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Tetrahedron Letters 47 (2006) 8993–8997

Tetrahedron Letters

Microwave-assisted synthesis of novel imidazolium-based ionic liquid crystalline dimers

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Received 1 August 2006; revised 22 August 2006; accepted 1 September 2006
Available online 30 October 2006

Abstract—Microwave promoted synthesis of novel imidazolium-based ionic liquid crystalline dimers containing calamitic–calamitic, calamitic–discotic and discotic–discotic moieties is reported. Classical reactions failed to produce these dimers. The thermotropic liquid crystalline properties of these salts were investigated by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. These salts, except the one having calamitic–discotic units, with bromide as counter ion were found to be mesomorphic over a wide temperature range.

Imidazolium-based ionic liquids have attracted considerable attention as environmentally benign solvents for various chemical reactions due to their interesting properties such as thermal stability, non-flammability, very low vapour pressure and reusability.[1] Furthermore, there is considerable interest in the structural features of ionic liquid crystals,[2] for example, as oriented solvents, which can impart selectivity to reactions by ordering reactants,[3] as templates for the synthesis of mesoporous and zeolitic materials,[4] and in the formation of ordered thin films.[5,6] The formation of supramolecular assemblies containing ionic liquids may find applications as heat carriers in solar thermal energy generators and as electrolytes for batteries and capacitors.[7] Alkali metal soaps were the first salts identified as displaying liquid crystalline properties, followed by alkylammonium, pyridinium, vinamidinium, phosphonium salts, etc.[8] A number of calamitic liquid crystalline imidazolium salts have been prepared recently and the formation of lamellar phases in these materials has been recognized.[9] The self-assembly of a non-liquid crystalline imidazolium ionic liquid and a hydroxyl-terminated liquid crystal leads to the formation of phase-segregated layered structures on the nanoscale. These materials have been found to exhibit two-dimensional ionic conductivities with a high anisotropy.[10] Recently, a number of anisotropic ionic functional materials have been reported by Kato.[11] Discotic ionic molecules containing 2,4,6-triarylpyridinium,[12] crown ethers,[13] 3,5-diaryl-1,2-dithiolium,[14] phthalocyanine[15] and tricycloquinazoline[16] moieties are also known to show mesomorphism. We have recently reported pyridinium and imidazolium-based ionic discotic liquid crystals with a triphenylene moiety.[17]

Compared to the large number of calamitic and discotic ionic molecules, only a few ionic liquid crystalline dimers and polymers are known. Veber and co-workers reported dimeric 2,4,6-triarylpyrylium tetrafluoroborate and symmetrically substituted ionic liquid crystalline dithiolium salts.[11,18] Ionic metallomesogens, composed of two mesogenic units, have been extensively studied.[19] Mesomorphic properties of oligomeric and main chain liquid crystalline viologens have been studied by Paleos et al.[20] and Bhowmik et al.,[21] respectively. The chemistry of ionic liquid crystals has recently been covered in a review article by Binnemans.[22] To the best of our knowledge ionic liquid crystalline dimers based on imidazolium moieties containing two mesogenic groups have not yet been explored. Hybridization of two different types of mesogens with imidazolium moieties may lead to novel materials with interesting properties. With this in mind, we have initiated a research programme to incorporate imidazolium-based ionic liquids in the supramolecular order of calamitic and discotic liquid crystals by attaching two calamitic, two discotic and a

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Keywords: Ionic liquid crystals; Triphenylene; Cyanobiphenyl; Discotic liquid crystals; Imidazolium salts; Microwaves.

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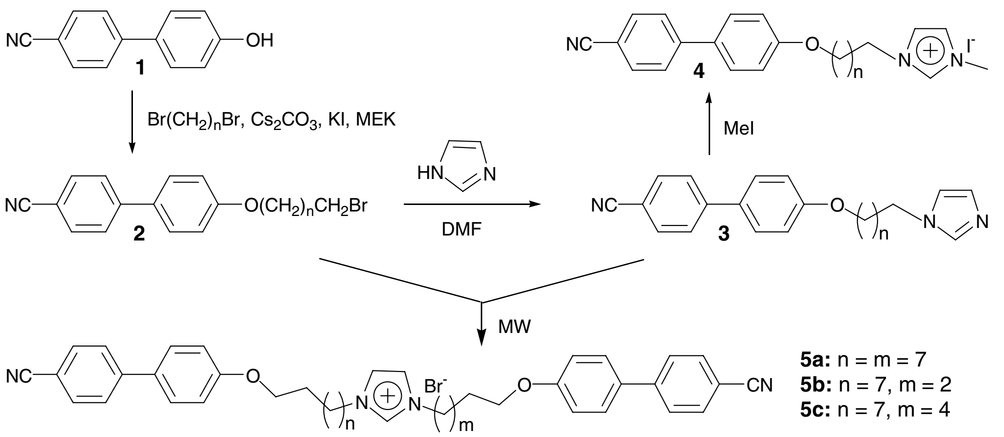
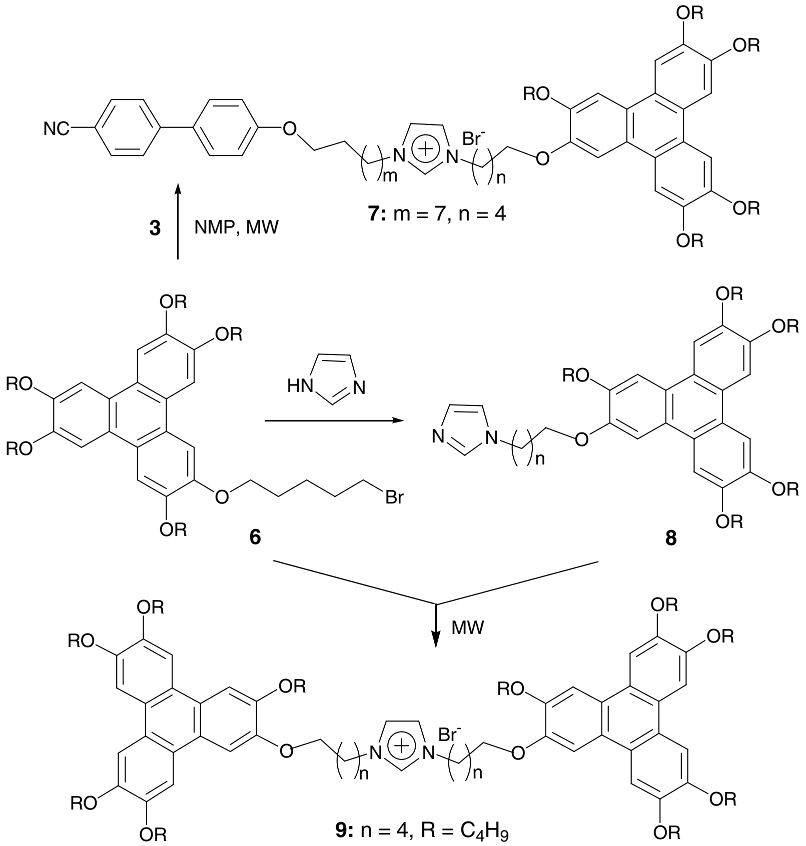
0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.09.167

hybrid of both the moieties, to imidazole. The most widely studied alkoxycyanobiphenyl and triphenylene units were chosen as the calamitic and discotic parts, respectively. A variety of monomeric, dimeric, oligomeric and polymeric liquid crystals have been derived from these two molecules.[23] Recently, alkoxycyanobiphenyls have also been connected to a discotic molecule to realize the biaxial nematic phase.[24]

The synthesis of imidazolium-based calamitic–calamitic ionic dimers is outlined in Scheme 1. Commercially available 4′-hydroxy-4-biphenylcarbonitrile **1** was alkylated under classical conditions with an excess of the appropriate α,ω-dibromoalkanes to obtain ω-brominated products **2**.[25] Imidazole-substituted alkoxycyanobiphenyls **3** were obtained by reacting **2** with imidazole in the presence of NaH. Liquid crystalline imidazolium salts **4** were obtained by the quaternization of **3** with methyl iodide. Ionic liquid crystalline calamitic–calamitic dimers **5** were obtained by attaching one more molecule of ω-brominated cyanobiphenyl to imidazoles **3**. Thus, the quaternization of **3** with ω-bromo-terminated cyanobiphenyl under microwave irradiation furnished dimers **5** in about 1 min. It should be noted



Scheme 1. Synthesis of imidazolium-based calamitic–calamitic dimers.



Scheme 2. Synthesis of imidazolium-based calamitic–discotic and discotic–discotic dimers.

that attempted quaternization under classical reaction conditions like reflux in toluene for 48 h did not produce any desired product. Similarly, calamitic–discotic and discotic–discotic salts were prepared as shown in Scheme 2. Since the synthetic details for the preparation of ionic dimers based on calamitic–discotic, discotic–discotic and calamitic–calamitic for different chain lengths are practically the same, only the procedure of **5a** is described.[26] Spectral data and elemental analysis of all the compounds were in good agreement with their structures.[27]

The phase transition temperatures of all the new compounds together with transition enthalpy values determined by DSC are given in Table 1. The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter operated at a scanning rate 5 °C min^{-1} both on heating and cooling. The textural observations of the mesophase were carried out using a polarizing light microscope provided with a heating stage and a central processor. The dimer series based on calamitic–calamitic moieties displayed SmC phases. Interestingly, calamitic–discotic hybrid **7** was found to be a non-liquid crystalline. On the other hand the dimer based on discotic–discotic moiety **9** showed a typical spine texture, which compared well with the texture of columnar phases shown by several other discotic liquid crystals.

Table 1. Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ mol^{-1}, in parentheses) of imidazolium-based ionic dimers

Compound	First heating scan	First cooling scan
4	Cr_1 73 (4.3) Cr_2 83 (1.4) Cr_3 92 (16.8) Cr_4 97 (16) I	I 70 (3) Sm A
5a	Cr 133 (72) I	I 102 (1.2) Sm C
5b	Cr 129 (54) I	I 95 (1.1) Sm C
5c	Cr 92 (23) Sm C 98 (1.2) I	I 96 (0.9) Sm C
7	Cr 135 (76) I	—
9	Cr 84 (26) Col_r 95 (2.5) I	I 92 (2.4) Col_r

Cr: Crystalline phase; SmC: smectic C phase; SmA: smectic A phase; I: isotropic phase.

The first compound of series **5a**, symmetrically substituted by two mesogenic groups through the central imidazolium moiety, showed only a monotropic SmC phase. Crystalline compound **5a** melted at 133 °C to the isotropic phase. However, on cooling the smectic phase appeared at 102 °C and was stable down to room temperature. Under the microscope it displayed a typical schlieren texture having only four brushes as shown in Figure 1a. The possibility of a nematic phase was ruled out as the uniaxial nematic phase usually exhibits a schlieren texture with two and four point singularities (two and four brushes). Compound **5b** also showed a monotropic SmC phase. On heating it melted at 129 °C and the phase appeared on cooling, at 95 °C, which was stable down to room temperature. Compound **5c** exhibited an enantiotropic SmC phase. Upon heating, it melted at about 92 °C to the SmC phase, which cleared at about 98 °C. On cooling, the smectic phase appeared within about one degree of supercooling. The compound did not crystallize and the phase remained stable down to room temperature. Compound **7** did not show any liquid crystalline phase. Crystalline compound **7** melted at 135 °C to the isotropic phase. Compound **9**, with two triphenylene moieties, exhibited a columnar mesophase. It melted at 84 °C to the columnar phase, which cleared at about 95 °C. On cooling, the columnar phase appeared at 92 °C. Like the other samples, it did not show any crystallization peak in DSC. The photomicrograph of the columnar texture is shown in Figure 1b.

The nature of the mesophases was confirmed by X-ray diffraction studies. The diffraction pattern of the SmC phase of calamitic–calamitic hybrid **5b** showed a diffuse peak in the wide-angle region with a spacing of about 0.43 nm and corresponds to the average lateral separation of the molecules in this fluid phase. Additionally, a single sharp peak was observed in the small angle region of the diffraction pattern (Fig. 2a). It has a spacing of about 2.7 nm at 40 °C, which is much lower than the full molecular length. Therefore, the tilt angle of the molecule in the SmC phase is found to be about 47°. The diffraction pattern of the ionic dimer made from

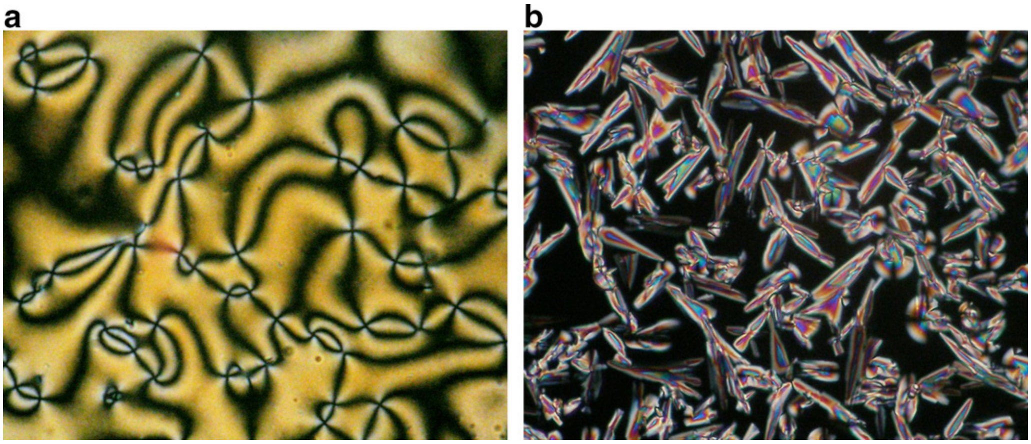


Figure 1. (a) Optical photomicrograph of compound **5a** at 90 °C on cooling from isotropic liquid; (b) Photomicrograph of the texture of the columnar phase of dimer **9** at 90 °C.

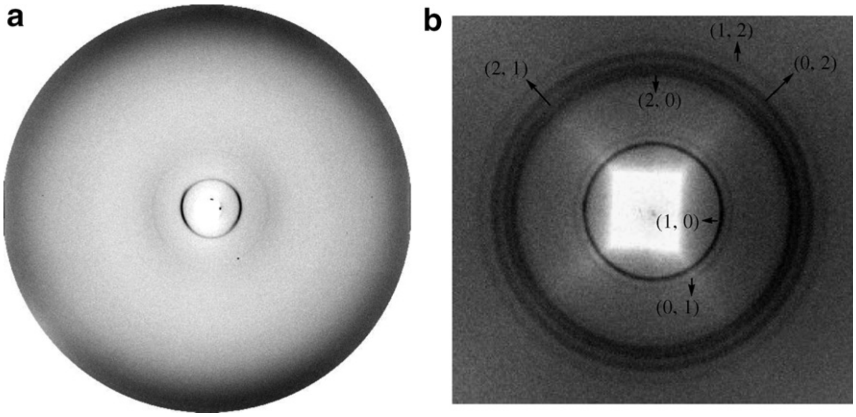


Figure 2. (a,b) X-ray diffraction patterns obtained for compounds **5b** and **9** at 40 °C and room temperature, respectively.

discotic–discotic moiety **9** is shown in Figure 2b. The sample was heated to the isotropic phase and then cooled to room temperature. The diffraction pattern was recorded at room temperature. In the small angle region, six reflections were observed, which can be indexed (as shown in the figure) on a simple rectangular lattice of lattice parameter $a = 3.48$ nm and $b = 3.03$ nm.

In conclusion, we have synthesized novel imidazolium-based ionic liquid crystalline dimers based on calamitic–calamitic, calamitic–discotic, discotic–discotic moieties using microwave irradiation. The quaternization of imidazole-substituted mesogens under classical reaction conditions failed to produce the desired quaternary salts. Polarizing optical microscopy and X-ray diffraction experiments showed smectic and columnar phases of the calamitic–calamitic and discotic–discotic hybrids, respectively.

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26. Synthesis of **5a**: In a typical reaction, **3** (20 mg, 0.052 mmol), **2** (23 mg, 0.057 mmol) were mixed in 1-methyl-2-pyrrolidinone (0.2 ml) in a small glass vial and loosely covered with a rubber septum. The mixture was heated in an unmodified household microwave oven at 360 W for 1 min. The vial was taken out and water (2 ml) was added and the mixture was centrifuged at 5000 rpm for 1 h. The supernatant liquid was removed and white solid was recrystallized twice from acetone to furnish **5a** (20 mg, 50%).
27. Selected data for compound **5a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.72 (s, 1H), 7.64 (d, $J = 8.3$ Hz, 4H), 7.59 (d, $J = 8.3$ Hz, 4H), 7.48 (d, $J = 8.7$ Hz, 4H), 7.26 (s, 2H), 6.94 (d, $J = 8.7$ Hz, 4H), 4.32 (t, $J = 7.4$ Hz, 4H), 3.96 (t, $J = 6.4$ Hz, 4H) 1.2–2.1 (m, 28H). IR (KBr, all the derivatives **5a**–**c** showed similar spectra): ν_{max} 2953, 2926, 2226, 1602, 1571, 1562, 1523, 1396, 1292, 1253, 1267, 1180, 1115, 1030, 853, 725, 660, 532 cm^{-1}. UV ($CHCl_3$, all the derivatives **5a**–**c** showed similar spectra): λ_{max} 307.6 nm. Elemental analysis: calculated for $C_{47}H_{55}N_4O_2Br$, C 71.65, H 7.04, N 7.11; found C 71.2, H 7.28, N 7.55. Selected data for compound **7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.85 (s, 1H), 7.81–7.83 (m, 6H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.51 (d, $J = 8.6$ Hz, 2H), 7.24 (s, 1H), 7.09 (s, 1H), 6.96 (d, $J = 8.7$ Hz, 2H), 4.45 (t, $J = 7.2$ Hz, 2H), 4.29 (t, $J = 7.2$ Hz, 2H), 4.25 (m, 12H), 3.95 (t, $J = 6.4$ Hz, 2H), 1.0–2.1 (m, 55H). IR (KBr): 2924, 2855, 1618, 1612, 1560, 1545, 1460, 1377, 1261, 1173, 1070, 1034, 835, 772, 721, 667. UV ($CHCl_3$): λ_{max} 305.2, 278, 265, 347.2 nm. Elemental analysis: calculated for $C_{68}H_{90}N_3O_7Br$, C 71.56, H 7.95, N 3.68; found C 71.1, H 7.95, N 4.08. Selected data for compound **9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.77 (s, 1H), 7.80–7.82 (m, 12H), 7.19 (s, 2H), 4.40 (t, $J = 7.3$ Hz, 4H), 4.23 (m, 24H), 1.2–2.1 (m, 82H). IR (KBr): 2924, 2855, 1618, 1612, 1560, 1545, 1460, 1377, 1261, 1173, 1070, 1034, 835, 772, 721, 667. UV ($CHCl_3$): λ_{max} 344.4, 305.2, 278.2, 269.6, 259 nm. Elemental analysis: calculated for $C_{89}H_{125}N_2O_{12}Br$, C 71.51, H 8.43, N 1.87; found C 71.1, H 8.45, N 2.15.