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Online publication date: 06 August 2010

To cite this Article Lai, Long-Li and Lin, Hong-Cheu(2000) 'Synthesis and mesogenic properties of azo-dye liquid crystals', Liquid Crystals, 27: 5, 707 — 709

To link to this Article: DOI: 10.1080/026782900202606

URL: http://dx.doi.org/10.1080/026782900202606

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LIQUID CRYSTALS, 2000, VOL. 27, NO. 5, 707–709

Preliminary communication

Synthesis and mesogenic properties of azo-dye liquid crystals

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(*Received 7 May 1999; accepted 20 December 1999*)

Azo-dye liquid crystals with strong amino electro-donating and moderately flexible carboxylate electron-withdrawing groups were synthesized, and their mesogenic properties were studied.

Azo-dye liquid crystals recently have attracted much attention for optical storage applications because of their easy availability, reasonable photo-fatigue resistance, and the marked transformation of their molecular shape upon E-to-Z photoisomerization [1, 2]. Azo-dyes have a reasonable dichroic ratio and are thus particularly suitable for low power consumption reflective liquid crystal devices [3]. In a guest–host (G–H) system dichroic dye is dissolved in a liquid crystal to improve the viewing angle and give better reflectance. In particular, three-layered G–H systems with subtractive colour mixing of yellow, magenta, and cyan are expected to allow the development of full-colour reflective displays [4]. Moreover, doping of dye in a self-supporting cholesteric polarizer can result in the different cholesteric pitch in different positions within the layer and thus broaden the bandwidth of the polarizer [5]. However, the solubility and the phase transition temperatures of the G–H systems are serious issues for application. Usually, the isotropization temperatures vary with the composition of G–H systems [6]. Addition of non-mesogenic dyes often causes the instability of the liquid crystal phase. Dyes which are themselves mesogenic minimize this effect. Therefore azo-dye liquid crystals are highly desirable as dopants.

Previous work in the azo-dye liquid crystal area has mostly concentrated on the alkoxy, nitro or cyano derivatives [1(*b*, *d*), 7] although some of the alkoxy and $-NO_2$ terminated azo-molecules did not even show any liquid crystalline phases [7(*a*, *c*)]. To our knowledge, only a few liquid crystalline molecules containing the amino together with the $-NO_2$ terminated functional groups have ever been synthesized [7(*g*, *e*)]. However, the introduction of the amino functional group often causes, to some extent, the bending of the molecule and consequently destabilizes the mesogenic phase. On the other hand, we have learned that the incorporation of the nitrogen-containing heterocyclic rigid core and the oxygen-containing flexible tail into the molecule may enhance the formation of the SmC phase [8]. In order to maintain the linearity of the molecules and formation of a wider SmC phase as a potential ferroelectric liquid crystal, we have introduced a piperazine moiety and an ester functionality into our system. Thus, a new family of azo-dye liquid crystals with strong amino electron-donating and moderately flexible carboxylate electron-withdrawing groups, as demonstrated in the figure, were recently synthesized. The purpose of maintaining the dialkyl amino group is to create a strong charge transfer in the system and to synthesize the desired chromophores with a suitable absorption wavelength in future work. We now wish to report our primary results.

The desired azo-dye molecules **1a–1d** were synthesized according to scheme 1. Compound **2** was obtained by reaction of the the *N*-phenylpiperazine with decenoyl chloride in dichloromethane in the presence of triethylamine, in almost quantitative yield. The diazonium salts **3a–3d** were prepared according to a literature method

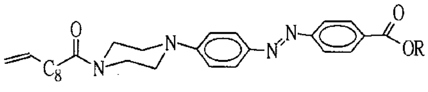

Figure.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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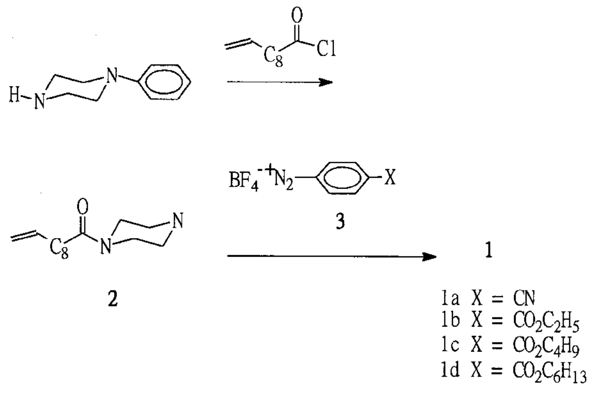
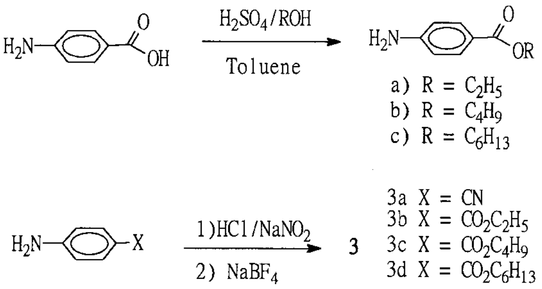


Scheme 1.

[9] as demonstrated in scheme 2. The esterification gave about 60% yields, and the diazotisation was carried out with almost quantitative yields.

The mesogenic behaviour and phase transitions, characterized by polarizing optical microscopy and differential scanning calorimetry (Perkin-Elmer DSC 7), are summarized in the table. Powder X-ray diffraction (XRD) patterns were obtained using a Siemens D-5000 X-ray diffractometer equipped with a TTK 450 temperature controller. The results show that all the compounds are mesomorphic, with a variety of SmA, SmC, and N phases. The smectic A phase was characterized by the focal-conic fan texture coexisting with homeotropic alignment; the tilted smectic C phase was characterized by the broken focal-conic fan texture coexisting with the schlieren texture. These results were also confirmed by XRD. The X-ray pattern in the SmC range showed only a sharp reflection in the small angle region, suggesting a smectic layer structure without regular arrangement in the intralayers. In the range of the SmC phase, the layer thickness decreased gradually with temperature to reach a minimum value, after which the thickness increased again until the isotropic phase was reached. This result was quite consistent. In the azomolecules **1c** and **1d** the *d*-spacings were quite similar: **1c**, 31.33 Å at 130°C, 31.24 Å at 150°C, 31.06 Å at 160°C, 31.36 Å at 170°C, and 31.55 Å at 180°C; **1d**, 33.44 Å at 110°C, 32.37 Å at 130°C, 32.11 Å at 150°C, 31.95 Å at 170°C, and 32.05 Å at 180°C. All of these *d*-spacings are much shorter than the calculated fully extended molecular length (~ 37.1 Å) due to molecular tilt in the SmC phase.



Scheme 2.

Additionally, compound **1a** shows only SmA and nematic phases. However, when the –CN group was replaced by the carboxylate functional group, the SmC phase, appeared as expected. The SmC phase in compounds **1b–1d** is in the range of 122.7–161.1°C, 125.2–189.0°C and 111.2–182.2°C, respectively. In a recent paper [8], we have already shown that the alkoxy-containing heterocyclic rigid core helps the formation of the SmC phase of liquid crystalline molecules. Now we may further regard that the carboxylate-containing heterocyclic rigid core produces similar results. In our case, the range of the SmC phase increases with the flexible chain lengths. The range of the SmC phase for compound **1b** is 38.4°C and that for compound **1d** is 71°C. Appropriate chain length, related to the molecular shape rather than dipole moment, is critical in generating the tilted SmC phase, as the increase of the chain length from C2 to C4 illustrates. It is noteworthy that when compounds **1c** and **1d** were cooled from the isotropic state, the polarizing optical microscope schlieren texture was observed with a little cracking for temperature below 155.9 and 153.0°C for **1c** and **1d**, respectively. However, from XRD study, it was proved that the cracking textures are still in the SmC phase.

Table. Phase transition temperatures (°C)[a] and corresponding enthalpies ($\mathrm{J\,g^{-1}}$), in parentheses, of the azo-dyes **1a–1d**. Phase transition temperatures and corresponding enthalpies were determined by the 2nd heating scans at a heating and cooling rate 10°C $\mathrm{min^{-1}}$. Cr = crystalline phase, SmX and SmX′ = unidentified smectic phases, I = isotropic liquid, H = heating, C = cooling.

Compound	Cr		SmX′		SmX		SmC		SmA		N		I
1a(H)	•	130.2(86.5)							•	136.5(0.1)	•	158.5(1.2)	•
1a(C)	•	110.2(75.9)							•	133.6(0.4)	•	155.7(1.0)	•
1b(H)	•	68.2(4.2)	•	80.4(0.7)	•	122.7(1.0)	•	161.1(0.5)	•	200.4(16.1)			•
1b(C)	•	61.5(4.4)			•	120.2(1.8)	•	157.7(0.3)	•	195.0(16.3)			•
1c(H)	•	65.2(3.4)			•	125.2(1.9)	•	189.0(17.9)					•
1c(C)	•	60.1(3.4)			•	122.2(1.6)	•	184.3(17.8)					•
1d(H)	•	111.2(28.6)					•	182.2(20.3)					•
1d(C)	•	65.2(18.2)			•	109.4(1.7)	•	177.5(19.1)					•

In conclusion, this work presents a successful approach to the synthesis of dye molecules exhibiting liquid crystalline phases. To the best of our knowledge, this is the first series of piperazine-containing dyes to possess the SmC phase. As stated at the beginning, these may help to improve the technology of reflective liquid crystal devices. The formation of the SmC phase in these dyes may also be useful in the area of ferroelectric liquid crystal displays.

We would like to thank the National Chi Nan University, Academia Sinica and National Science Council of the Republic of China through Grant No. NSC 88-2113-M-260-001 and NSC 88-2113-M-001-048. Without their support, it would have been impossible to complete this work.

Appendix

Products **1a–1d** were identified as the required materials and judged to be pure by ^{1}H and ^{13}C NMR spectroscopy. Elementary analyses for C, H and N were also satisfactory.

1a. ^{1}H NMR: δ (CDCl$_3$) 1.32–1.70 (m, 12H, 6CH$_2$), 2.03 (quint, 2H, CH$_2$), 2.38 (t, 2H, CH$_2$), 3.44 (s, b, 4H, 2CH$_2$), 3.68 (s, b, 2H, CH$_2$), 3.81 (s, b, 2H, CH$_2$), 4.89–5.05 (m, 2H, –CH$_2$), 5.71–5.88 (m, 1H, –CH), 6.99 (d, 2H, $J = 9.16$ Hz, 2 × Ar–H), 7.94 (d, 2H, $J = 9.17$ Hz, 2 × Ar–H), 7.96 (d, 2H, $J = 8.92$ Hz, 2 × Ar–H), 8.34 (d, 2H, $J = 9.01$ Hz, 2 × Ar–H). ^{13}C NMR: δ (CDCl$_3$) 25.18, 28.81, 28.99, 29.29, 29.37, 33.21, 33.69, 40.88, 44.90, 47.40, 47.58, 114.08, 114.33, 122.79, 124.59, 125.66, 139.07, 145.33, 147.75, 153.30, 156.16, 171.81. Anal: calc. for $C_{28}H_{35}N_5O$, C 73.49, H 7.71, N 15.30; found C 73.08, H 7.83, N 15.27%.

1b. ^{1}H NMR: δ (CDCl$_3$) 1.32–1.63 (m, 15H, 6CH$_2$ + Me), 2.04 (quint, 2H, CH$_2$), 2.35 (t, 2H, CH$_2$), 3.32 (s, b, 4H, 2CH$_2$), 3.60 (s, b, 2H, CH$_2$), 3.78 (s, b, 2H, CH$_2$), 4.40 (t, 2H, OCH$_2$), 4.94–5.05 (m, 2H, =CH$_2$), 5.71–5.88 (m, 1H, =CH), 6.91 (d, 2H, $J = 8.80$ Hz, 2 × Ar–H), 7.88 (d, 2H, $J = 8.48$ Hz, 2 × Ar–H), 7.91 (d, 2H, $J = 8.74$ Hz, 2 × Ar–H), 8.18 (d, 2H, $J = 8.48$ Hz, 2 × Ar–H). ^{13}C NMR: δ (CDCl$_3$) 14.03, 24.93, 28.56, 28.74, 29.01, 29.07, 32.91, 33.45, 40.69, 44.68, 47.29, 60.79, 113.82, 114.30, 121.86, 124.89, 130.18, 130.81, 138.78, 145.23, 152.64, 155.13, 165.78, 171.55. Anal: calc. for $C_{30}H_{39}N_4O_3$, C 71.40, H 7.99, N 11.10; found C 71.22, H 7.91, N 11.05%.

1c. ^{1}H NMR δ (CDCl$_3$) 0.99 (t, 3H, Me), 1.31–1.80 (m, 16H, 8CH$_2$), 2.04 (quint, 2H, CH$_2$), 2.35 (t, 2H, CH$_2$), 3.36 (s, b, 4H, 2CH$_2$), 3.63 (s, b, 2H, CH$_2$), 3.79 (s, b, 2H, CH$_2$), 4.40 (t, 2H, OCH$_2$), 4.90–5.03 (m, 2H, =CH$_2$), 5.72–5.89 (m, 1H, =CH), 6.94 (d, 2H, $J = 8.80$ Hz, 2 × Ar–H), 7.87 (d, 2H, $J = 8.48$ Hz, 2 × Ar–H), 7.91 (d, 2H, $J = 8.74$ Hz, 2 × Ar–H), 8.19 (d, 2H, $J = 8.48$ Hz, 2 × Ar–H). ^{13}C NMR: δ (CDCl$_3$) 13.65, 19.14, 25.11, 28.74, 28.93, 29.24, 29.29, 30.63, 33.11, 33.63, 40.86, 44.89, 47.76, 64.87, 114.04, 114.52, 122.04, 125.05, 130.35, 131.04, 138.97, 145.46, 152.84, 155.33, 166.04, 171.64. Anal: calc. for $C_{32}H_{43}N_4O_3$, C 72.15, H 8.33, N 10.52; found C 72.11, H 8.36, N 10.46%.

1d. ^{1}H NMR: δ (CDCl$_3$) 0.91 (t, 3H, Me), 1.31–1.80 (m, 20H, 10CH$_2$), 2.05 (quint, 2H, CH$_2$), 2.35 (t, 2H, CH$_2$), 3.35 (s, b, 4H, 2CH$_2$), 3.62 (s, b, 2H, CH$_2$), 3.79 (s, b, 2H, CH$_2$), 4.40 (t, 2H, OCH$_2$), 4.90–5.03 (m, 2H, =CH$_2$), 5.72–5.88 (m, 1H, =CH), 6.94 (d, 2H, $J = 8.90$ Hz, 2 × Ar–H), 7.88 (d, 2H, $J = 8.48$ Hz, 2 × Ar–H), 7.91 (d, 2H, $J = 8.84$ Hz, 2 × Ar–H), 8.16 (d, 2H, $J = 8.50$ Hz, 2 × Ar–H). ^{13}C NMR: δ (CDCl$_3$) 13.88, 22.39, 25.10, 25.55, 28.52, 28.73, 28.91, 29.24, 31.30, 33.10, 33.62, 40.85, 44.88, 47.52, 47.74, 65.15, 114.02, 114.50, 122.03, 125.02, 130.33, 131.04, 138.95, 145.45, 152.84, 155.32, 166.02, 171.60. Anal: calc. for $C_{34}H_{47}N_4O_3$, C 72.82, H 8.63, N 9.99; found, C 72.76, H 8.58, N 9.98%.

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