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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Lai, Long-Li , Wang, Eshin , Lee, Long-Je , Chen, Jo-Jin and Yang, Dee-Way(2011) 'H-Bonded complexes of *N, N*-disubstituted aminophenylazo-(4)-pyridine and benzoic acid derivatives: preparation, mesogenic study and molecular modelling', *Liquid Crystals*, 28: 1, 157 – 159

To link to this Article: DOI: 10.1080/02678290010001734

URL: <http://dx.doi.org/10.1080/02678290010001734>

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Preliminary communication

H-Bonded complexes of *N,N*-disubstituted aminophenylazo-(4)-pyridine and benzoic acid derivatives: preparation, mesogenic study and molecular modelling

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(Received 4 February 2000; accepted 7 March 2000)

N,N-Disubstituted aminophenylazo-(4)-pyridine forms complexes with a series of *m*-alkoxy benzoic acids by intermolecular hydrogen bonding; liquid crystalline phases of the resulting complexes are thus induced.

Azo-dye liquid crystals recently have attracted much attention for their potential application in optical storage systems because of their easy availability, reasonable photo-fatigue resistance and the marked transformation of the molecular shape upon *E*-to-*Z* photoisomerization [1, 2]. Azo-dyes have a reasonable dichroic ratio and are thus particularly suitable for lower power consumption reflective liquid crystal devices [3]. In a guest–host system (G-H) the dichroic dye is dissolved in a liquid crystal to improve the viewing angle and provide better reflectance. In particular, three-layered G-H systems with subtractive colour mixing of yellow, magenta and cyan are expected to be used for developing full-colour reflective displays [4]. However, the solubility and the phase transition temperatures of the G-H systems may be serious problems in applications development. Clearing temperatures usually vary with the components of the G-H systems; the addition of non-mesogenic dyes often causes instability of the liquid crystalline phase in these systems [5]. Dyes which are themselves mesogenic minimize this effect; azo-dye liquid crystals are therefore highly desirable as dopants.

In a previous paper [6], we reported the successful synthesis of a series of crystalline azo-dye compounds containing an amino electron-donating functionality and a carboxylate electron-withdrawing group, as shown as structure **1** (see the figure), which shows a yellow colour in CHCl₃ solution. To obtain compounds with magenta or cyan colour, i.e. further to decrease the LUMO and HOMO energy gap of the molecules, it may be

necessary to synthesize compounds with stronger electron-withdrawing groups, such as CN or NO₂, replacing the carboxylate moiety. Although we can achieve our purpose by such a strategy, the diversity of the liquid crystalline molecules is, to some extent, limited, as the CN and NO₂ functional groups are short and no further attachments can be linked to them. Another method for reducing the LUMO and HOMO energy gap of the molecules is to introduce a heteroaromatic system, such as the pyridine ring, to replace the benzene carboxylate moiety. By following literature methods we prepared the pyridine-containing azodye **2** [7]. It was characterized as follows. ¹H NMR for **2** δ (CDCl₃): 0.85 (3H, s, Me), 1.25–1.30 (12H, m, 6 × CH₂), 1.64 (2H, quint, CH₂), 2.35 (2H, t, CH₂), 3.40 (4H, t, 2 × CH₂), 3.65 (2H, t, CH₂), 3.79 (2H, t, CH₂), 6.94 (2H, d, *J* = 9.0 Hz, 2 × Ar-H), 7.63 (2H, d, *J* = 6.3 Hz, 2 × Ar-H), 7.90 (2H, d, *J* = 9.0 Hz, 2 × Ar-H), 8.71 (2H, d, *J* = 6.3 Hz, 2 × Ar-H). Anal. calc. for C₂₅H₃₅N₅O C 71.23, H 8.37, N 16.61; found C 71.16, H 8.39, N 16.58%.

This compound showed only highly ordered smectic transitions (see the table); however, low viscosity mesogenic phases were induced by the inter-molecular hydrogen bonding of **2** with a series of *m*-alkoxy benzoic acids. As the pyridine ring can be replaced by other heteroaromatics further to reduce the LUMO and HOMO energy gap of the molecules, it may be possible to prepare other heteroaromatic azo-dye molecules in the future, showing the magenta or cyan colour, to be used for the development of the full colour reflective displays. Although the thermomesomorphic H-bonded complexes between pyridyl derivatives and carboxylic

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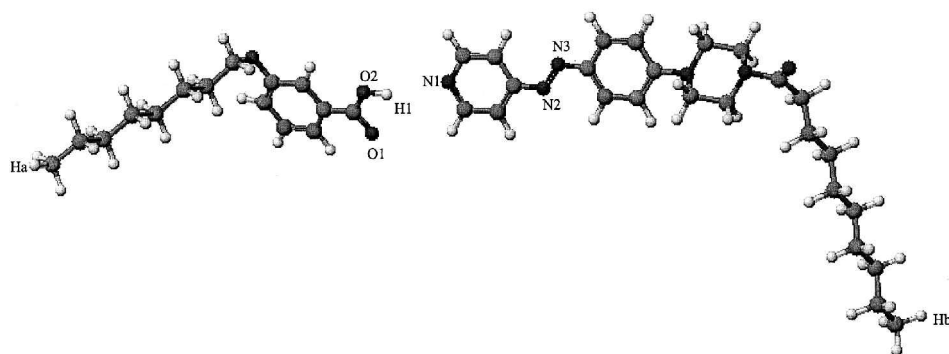
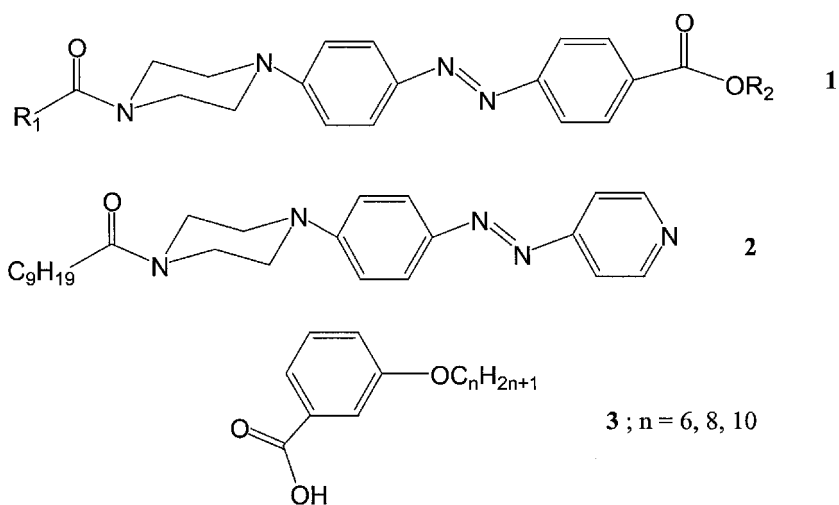
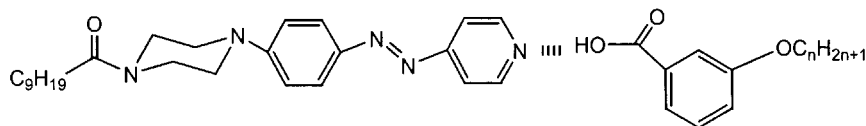


Figure. Structures of compounds **1**, **2** and **3**, and modelling of complex **PAMB8**. Distance of hydrogen bond between H1 and N1: 2.65 Å; distance Ha–Hb = 37.03 Å; energy of H-bond: 2.82 kcal mol⁻¹.

Table. Phase transition temperature (°C) and corresponding enthalpies (J g⁻¹) in parentheses, of hydrogen-bonded complexes from a 1:1 molar ratio of pyridyl azodye **2** and *m*-alkoxybenzoic acid **3** (*n* = 6, 8, 10). The phase transition temperatures and corresponding enthalpies of the hydrogen bonded complexes were determined by 2nd DSC scans at a heating and cooling rate of 10°C min⁻¹ between 50 and 140°C. Cr = crystalline, SmX = unidentified smectic phase, I = isotropic liquid. **PAMB_n** = hydrogen-bonded complex of **2** and **3** (*n* = 6, 8, 10).



PAMB_n

| | | | | | | | | | | | | |
|---------------|-----|---|--------------------------|---|-----|---|---------------------------------|---|-----|---|----------------------------|---|
| Azodye 2 | Cr1 | ⇌ | 110.7(8.1) 70.4(12.7) | ⇌ | Cr2 | ⇌ | 123.(57.6) 102.9(67.4) | I | | | | |
| PAMB6 | Cr | ⇌ | 68.2 | ⇌ | SmX | ⇌ | 87.2(15.8) 76.8 ^a | ⇌ | SmC | ⇌ | 123.6(18.6) 114.2(14.3) | I |
| PAMB8 | Cr1 | ⇌ | 79.4(1.9) 68.8 | ⇌ | Cr2 | ⇌ | 98.7(43.9) 71.2 ^b | ⇌ | SmC | ⇌ | 125.2(16.5) 117.0(15.2) | I |
| PAMB10 | Cr1 | ⇌ | 78.7(1.2) 66.7 | ⇌ | Cr2 | ⇌ | 98.0(37.4) 70.4 ^c | ⇌ | SmC | ⇌ | 124.0(14.8) 115.4(13.8) | I |

^a The peaks are overlapped and their total enthalpy is 15.4 J g⁻¹.

^b The peaks are overlapped and their total enthalpy is 11.2 J g⁻¹.

^c The peaks are overlapped and their total enthalpy is 10.7 J g⁻¹.

acids have been investigated [8], our different approach may open up another useful azo-dye liquid crystal area. Mesogenic behaviour in other nitrogen-containing heterocycles with narrower HOMO and LUMO energy gaps can be induced similarly. Now we wish to report the preliminary results.

To study the liquid crystalline properties of hydrogen bonded complexes, compound **2** and one equivalent of the *m*-alkoxy benzoic acid **3** (see the figure) were dissolved in tetrahydrofuran (THF); the solution was maintained in a fume hood for 48 h while the THF was allowed to evaporate spontaneously. The resulting solid was ground and thoroughly blended for the study of liquid crystalline properties. The mesogenic behaviours and phase transitions were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (Perkin-Elmer DSC 7); see the table. Powder X-ray diffraction (XRD) patterns were obtained from a Siemens D-5000 X-ray diffractometer equipped with a TTK 450 temperature controller. The H-bonded complexes of **2** and **3**, known as **PAMB_n** all show a smectic C phase in their heating and cooling processes, which was characterized by the broken focal-conic fan texture coexisting with the schlieren texture through POM; this is different from the mesogenic behaviour of the *m*-alkoxy benzoic acid derivatives, e.g. compound **2** ($n = 6, 8, 10$) showed no LC phases. Complex **PAMB8** was also studied by XRD; the *d*-spacing distances in the SmC phase were 36.51 Å at 110°C during heating and 36.60 Å at 110°C and 37.21 Å at 90°C during cooling, respectively. 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 between the layers. Although we changed the tail lengths of the acid **2**, the mesogenic range for complexes **PAMB_n**, from smectic C to isotropic liquid of SmX phases, did not vary much from each other. The SmC range was about 50°C for these H-bonded complexes.

As compound **2** contains five nitrogen atoms in the structure, it is quite interesting to know which nitrogen atom forms the hydrogen bonding with the *m*-alkoxybenzoic acid. MM3 geometry studies[†] revealed that H-bonding interactions could occur between **2** and **3** ($n = 8$). The H-bond distance between the carboxylic proton of **3** ($n = 8$) and the pyridyl nitrogen of **2** was calculated to be 2.65 Å, and this interaction lowered the energy of the system by 2.82 kcal mol⁻¹. Significantly, the distance between Ha of **3** ($n = 8$) and Hb of **2** was

calculated to be 37.03 Å (see the figure), which is consistent with the result obtained by XRD (37.21 Å).

In conclusion, this work presents a successful approach to the preparation of mesogenic azo-dye complexes through intermolecular hydrogen bonding. This different approach may open up another useful azo-dye liquid crystal area. Mesogenic behaviour in other nitrogen-containing heterocycles with the narrower HOMO and LUMO energy gaps can be induced similarly. We are optimistic that liquid crystals with suitable different colours can be prepared in the future. The technology of reflective liquid crystal devices may thus be further developed, and the formation of the SmC phase in these dyes may also be useful in the area of ferroelectric liquid crystal displays.

We thank National Chi Nan University and National Science Council (NSC 89-2113-M-260-001) for financial support; also Dr. H.-C. Lin in Academia Sinica and Dr. C.-H. Lin, respectively, for valuable discussion in determining mesogenic phase transitions and the MM3 study of the hydrogen bonding system.

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[†]Semi-empirical calculation was carried out by using CAChe provided by Oxford Molecular Ltd (CAChe Scientific Beaverton, Oregon).