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A new liquid crystal compound based on an ionic imidazolium salt

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Abstract—The preparation of 1,3-bis-(4-dodecyloxy-phenyl)-3*H*-imidazol-1-ium trifluoro-methanesulfonate is described from the 4-dodecyloxy phenylamine derivative. This new imidazolium salt exhibits a lamellar liquid crystal mesophase between 119 and 172 °C. The Smectic A phase has been characterised by polarising optical microscopy, differential scanning calorimetry and X-ray diffraction. In addition the lamellar crystallographic structure obtained on single crystal is reported and corroborated the self-assembly of molecules in the mesomorphic state.

Convergence of the two distinct fields of ionic liquid and liquid crystal chemistry could lead to a vast new range of materials for research and industry. Interest in this has been driven in large part by the views that ionic liquids have potential, especially as green solvents for organic reactions[1] and that liquid crystals are systems, which provide self-organised orientational ordering at the nanometric level.[2] The association of order and mobility opens the door to investigations, for example, of reactions in ordered solvents in the hope of obtaining better selectivity and of improved performance in electronic devices based on the transport of ions[3] or electrons.[4] Recently, solvents based on imidazolium salt have been used with success in dye-sensitised solar cells[5] and light-emitting electrochemical cells,[6] and to prepare gold nanoparticules or nanorods.[7] Despite growing interest in the properties of ionic liquids, which are frequently based on imidazolium compounds, very little is known of systems in which such liquids also form liquid crystals.[8]

Herein, we wish to report that the introduction of alkyl chains on aryl substituents can cause imidazolium precursors of *N*-heterocyclic carbenes (NHCs) to exhibit liquid crystal properties. *N*-heterocyclic carbenes as ligands in coordination chemistry have recently received growing interest because of their electronic properties comparable to phosphine ligands.[9] In contrast, imidazolium precursors of NHCs have received less attention but these cationic molecules are potentially useful in the search of liquid crystalline ionic liquids.

Compound **A**[10] was obtained in a two-step procedure from aniline derivative (Scheme 1). Condensation with glyoxal followed by treatment with chloromethyl pivalate in the presence of one equivalent of silver triflate gave the corresponding imidazolium salt **A** in 60% yield.[11] The triflate salt is air stable and could be purified by column chromatography on silica. The CH (imidazolium) proton appears in the ^{1}H NMR spectrum at 9.64 ppm as a triplet with a $^4J_{HH} = 1.65$ Hz. Single crystals of **A**[12] suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH_2Cl_2 solution. The molecular structure is shown in Figure 1a/b. The solid state array is formed by interdigitation of the extended but smightly curved, approximatively 29 Å long molecules. The most interesting feature of this array is its lamellar structure, in which the layers are separated by $d_1 = 29.2$ Å. Another repeating distance, $d_2 = 9.0$ Å, is due to the packing of the imidazolium entities. The rigid rings as well as the anions are fully segregated from the flexible chains. Clearly, the observed arrangements favour liquid crystalline properties.

Keywords: Imidazolium salt; Liquid crystals; Mesophase; Self-assembly.

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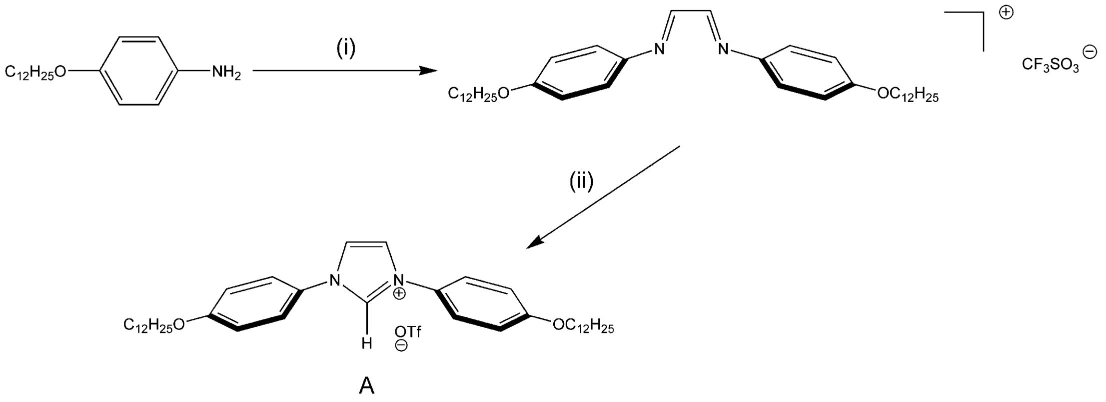

Scheme 1. Reagents and conditions: (i) glyoxal, ethanol reflux; (ii) AgOTf, chloromethyl pivalate; CH_2Cl_2 48 h under inert atmosphere.

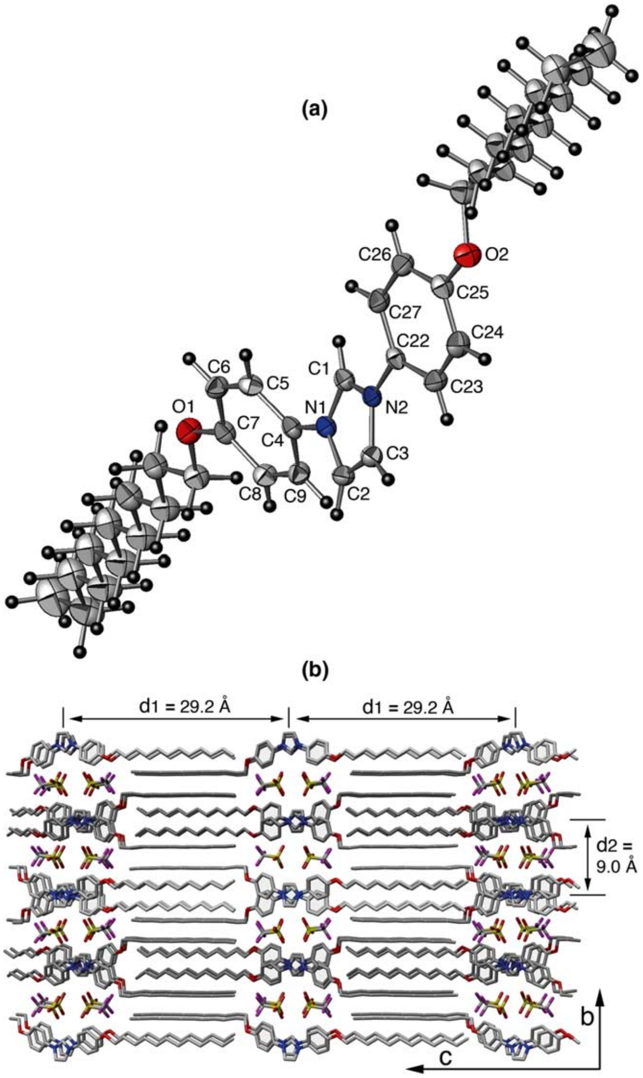

Figure 1. (a) ORTEP drawing of imidazolium compound **A** (50% thermal ellipsolids). (b) Packing of molecules **A** in the crystal. We observe a segregation between the rigid part and the alkyls tails. The alkyl tails connect the layers by their interdigitation.

The mesomorphic behaviour and phase transition temperatures were characterised by polarising optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffractometry (XRD). The DSC thermograms of compound, recorded from 50 to 190 °C, show two sharp peaks. One, at 119 °C (ΔH = 53.75 kJ/mol), corresponds to the melting of the crystal into a liquid crystalline phase, whereas the other, at 177 °C (ΔH = 2.71 kJ/mol), can be attributed to clearing of the liquid crystal into an isotropic melt. The reverse transitions, induced by cooling, take place at 172 °C (ΔH = 2.80 kJ/mol) and, with a hysteresis of ~20 °C, at 96 °C (ΔH = 54.75 kJ/mol). The high stability of the compound was demonstrated by the absence of significant perturbation of the DSC patterns following several heating–cooling cycles. The optical textures observed during slow cooling from the isotropic melt showed the emergence of a Smectic A phase (appearance of Bâtonnet rods, turning into wide, fan-like, focal-conic textures) (Fig. 2).

The Smectic structure of the liquid crystal phase was confirmed by XRD studies. The X-ray pattern (Fig. 3a) of the Smectic A form recorded at 119 °C contains a diffuse band at 4.6 Å (wide angle), which shows that the alkyl chains have a liquid-like structure and are segregated from the aromatic cores. However, the presence of two sharp reflections at 30.89 and 15.26 Å (small angle) in a ratio of 1:2 indicates unambiguously the presence of layers.

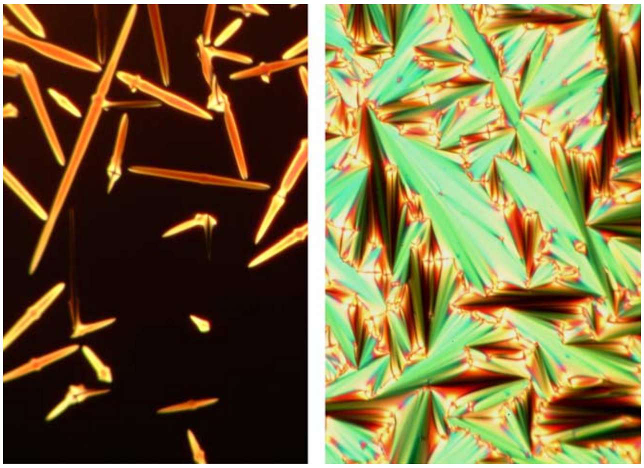

Figure 2. (Left) Corresponding when the Smectic A emerges as batônnet from the isotropic liquid. (Right) Typical texture of Smectic A phase with fan-like, focal-conic and positive units.

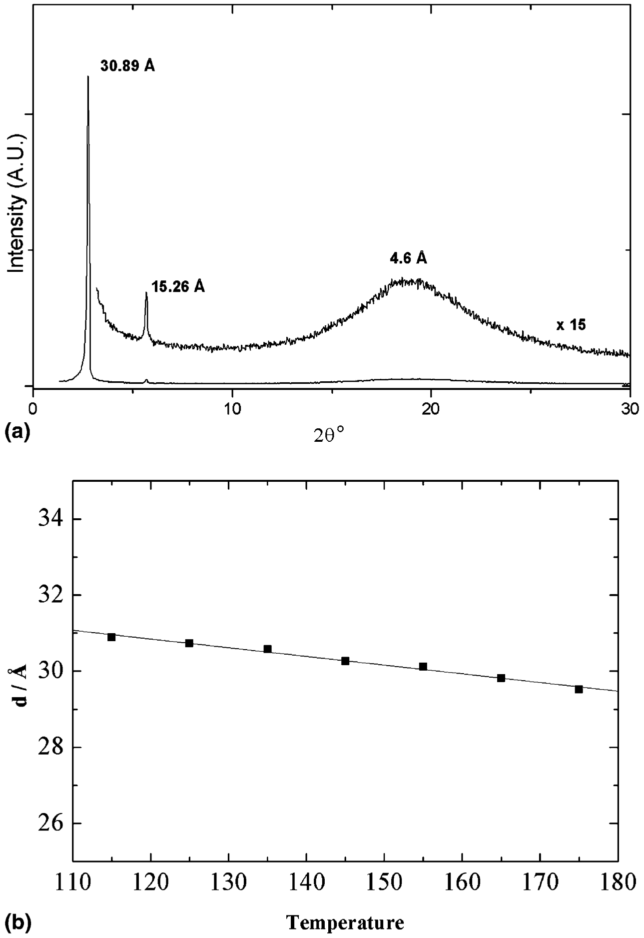

Figure 3. (a) Powder X-ray diffraction pattern of compound **A** in the liquid crystal state ($T = 119\ ^\circ C$). For clarity, the intensity at Bragg angles $2\theta > 3^\circ$ is multiplied 15-fold. (b) Temperature dependence of the layer thickness of the Smectic A.

Additionally, we have investigated the temperature dependence of the layer thickness of the Smectic A phase as a function of the temperature (Fig 3b). The spacing of the layer found in the liquid crystal state (around 31 Å) compares well with that (29.2 Å) in the X-ray structure of the crystal recorded at 173 K.

In conclusion, we report a fully characterised new mesomorphic compound based on an imidazolium unit. We are now investigating the ability of this compound to form thermotropic complexes with, for example, palladium(II). We are also attempting to introduce different tails and anions in order to obtain room-temperature ionic liquid crystals.

Acknowledgements

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10. Full synthetic details will be given elsewhere. The new compound was characterised by NMR and elemental analyses. To a mixture of bis-imine (0.770 g, 1.33 mmol) and AgOTf (0.446 g, 1.73 mmol) were added dry CH_2Cl_2 (15 ml) and then chloromethyl pivalate (310 µl, 2.13 mmol). The Schlenk tube was stirred in dark at 50 °C, under argon atmosphere, for 20 h. The solution was cooled to rt, the mixture was filtered through Celite, the solvent was evaporated and the crude product was purified by silica gel column chromatography first with CH_2Cl_2 as eluent and then CH_2Cl_2–MeOH (20:1). The compound was subsequently crystallised from dichlomethane by addition of hexane. The imidazolium triflate deposited as colorless crystals (0.600 g, 8.12 mmol, 61%). Anal. Calcd for $C_{40}H_{61}F_3N_2O_5S$ ($M_r = 738.98$): C 65.01, H 8.32, N 3.79, S 4.34. Found: C 64.78, H 8.58, N 3.56, S 4.25. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ 9.59 (t, N–CH–N imidazolium, $^4J = 1.65$ Hz), 7.67 (d, 2H, N–CH–CH–N imidazolium, $^4J = 1.6$ Hz), 7.64 (m, 2H, aromatic, AA′ system, $^3J = 9.0$ Hz), 7.01 (m, 2H, aromatic, BB′ system, $^3J = 9.0$ Hz), 3.95 (t, 2H, CH_2–O, $^3J = 6.6$ Hz), 1.79 (m, 2H, CH_2–CH_2–O), 1.43 (m, 2H, CH_2–CH_2–CH_2–O), 1.28 (s broad, 32H, aliphatic), 0.89 (t, 3H, CH_3, $^3J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C) δ 14.10 ppm (–CH_3), 22.69, 25.97, 29.10, 29.36, 29.41, 29.60, 29.63, 29.65, 29.68, 31.92, 68.65 (O–CH_2), 115.95, 122.02, 122.81, 123.44, 126.86, 132.40, 160.64.
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12. *Crystal data* for **A**: $C_{40}H_{61}F_3N_2O_5S$, $M_w = 738.98$ g, monoclinic; $a = 8.860(1)$ Å, $b = 17.452(3)$ Å, $c = 25.969(5)$ Å, $\beta = 90.54(5)^\circ$, $V = 4015.3$ Å^3, $T = 173$ K, *C*, space group $P2_1/a$ (no. 14), $Z = 4$, $D_c = 1.222$ g cm^{-3}, μ(Mo Kα) = 0.138 mm^{-1}, a total of 27,812 reflections, $1.41^\circ < \theta < 29.97^\circ$, 11,644 independent reflections with 5887 having $I > 2\sigma(I)$, 460 parameters, final results: $R_1 = 0.09$; $R_{w2} = 0.19$, Goof = 1.078, maximum residual electronic density = 0.281 e$^-$ Å^{-3}. CCDC reference number 249105.