ as a light yellow solid. Yield: 82%, m.p. 169°C. ^{1}H NMR (400 MHz, DMSO): 9.10 (s, 2H, imidazolium ring), 7.82 (d, 4H, J=8.8 Hz, Ar–H), 7.77 (s, 2H, imidazolium ring), 7.70 (s, 2H, imidazolium ring), 7.09 (d, 4H, m, J=9.2 Hz, Ar–H), 4.17 (t, 4H, J=14.4 Hz, N–CH_2), 4.07 (t, 4H, J=12.4 Hz, OCH_2), 3.85 (s, 6H, N-CH_3), 1.74–1.85 (m, 8H, CH_2), 1.45–1.49(m, 4H, CH_2), 1.31–1.35 (m, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO): 24.83, 25.18,



(a) (b)

Figure 1. Optical micrographs (×200) of $\mathbf{DC_{10}}$ showing the schlieren texture of its mesophase at (a) 162°C and (b) at 150°C on cooling.

28.29, 29.24, 35.68, 48.70, 67.74, 114.90, 122.22, 123.56, 124.07, 136.43, 146.08, 160.83. Elemental analysis: calculated for $C_{32}H_{44}B_2F_8N_6O_2$, C 53.50, N 11.70, H 6.17; found, C 53.86, N 11.48, H 5.96%.

4,4′-Bis(1-decyloxy-3-methylimidazolium tetrafluoroborate)azobenzene ($\mathbf{DD_{10}}$) was synthesised according to the procedure use for $\mathbf{DD_6}$. The target material was obtained as light yellow solid with a yield of 89%. ^{1}H NMR (400 MHz, DMSO): 9.08 (s, 2H, imidazolium ring), 7.82 (d, 4H, J=8.8 Hz, Ar–H), 7.76 (s, 2H, imidazolium ring), 7.69 (s, 2H, imidazolium ring), 7.09 (d, 4H, m, J=8.8 Hz, Ar–H), 4.14 (t, 4H, J=14.4 Hz, N–CH_2), 4.05 (t, 4H, J=12.8 Hz, OCH_2), 3.84 (s, 6H, N–CH_3), 1.72–1.79 (m, 8H, CH_2), 1.40–1.43(m, 24H, CH_2). ^{13}C NMR (100 MHz, DMSO): 24.83, 25.18, 28.29, 29.24, 35.68, 67.87, 114.89, 122.21, 123.55, 124.05, 136.41, 146.04, 160.86. Elemental analysis: calculated for $C_{40}H_{60}B_2F_8N_6O_2$, C 57.84, N 10.12, H 7.28; found, C 57.76, N 10.36, H 7.41%.

3. Results and discussion

Liquid crystalline properties

The mesomorphic behaviour of the new azobenzene derivatives was examined using DSC, POM and XRD measurements.

Figure 1 shows POM micrographs of compound $\mathbf{DC_{10}}$ in its mesophase. Schlieren textures observed in both heating and cooling runs indicate enantiotropic smectic C (SmC) behaviour. In contrast, owing to their high crystalline temperatures, no mesophase was observed for $\mathbf{DC_6}$, $\mathbf{DD_6}$ and $\mathbf{DD_{10}}$.

The phase behaviours of the new compounds were further confirmed by DSC. The DSC curves of $\mathbf{DC_n}$ compounds obtained in heating and cooling runs are shown in Figure 2. In the DSC measurements of $\mathbf{DC_{10}}$, an exothermic peak appeared at 163°C when compound $\mathbf{DC_{10}}$ was cooled from the molten state, confirming a phase transition from isotropic phase to SmC phase. Another exothermic peak at 140°C is assigned to the crystallisation. Two endothermic peaks at 156 and 169°C were observed in the second heating run, which were attributed to crystal–SmC and SmC–isotropic phase transitions, respectively.

All the transition temperatures and associated enthalpies are summarised in Table 1. The results indicate that imidazolium salts with fluorinated anions tend to have lower melting points than

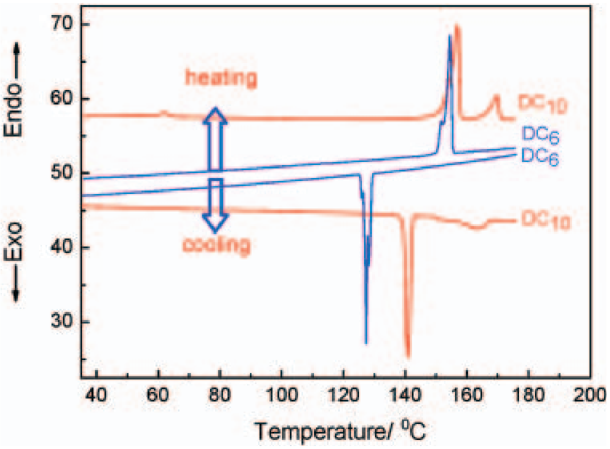


Figure 2. DSC curves of $\mathbf{DC}_n$.

Table 1. Phase transition temperatures (°C) and enthalpies ($\mathrm{kJ\,mol^{-1}}$, in parentheses) of **DC*n*** and **DD*n*** determined by DSC (second heating cycle, $10^{\circ}\mathrm{C\,min^{-1}}$). (Cr=crystal; SmC=smectic C phase; I=isotropic liquid).

Compound	Transition	Heating	Transition	Cooling
DC$_6$	Cr_1–Cr_2	154 (72.0)	I–Cr	127 (65.4)
	Cr_2–I			
DC$_{10}$	Cr_1–Cr_2	77 (8.6)	I–SmC	163 (10.5)
	Cr_2–SmC	156 (45.6)	SmC–Cr	140 (45.0)
	SmC–I	169 (10.1)		
DD$_6$	Cr–I	143 (66.6)	I–Cr	117 (61.3)
DD$_{10}$	Cr_1–Cr_2	77 (8.6)	I–Cr_3	147 (41.3)
	Cr_2–Cr_3	98 (10.4)	Cr_3–Cr_2	92 (9.8)
	Cr_3–I	155 (43.2)	Cr_2–Cr_1	73 (7.8)

compounds with non-fluorinated anions, and the ionic interaction of imidazolium salts with Br anions is much stronger than that with BF_4 anions (*19*). We found that the chemical shift of the CH proton of imidazolium ring depends on the anion. With an alkyl chain length of $n=10$, the CH proton of imidazolium ring of imidazolium salts with Br anions has lower chemical shift at 9.12 ppm, the imidazolium salts with BF_4 anions has higher chemical shift at 9.08 ppm. The imidazolium salts with an alkyl chain length of $n=6$ has the similar trend, which may also reflect the strength of the ionic interaction between the imidazolium cations and the Br anions (*12*).

No liquid crystalline phases were detected in **DB$_n$** compounds since the crystalline temperature is much higher than the mesophase temperature. In contrast, the covalent incorporation of imidazolium ion groups into **DB$_{10}$** enabled **DC$_{10}$** to exhibit smectic phases. Hence, the ionic interaction between imidazolium salts can induce and stabilise a SmC phases (*20*). It was also found that the mesomorphic temperature range of **DC$_{10}$** with a longer alkyl spacer is much wider than that of **DC$_6$**, indicating that the length of a flexible chain also plays an important role in stabilising the SmC phase.

In addition, no liquid crystalline phases were observed for **DD$_n$** compounds We suppose that the ionic interaction of imidazolium salts with Br anions is much stronger than that with BF_4 anions, so **DC$_n$** have a stronger tendency to form a three-dimensional lattice, which is favourable for stabilisation of the smectic phases in ionic LCs, between the cations and the anions within the layers compared with the compounds **DD$_n$** (*4*).

Mesophase structure of DC$_{10}$

In order to obtain further information on the molecular arrangements in the mesophase, variable temperature XRD measurements were performed on **DC$_{10}$**. Figure 3 shows the XRD patterns of **DC$_{10}$** in the crystalline state (at 25°C) and the mesophase (at 150°C), during the cooling scan.

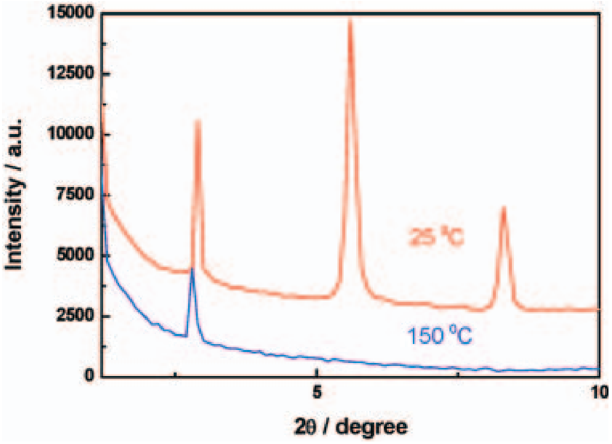
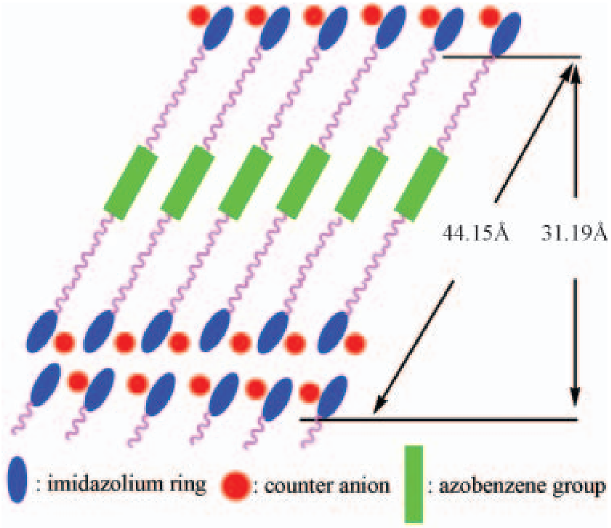


Figure 3. X-ray diffraction patterns of **DC$_{10}$** at different temperatures upon cooling from the isotropic phase.

It is apparent that the salt displays layered structures in both the crystal and liquid crystalline phases, with one or more peaks in the low-angle region of the diffraction pattern. The layer spacing (*d*) was calculated by using Bragg's law. The XRD pattern of **DC$_{10}$** at 140°C shows one sharp diffraction peak in the small-angle region, implying the formation of a layered structure. On the other hand, a broad diffraction peak in the wide-angle region indicates liquid-like arrangement of the molecules within the layers. The layer spacing (31.19 Å) is much smaller than the calculated molecular lengths, and the *d*/*l* ratio is 0.7, which confirms the conclusion that a SmC phase is observed in **DC$_{10}$**.



Scheme 2. Schematic model of interdigitated structure for **DC$_{10}$** in the SmC phase.

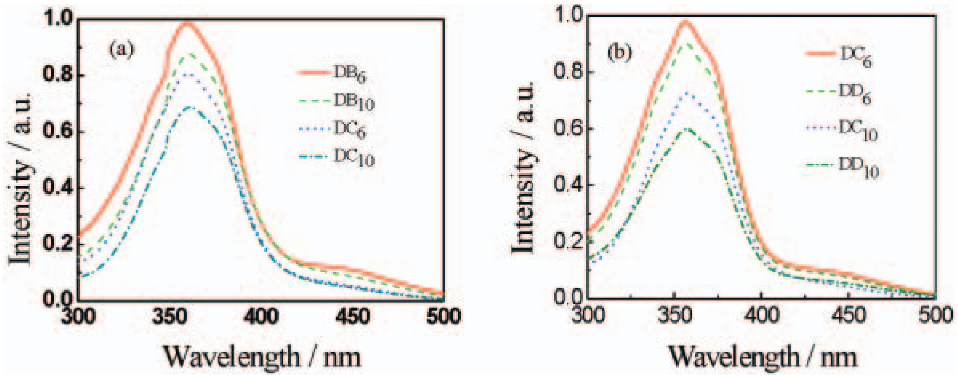


Figure 4. UV–visible spectra of (a) **DB*n*** and **DC*n*** in chloroform and (b) **DC*n*** and **DD*n*** compounds in methanol.

A model for the arrangement of the mesogenic groups of **DC$_{10}$** in the smectic layers is shown in Scheme 2. In this model, the molecules of **DC$_{10}$** are arranged in a monolayer with the molecular long axis tilted with respect to the layer normal (SmC) (*26*). The azobenzene part can be considered as the centre of the molecules, whereas the imidazolium ion group can be considered more or less as a part of one of the tails. The azobenzene groups are facing each other in the lateral direction and the interaction of the azobenzene groups keeps the orientation order of liquid crystal molecules within the layer. The imidazolium salt parts become associated with each other to form a smectic layer (SmC) and all the layers are further linked with the imidazolium ions through electrostatic interactions (*27*). We consider that the organisation of the imidazolium salt parts contributes to the formation of the smectic layer structure through electrostatic interactions.

UV–visible spectra

UV–visible spectra of **DB*n*** and **DC*n*** in CHCl$_3$ solution are shown in Figure 4 (the concentrations were ca. 10^{-4}M). The compounds all exhibit an absorption maximum at ca. 360 nm and weak shoulders at ca. 460 nm, which are related to π–π^* and n–π^* transitions of the azobenzene trans–cis configuration (*28*), respectively (as shown in Figure 4(a)). These results suggest that the imidazolium salts have no influence on the arrangement of the azobenzene groups in CHCl$_3$ solution.

In order to study the effect of anion on the UV–visible spectra, the optical properties of **DC$_n$** and **DD$_n$** in methanol solution were also analysed. As shown in Figure 4(b), all the compounds have the similar absorption maximum, so the anions have no influence on the optical properties of the azobenzene groups in methanol solution.

4. Conclusions

In conclusion, the synthesis and characterisation of imidazolium-substituted azobenzene derivatives were explored in detail. The compounds **DC*n*** and **DD*n*** have been characterised by DSC, POM, XRD and UV–visible spectroscopic measurements. The effect of the length of a flexible chain on the thermal properties of monomers **DC*n*** and **DD**$_n$ was studied. The results showed that only monomer **DC$_{10}$** exhibits monolayer smectic C phase textures and no liquid crystalline phases were observed for **DD$_n$**. Ionic interaction between imidazolium salts and the flexible chain plays an important role for the stabilisation of the smectic phases. The ionic interaction of imidazolium salts with Br anions is much stronger than that with BF$_4$ anions, so **DC*n*** have a stronger tendency to form a three-dimensional lattice between the cations and the anions, which is favourable for stabilisation of the smectic phases in ionic LCs. The UV results of these imidazolium-substituted azobenzene derivatives suggest that the imidazolium salts have no influence on the arrangement and configuration of the azobenzene groups in solution.

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