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Preliminary communication

Conductive liquid crystalline compounds having a piperazine structure

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New conductive thermotropic liquid crystalline materials having a piperazine ring in the central core: 1-[4-(9-decenyloxy)phenyl]-4-alkylpiperazines (**6**) were synthesized. The mesomorphic behaviours of these compounds and their conductivity in the liquid crystal phase were measured. The principal features of these compounds are to exhibit a smectic B phase around room temperature (for example **6**: Cr 50 SmB 81 I, °C) and to exhibit a large dark current (**6d**: 430 μA cm^{-2}, applied voltage 20 V, at 70°C) in the smectic B phase.

The photoconductive behaviour of nematic and smectic liquid crystalline phases have previously been studied [1–3]. Photoconductive behaviour has been reported in the smectic A (SmA) phase of thiobenzothiazole-type compounds and in the discotic liquid crystalline phase of triphenylene-type compounds [2–4]. Moreover, dark conductivity in the nematic liquid crystalline state has been studied, and ionic conduction was dominant [1]. In the measurement of SmA phase dark current, about 100 nA of dark current were reported [2]. In this paper we now report the dark current of 1-[4-(9-decenyloxy)-phenyl]-4-alkylpiperazines (**6**) which have two basic nitrogens in their central core. These compounds exhibit the smectic B (SmB) phase, which must be advantageous for transport of charge. That is, in the transport of charge, the degree of assembly of molecules must be important.

The compounds **6** were synthesized by the route shown in figure 1. Measurement of transition temperatures and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers, a differential scanning calorimeter, and X-ray diffraction (XRD). Phase transition temperatures for compounds **6** are given in table 1.

Observations on their textures indicates that these compounds exhibit the natural SmB phase texture. To confirm this result, conoscopic figures and XRD were measured for the LC phase of compounds **6**. The results support the assignment of the liquid crystalline phase as SmB. That is, a uniaxial conoscopic figure was observed,

Table 1. Phase transition temperatures for compounds **6**. Cr = crystal, SmB = smectic B phase, I = isotropic.

Compound	*R*	Transition temperature/°C [1]
6a	C_8H_{17}	Cr $\underset{41}{\overset{50}{\rightleftarrows}}$ SmB $\underset{80}{\overset{80}{\rightleftarrows}}$ I
6b	$C_{10}H_{21}$	Cr $\underset{45}{\overset{61}{\rightleftarrows}}$ SmB $\underset{83}{\overset{83}{\rightleftarrows}}$ I
6c	$C_{11}H_{23}$	Cr $\underset{47}{\overset{55}{\rightleftarrows}}$ SmB $\underset{82}{\overset{82}{\rightleftarrows}}$ I
6d	$C_{12}H_{25}$	Cr $\underset{43}{\overset{56}{\rightleftarrows}}$ SmB $\underset{81}{\overset{81}{\rightleftarrows}}$ I

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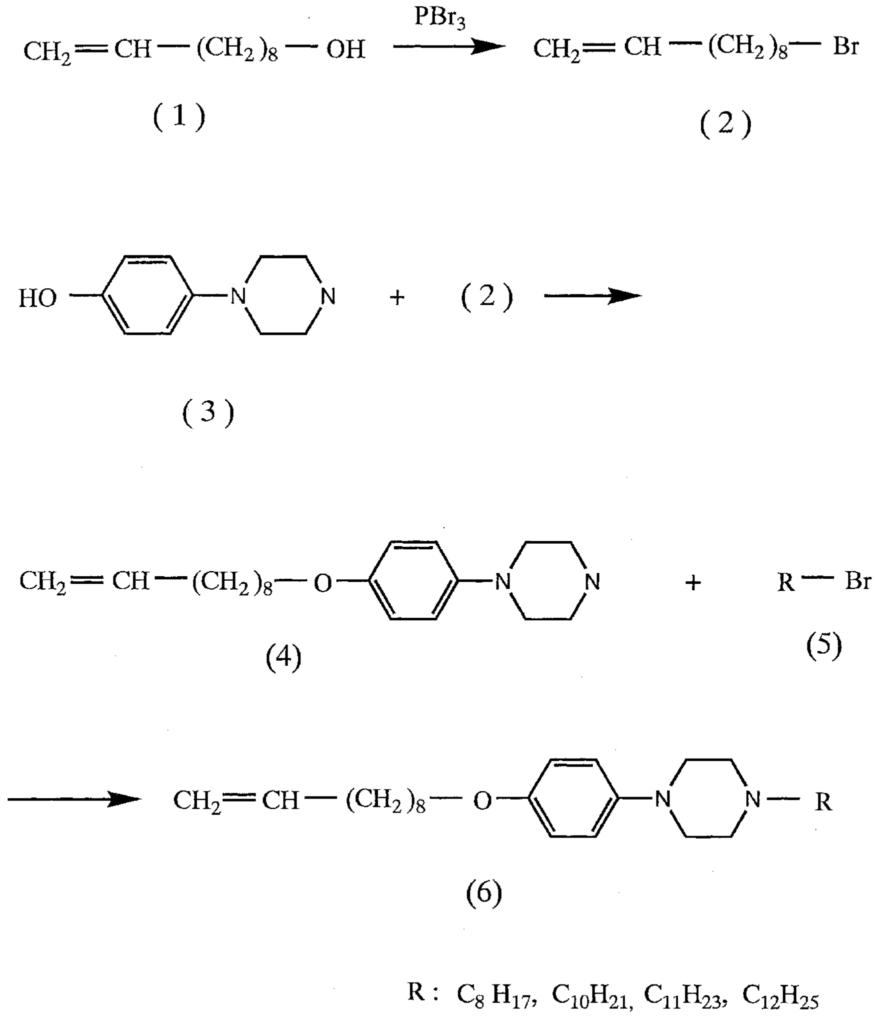

Figure 1. Synthetic pathway for the conductive liquid crystal compounds **6**.

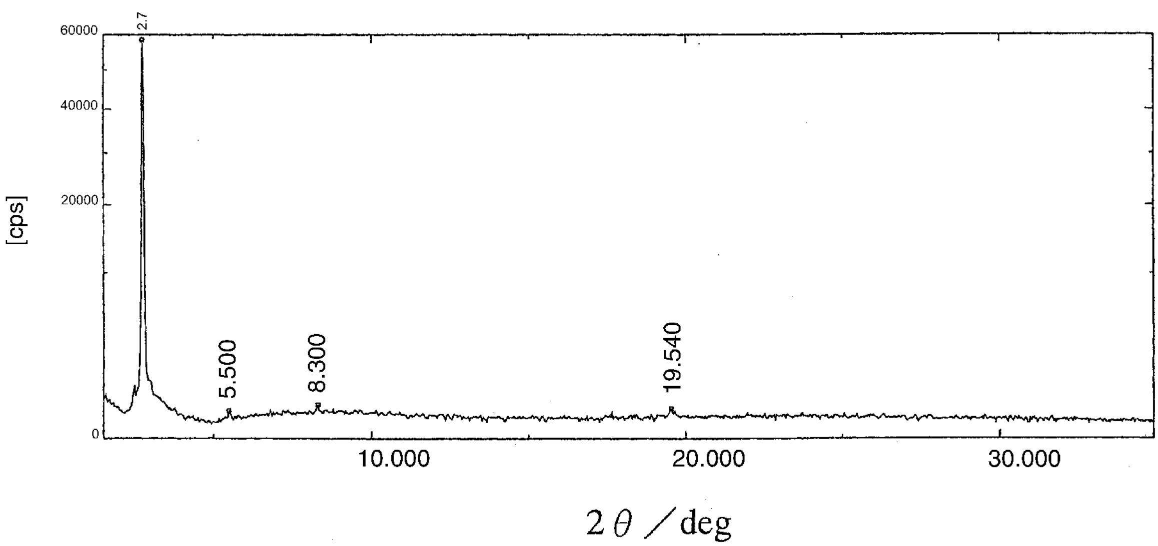

Figure 2. X-ray diffraction pattern of the compound **6d**.

Table 2. Dark current of compounds **6** in the smectic B phase.

Compound	R	Dark current/μA cm^{-2}, at 70°C (Applied voltage 20 V, cell gap 15 μm)
6a	C_8H_{17}	310
6b	$C_{10}H_{21}$	340
6c	$C_{11}H_{23}$	330
6d	$C_{12}H_{25}$	430

and the diffraction pattern of a typical SmB phase was obtained. For example, in compound **6d**, the sharp peak in the small angle region indicated that the layer spacing of this phase is 32.2 Å; the small peak in the wide angle region indicate that the lateral distance between molecules is 4.5 Å (figure 2). As the layer spacing is nearly equal to the molecular length of compound **6d**, these compounds seem to be arranged in mono layers.

The electrical dark current of the 1-[4-(9-decenyloxy)-phenyl]-4-alkylpiperazines was measured for homogeneous alignment in a liquid crystalline cell (cell spacing 15 μm, effective area of electrode 0.16 cm^2) by using an Advantest 8340A instrument and a Mettler FP90 control processor (table 2). The compounds exhibit a dark current of 310–430 μA cm^{-2} (applied voltage 20 V). Generally, the dark current of liquid crystalline compounds is several nA cm^{-2}, so these values are the largest seen in thermotropic liquid crystalline materials. The currents are electric, not ionic, judging from the response times of less than 1 μs. In the case of ionic transport the response time is several μs in a 15 μm liquid crystal cell.

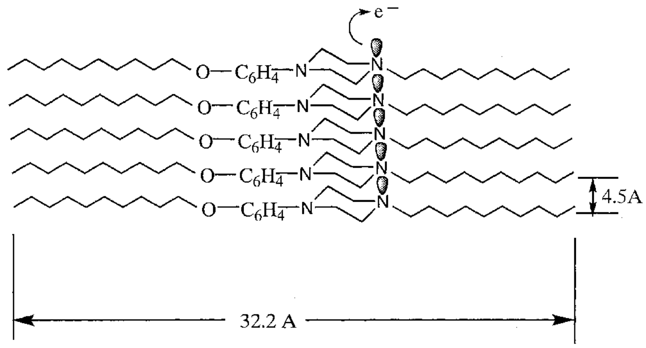

Figure 3. Molecular arrangement of compounds **6** in the smectic B phase.

Compounds **6** exhibit the SmB phase, in which the liquid crystalline molecules are arranged side by side. The basic nitrogen atoms must therefore be gathered together as shown in figure 3. The density of molecules in the SmB phase is higher than in the SmA phase. These factors must be favourable for conduction by hole transfer.

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