Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Study of the mesogenic behaviour of hydrogen-bonded complexes prepared from aminophenylazopyridines and benzoic acid derivatives

Long-Li Lai[a]; Long-Je Lee[a]; Eshin Wang[a]; Feng-Ya Su[a]
[a] Department of Applied Chemistry, National Chi Nan University, Puli, Taiwan 545, ROC,

To cite this Article Lai, Long-Li , Lee, Long-Je , Wang, Eshin and Su, Feng-Ya(2001) 'Study of the mesogenic behaviour of hydrogen-bonded complexes prepared from aminophenylazopyridines and benzoic acid derivatives', Liquid Crystals, 28: 3, 381 — 386

To link to this Article: DOI: 10.1080/02678290010013957

URL: http://dx.doi.org/10.1080/02678290010013957

LIQUID CRYSTALS, 2001, VOL. 28, NO. 3, 381–386

Study of the mesogenic behaviour of hydrogen-bonded complexes prepared from aminophenylazopyridines and benzoic acid derivatives

LONG-LI LAI*, LONG-JE LEE, ESHIN WANG and FENG-YA SU
Department of Applied Chemistry, National Chi Nan University, Puli,
Taiwan 545, ROC

(*Received 27 June 2000; accepted 30 August 2000*)

Complexes have been formed between *N*,*N*-disubstituted aminophenylazopyridines and a series of alkoxybenzoic acids by intermolecular hydrogen bonding; liquid crystalline phases of the resulting complexes are induced thereby.

1. Introduction

Azo dye liquid crystals have recently attracted much attention for their potential application in optical storage systems because of their easy availability, good photo-fatigue resistance and the marked transformation of the molecular shape on *E*–*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 (GH) system the dichroic dye is dissolved in a liquid crystal to improve the viewing angle and give better reflectance. In particular, three-layered GH 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 phase transition temperatures of the GH systems are serious problems for applications. Usually, the clearing temperatures vary with the components of the GH systems. Addition of the non-mesogenic dyes often causes instability of the liquid crystalline phase [5]; dyes which are themselves mesogenic minimize this effect. Azo dye liquid crystals are therefore highly desirable as dopants.

Previously, we successfully synthesized a series of yellow crystalline azo dyes containing an amino electron-donating functionality and a carboxylate electron-withdrawing group [6]. To obtain compounds with magenta or cyan colour, i.e. to decrease further the LUMO and HOMO energy gap of the molecules, it may be possible to synthesize compounds with stronger electron-withdrawing groups, such as CN or NO$_2$, to replace the carboxylate moiety. Although we could achieve this purpose by such a strategy, the diversity of the liquid crystalline molecules is limited, as the CN and NO$_2$ functional groups are short and no further attachments can be linked to them. Another method for reducing the LUMO and HOMO energy gap is to introduce a heteroaromatic system, such as the pyridine ring, to replace the benzene carboxylate moiety. Recently, we prepared pyridine-containing azo dyes by literature methods [7], and found that these compounds showed only highly-ordered smectic transitions; however, low viscosity mesogenic phases could be induced by inter-molecular hydrogen bonding with a series of *m*-alkoxy benzoic acids [8]. 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 dyes with magenta or cyan colours for the development of full colour reflective displays in the future. Although thermo-mesomorphic H-bonded complexes between pyridyl derivatives and carboxylic acids have already been investigated [9], our 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 gap can be induced similarly; we now wish to report our completed work.

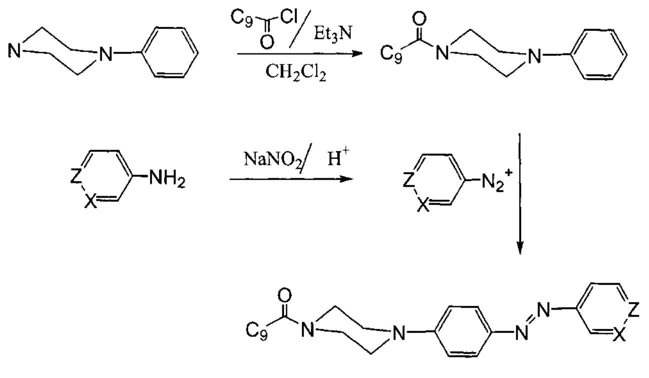
2. Experimental

Chemicals used in this work were commercially available from ACROS. The 4-pyridylazo dye **1** and 3-pyridylazo dye **2** were prepared by literature methods, as shown in the scheme [6, 7] and characterized by

---

*Author for correspondence; e-mail: lilai@ncnu.edu.tw

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010013957



1. X = C, Z = N; **2**. X = N, Z = C

Scheme.

^{1}H NMR spectroscopy and elemental analysis†. 3-Alkoxy benzoic acids **3** and 4-alkoxy benzoic acids **4** were also synthesized according to literature methods [9]. The hydrogen bonded complexes *l*-PA-*m*-AB*n* (*l*, *m* = 3 or 4, *n* = 6, 8, 10, 12) were prepared by dissolving a 1 : 1 molar ratio of the azo dye and benzoic acid derivatives in sufficient amounts of tetrahydrofuran (THF). The resulting solution was then 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 its liquid crystalline properties. ^{1}H NMR spectra were measured by a Bruker AC 300 FT NMR spectrometer. The mesogenic behaviour and phase transitions were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (Perkin-Elmer DSC 7). Phase transition temperatures and enthalpies were determined by 2nd DSC scans at a heating/cooling rate of 10°C min^{-1}, between 50 and 150°C (see the tables). Powder X-ray diffraction (XRD) patterns were obtained from a Siemens D-5000 X-ray diffractometer equipped with a TTK 450 temperature controller. Semi-empirical calculation was carried out by using CAChe program provided by Oxford Molecular Ltd (CAChe Scientific Beaverton, Oregon.).

3. Results and discussion

Complexes 4-PA-3-AB*n* were prepared from pyridylazo dye **1** with one equivalent of 3-alkoxybenzoic acid **3** (*n* = 6, 8, 10, 12). Compound **1** shows no liquid crystalline phase during heating and only a highly ordered smectic phase on cooling (table 1). The alkoxybenzoic acid derivatives **3** (*n* = 6, 8, 10) also show no liquid crystalline properties during heating or cooling processes (table 2). Compound **3** (*n* = 12) shows two crystalline phases during heating and two crystalline phases and one highly ordered smectic phase during cooling. However, complexes 4-PA-3-AB*n* (*n* = 6, 8, 10, 12) all show a SmC phase during heating and cooling, characterized by the broken focal-conic fan texture coexisting with the schlieren texture, as seen in POM.

Complexes 4-PA-3-AB8 and 4-PA-3-AB12 were studied by XRD. The *d*-spacings in the SmC phase for 4-PA-3-AB8 are 36.51 Å at 110°C during heating and 36.60 Å at 110°C and 37.21 Å at 90°C during cooling. The *d*-spacings in the SmC phase for 4-PA-3-AB12 are 39.73 Å at 95 and 115°C and 39.43 Å at 115°C during heating; and 39.58 Å at 105°C, 39.92 Å at 95°C and 40.32 Å at 75°C during cooling. Although the tail lengths of the acids **3** were varied, the mesogenic range for complexes 4-PA-3-AB*n*, from SmC to isotropic liquid or SmX phases, were similar. The SmC temperature range is about 45–60°C for these H-bonded complexes.

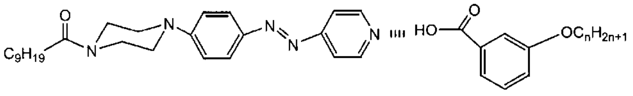
Complexes 4-PA-4-AB*n* were prepared from pyridylazo dye **1** with one equivalent of 4-alkoxybenzoic acid **4** (*n* = 8, 10, 12). The alkoxybenzoic acid derivatives (*n* = 6, 8, 10, 12) show nematic and/or SmC phases during heating and cooling (table 3) [9*b*, 10]. With a shorter alkyl chain, the nematic phase is preferred. Conversely, when the chain is longer, the SmC phase is preferred. Complexes 4-PA-4-AB*n* (*n* = 8, 10, 12) all show SmC and SmA phases during heating and cooling, which were characterized by the broken focal-conic fan texture coexisting with the schlieren texture, and the broken focal-conic fan texture, respectively, by POM (table 4).

Complex 4-PA-4-AB10, representing this series of complexes, was studied by powder XRD. The *d*-spacings in the SmA phase are 42.85 Å at 170°C, 42.23 Å at 150°C and 42.18 Å at 140°C during cooling. The *d*-spacings in the SmC phase for 4-PA-4-AB10 are 41.98 Å at 120°C and 41.86 Å at 100°C during cooling. The *d*-spacings gradually increase to a maximum at 170°C. Below the phase change point (122.1°C), i.e. in the SmC region, the increasing *d*-spacing arises from the decreasing angle θ between the Z and the molecular axes. Above the phase-changing point, i.e. in the SmA region, the increasing *d*-spacing may arise from the reduced interaction between molecular layers on heating. The temperature ranges of the SmA phase (about 50°C) for complexes 4-PA-4-AB*n*

---

† ^{1}H NMR for **1**: δ ($CDCl_3$) 0.85 (3H, s, Me), 1.25–1.30 (12H, m, 6 × CH_2), 1.64 (2H, quint, CH_2), 2.35 (2H, t, CH_2), 3.40 (4H, t, 2 × CH_2), 3.65 (2H, t, CH_2), 3.79 (2H, t, CH_2), 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). Elemental analysis: calcd for $C_{25}H_{35}N_5O$, C 71.23, H 8.37, N 16.61; found, C 71.16, H 8.39, N 16.58%. ^{1}H NMR for **2**: δ ($CDCl_3$) 0.86 (3H, s, Me), 1.25–1.30 (12H, m, 6 × CH_2), 1.64 (2H, quint, CH_2), 2.35 (2H, t, CH_2), 3.38 (4H, t, 2 × CH_2), 3.65 (2H, t, CH_2), 3.79 (2H, t, CH_2), 6.95 (2H, d, J = 9.0 Hz, 2 × Ar–H), 7.38–7.42 (1H, m, Ar–H), 7.90 (2H, d, J = 9.0 Hz, 2 × Ar–H), 8.10 (1H, 2d, J = 6.0, 2.4 Hz, Ar–H), 8.61 (1H, d, J = 6.3 Hz, Ar–H), 8.71 (1H, d, J = 6.3 Hz, Ar–H). Elemental analysis: calcd for $C_{25}H_{35}N_5O$, C 71.23, H 8.37, N 16.61; found, C 71.25, H 8.47, N 16.61%.

Table 1. Phase transition temperatures (°C) and corresponding enthalpies (J g^{-1}), in parentheses, of hydrogen-bonded complexes from a 1:1 molar ratio of pyridylazo dye-1 and 3-alkoxybenzoic acids (*n* = 6, 8, 10, 12). Cr = crystalline, SmX = unidentified smectic phase, SmC = Smectic C phase, I = isotropic liquid.

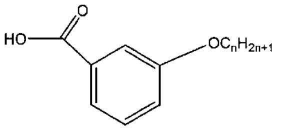


4-PA-3-ABn

Azo dye-1	$\mathrm{Cr1} \xrightleftharpoons[70.4(12.7)]{110.7(8.1)} \mathrm{Cr2}\ \mathrm{SmX} \xrightleftharpoons[102.9(67.4)]{123.0(57.6)} \mathrm{I}$
4-PA-3-AB6	$\mathrm{Cr} \xleftarrow[68.2]{} \mathrm{SmX} \xleftarrow[76.8^{a}]{} \mathrm{SmC};\ \mathrm{Cr} \xrightarrow{87.2(15.8)} \mathrm{SmC} \xrightleftharpoons[114.2(14.3)]{123.6(18.6)} \mathrm{I}$
4-PA-3-AB8	$\mathrm{Cr1} \xrightleftharpoons[68.8]{79.4(1.9)} \mathrm{Cr2}\ \mathrm{SmX} \xrightleftharpoons[71.2^{b}]{98.7(43.9)} \mathrm{SmC} \xrightleftharpoons[117.0(15.2)]{125.2(16.5)} \mathrm{I}$
4-PA-3-AB10	$\mathrm{Cr1} \xrightleftharpoons[66.7]{78.7(1.2)} \mathrm{Cr2}\ \mathrm{SmX} \xrightleftharpoons[70.4^{c}]{98.0(37.4)} \mathrm{SmC} \xrightleftharpoons[115.4(13.8)]{124.0(14.8)} \mathrm{I}$
4-PA-3-AB12	$\mathrm{Cr1} \xrightarrow{85.4(33.4)} \mathrm{SmC} \xrightleftharpoons[112.6(13.4)]{120.0(13.5)} \mathrm{I}$

[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}.

Table 2. Phase transition temperature (°C) and corresponding enthalpies (J g^{-1}), in parentheses, of 3-alkoxybenzoic acids (*n* = 6, 8, 10, 12). Cr = crystalline, SmX = unidentified smectic phase, I = isotropic liquid.



3-alkoxybenzoic acid 3

n = 6	$\mathrm{Cr} \xrightleftharpoons[48.9(102.5)]{69.8(102.2)} \mathrm{I}$
n = 8	$\mathrm{Cr} \xrightleftharpoons[60.9(133.5)]{73.9(132.3)} \mathrm{I}$
n = 10	$\mathrm{Cr} \xrightleftharpoons[56.3(123.8)]{71.9(121.7)} \mathrm{I}$
n = 12	$\mathrm{Cr} \xrightleftharpoons[68.9(5.8)]{76.2(5.1)} \mathrm{Cr1} \xleftarrow[76.5]{} \mathrm{SmX} \xleftarrow[79.6^{a}]{} \mathrm{I};\ \mathrm{Cr1} \xrightarrow{89.1(109.7)} \mathrm{I}$

[a] The peaks are overlapped and their total enthalpy is 121.2 J g^{-1}.

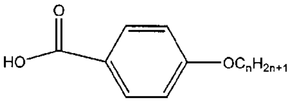
are similar, but the range of the SmC phase increases from 37 to 60°C, when the carbon number of the alkoxy chain increases from 8 to 12 (during cooling).

Complexes 3-PA-4-AB*n* were prepared from pyridylazo dye **2** with one equivalent of 4-alkoxybenzoic acid **4** (*n* = 6, 8, 10, 12). They show a SmA phase during heating and cooling, characterized in POM by the broken focal-conic fan texture (table 5). Changing the length of the acid **4** molecule has little effect on the mesogenic range; the SmA temperature range is about 30–40°C during cooling. The XRD reflection pattern for the SmC and SmA phases for the above-mentioned complexes show only a sharp reflection in the small angle region, suggesting a smectic layer structure without regular arrangement in the intralayers.

As the pyridylazo dye **1** molecule contains five nitrogen atoms in its structure, it is interesting to know which nitrogen atom interacts with the proton of the alkoxybenzoic acid. MOPAC geometry studies revealed that N and H interactions could occur between the dye molecules and the benzoic acid derivatives. For complex 4-PA-3-AB8, the distance between the carboxylic proton of **3** (*n* = 8) and the pyridyl ending nitrogen of **1** is calculated to be 1.99 Å; the distance between the pyridyl hydrogen and the oxygen of the C=O moiety is 3.08 Å. The heat of formation according to the MOPAC studies is − 139.97 kcal mol^{-1} for 3-alkoxybenzoic acid **3** (*n* = 8), 14.55 kcal mol^{-1} for azo dye **1** and − 126.48 kcal mol^{-1} for the 4-PA-3-AB8 system. The interaction between the dye **1** and the acid molecule **3** (*n* = 8) lowers the energy of the system by 1.06 kcal mol^{-1}‡. This contribution is mainly from the interaction between the carboxylic proton of **3** (*n* = 8) and the pyridyl ending nitrogen of **1**; there is a minor contribution from the interaction between the oxygen of the C=O moiety of **3** (*n* = 8) and the pyridyl hydrogen of **1**. Significantly, the distance between the end carbon (Ca) of **1** and the end carbon

‡Compound 4-PA-3-AB8 has been studied by the MM3 method with similar results [8].

Table 3. Phase transition temperature (°C) and corresponding enthalpies (J g^{-1}), in parentheses, of 4-alkoxybenzoic acids ($n = 6, 8, 10, 12$). Cr = crystalline, SmX = unidentified smectic phase, SmC = smectic C phase, N = nematic phase, I = isotropic liquid.



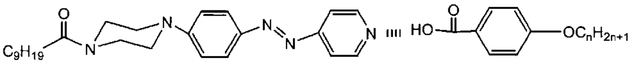
4-alkoxybenzoic acid 4

$n = 6$	$\mathrm{Cr} \xrightleftharpoons[89.5(53.1)]{104.5(54.5)} \mathrm{N} \xrightleftharpoons[145.1(8.6)]{148.6(9.7)} \mathrm{I}$
$n = 8$	$\mathrm{Cr} \xrightleftharpoons[48.1(48.3)]{73.9(5.7)} \mathrm{SmC} \xrightleftharpoons[91.2(44.8)]{98.3(45.8)} \mathrm{N} \xrightleftharpoons[137.89(7.2)]{140.0(7.2)} \mathrm{I}$
$n = 10$	$\mathrm{Cr} \xrightleftharpoons[70.9(78.3)]{85.9(75.9)} \mathrm{SmX} \xrightleftharpoons[89.4(41.6)]{96.0(41.7)} \mathrm{SmC} \xrightleftharpoons[118.2(9.5)]{121.8(5.7)} \mathrm{N} \xrightleftharpoons[137.1(5.9)]{140.8(8.8)} \mathrm{I}$
$n = 12$	$\mathrm{Cr} \xrightleftharpoons[61.3(10.7)]{75.6(10.4)} \mathrm{SmX1} \xrightleftharpoons[76.1(1.4)^{a}]{} \mathrm{SmX} \xrightleftharpoons[82.9(17.7)]{89.2(26.1)} \mathrm{SmC} \xrightleftharpoons[118.5]{122.3} \mathrm{N} \xrightleftharpoons[120.3^{b}]{124.5^{a}} \mathrm{I}$

[a] The peaks are overlapped and their total enthalpy is 20.6 J g^{-1}.

[b] The peaks are overlapped and their total enthalpy is 14.5 J g^{-1}.

Table 4. Phase transition temperature (°C) and corresponding enthalpies (J g^{-1}), in parentheses, of hydrogen-bonded complexes from a 1 : 1 molar ratio of pyridylazo dye-1 and 4-alkoxybenzoic acids ($n = 8, 10, 12$). Cr = crystalline, SmX = unidentified smectic phase, SmC = smectic C phase, SmA = smectic A phase, I = isotropic liquid.



4-PA-4-ABn

Azo dye-1	$\mathrm{Cr1} \xrightleftharpoons[70.4(12.7)]{110.7(8.1)} \substack{\mathrm{Cr2}\\ \mathrm{SmX}} \xrightleftharpoons[102.9(67.4)]{123.0(57.6)} \mathrm{I}$
4-PA-4-AB8	$\mathrm{Crl} \xrightleftharpoons[70.7(10.8)]{87.7(13.0)} \substack{\mathrm{Cr2}\\ \mathrm{SmX}} \xrightleftharpoons[92.3(13.0)]{127.4(14.8)} \mathrm{SmC} \xrightleftharpoons[129.2(1.9)]{136.3(2.6)} \mathrm{SmA} \xrightleftharpoons[174.3(24.3)]{184.2(33.6)} \mathrm{I}$
4-PA-4-AB10	$\mathrm{Crl} \xrightleftharpoons[58.1(15.6)]{80.2(14.1)} \substack{\mathrm{Cr2}\\ \mathrm{SmX}} \xrightleftharpoons[76.1(12.6)]{115.1(12.6)} \mathrm{SmC} \xrightleftharpoons[122.1(2.7)]{130.6(2.9)} \mathrm{SmA} \xrightleftharpoons[170.4(19.6)]{181.8(31.2)} \mathrm{I}$
4-PA-4-AB12	$\mathrm{Crl} \xrightarrow{94.1(23.2)} \mathrm{Cr2} \xrightleftharpoons[59.7(30.1)]{102.3(2.7)} \mathrm{SmC} \xrightleftharpoons[120.3(2.5)]{127.7(1.7)} \mathrm{SmA} \xrightleftharpoons[170.0(22.9)]{179.8(28.8)} \mathrm{I}$

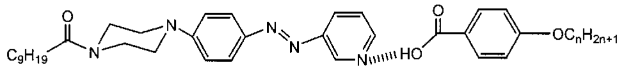
(Cb) of **3** was calculated to be 39.54 Å (figure 1), which is comparable with the result obtained by XRD (37.21 Å).

For complex 4-PA-4-AB10, the distance between the carboxylic proton of **4** ($n = 10$) and the pyridyl ending nitrogen of **1** is calculated to be 1.76 Å, and the distance between the pyridyl hydrogen and the oxygen of the C=O moiety is 2.48 Å. The heat of formation according to MOPAC studies is 14.55 kcal mol^{-1} for azo dye **1** and − 151.94 kcal mol^{-1} for 4-alkoxybenzoic acid **4** ($n = 10$). The 4-PA-4-AB10 system was similarly investigated and the heat of formation calculated to be − 139.17 kcal mol^{-1}. This interaction lowers the energy of the system by 1.78 kcal mol^{-1}. This contribution is mainly from the interaction between the carboxylic proton of **4** ($n = 10$) and the pyridyl ending nitrogen of **1**; a minor contribution comes from the interaction between the oxygen of the C=O moiety of **4** ($n = 10$) and the pyridyl hydrogen of **1**. Significantly, the distance between the end carbon (Ca) of **1** and the end carbon (Cb) of **4** was calculated to be 44.52 Å (figure 2), which is comparable with the result obtained by XRD (42.85 Å).

4. Conclusion

This work presents a successful approach to the formation of mesogenic azo dye complexes; the energy reduction by interaction of the dye and benzoic acid derivatives may be regarded as resulting from the H-bonding interaction. Our new approach may open up another useful azo dye liquid crystal area. It maybe possible to induce mesogenic behaviour in other nitrogen-containing heterocycles with narrower HOMO and LUMO energy gap. We are optimistic that liquid crystals with suitable different colours can be prepared similarly in the future. Reflective liquid crystal device technology

Table 5. Phase transition temperature (°C) and corresponding enthalpies (J g^{-1}), in parentheses, of hydrogen-bonded complexes from a 1:1 molar ratio of pyridylazo dye-2 and 4-alkoxybenzoic acid ($n = 6, 8, 10, 12$). Cr = crystalline, SmX = unidentified smectic phase, SmA = smectic A phase, I = isotropic liquid.



3-PA-4-ABn

Azo dye-2	Cr1	108.3(84.2) 87.5	SmA	 93.9^{a}			I
3-PA-4-AB6	Cr1	94.5 59.7(49.0)	SmA	98.3^{b} 89.8(10.5)			I
3-PA-4-AB8	Cr1	91.3(45.8) 73.4(56.1)	SmA	95.9(10.3) 94.6(10.4)			I
3-PA-4-AB10	Cr1	96.7(39.6) 65.7(44.3)	SmA	103.4(9.9) 99.0(16.4)			I
3-PA-4-AB12	Cr1	89.2(63.5) 68.4(43.5)	SmX SmA	94.7 98.2(12.1)	SmA	102.1^{c}	I

[a] The peaks are overlapped and their total enthalpy is 10.4 J g^{-1}.
[b] The peaks are overlapped and their total enthalpy is 67.7 J g^{-1}.
[c] The peaks are overlapped and their total enthalpy is 41.9 J g^{-1}.

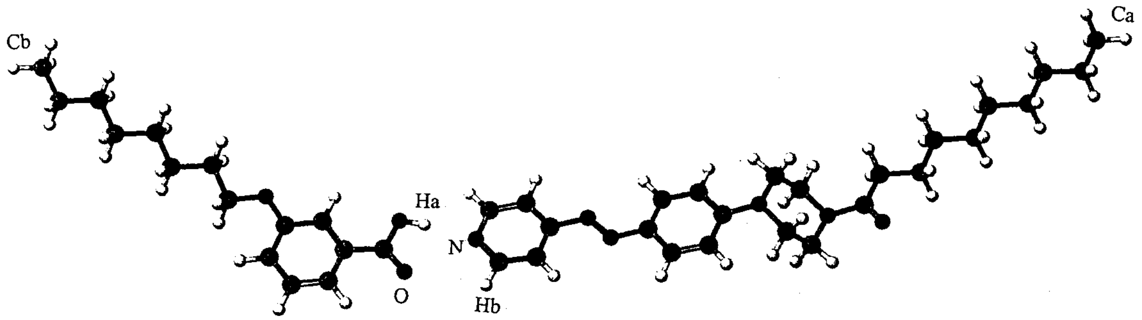


Figure 1. The calculated distances Ha–N and Hb–O are 1.99 and 3.08 Å, respectively. The calcuated Ca–Cb distance is 39.54 Å; the corresponding distance observed by XRD is 37.21 Å. The energy lowering by H-bond interactions is calculated to be 1.06 kcal mol^{-1}.

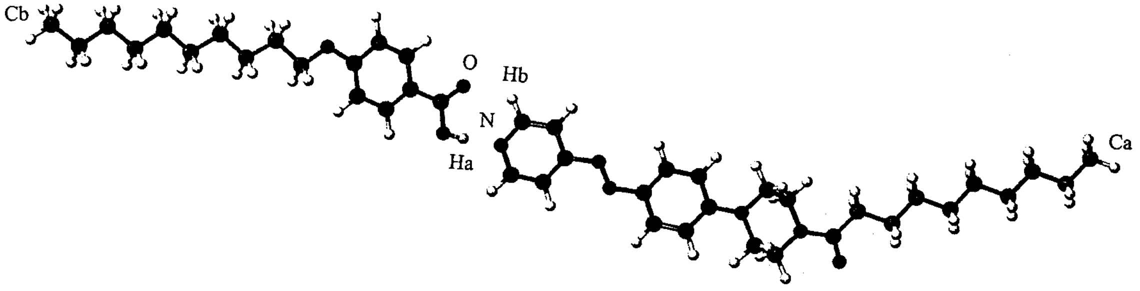


Figure 2. The calculated distances Ha–N and Hb–O are 1.76 and 2.48 Å, respectively. The calculated Ca–Cb distance is 44.52 Å; the corresponding distance observed by XRD is 42.85 Å. The energy lowering by H-bond interactions is calculated to be 1.78 kcal mol^{-1}.

may be further developed in this way, 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 the National Science Council (NSC 89-2113-M-260-001) for financial support.

References

[1] (*a*) Ruslim, C., and Ichimura, K., 1998, *Chem. Lett.*, 789; (*b*) Kozlovsky, M. V., Shibaev, V. P., Stakhanov, A. I., Weyrauch, T., and Haase, W., 1998, *Liq. Cryst.*, **24,** 759; (*c*) Shivaev, V. P., Kostomin, S. A., and Ivanov, S. A., 1996, in *Polymers as Electrooptical and Photooptical Active Media*, edited by V. P. Shibaev (Berlin: Springer), pp. 37–110; (*d*) Ikeda, T., and Tsutsumi, O., 1995, *Science*, **268,** 1873; (*e*) Anderle, K., and Wendorff, J., 1994, *Mol. Cryst. liq. Cryst.*, **243,** 51.

[2] (*a*) Hermann, D. S., Rudquist, P., Ichimura, K., Kudo, K., Komitov, L., and Lagerwall, S. T., 1997, *Phys. Rev. E*, **55,** 2857; (*b*) Sasaki, T., Ikeda, T., and Ichimura, K., 1994, *J. Am. chem. Soc.*, **116,** 625.

[3] Bauman, D., 1988, *Mol. Cryst. liq. Cryst.*, **159,** 197.

[4] (*a*) Sunohara, K., Naito, K., Tanaka, M., Naikai, Y., Kamiura, N., and Taira, K., 1996, *SID'96 Dig.*, 103; (*b*) Taira, K., Iwanaga, H., Hotta, A., Nakai, Y., Ohtake, T., and Sunohara, K., 1996, *AM-LCD'96*, 333.

[5] (*a*) Naoum, M. M., Saad, G. R., Nessim, R. I., and Abdel Azis, T. A., 1998, *Liq. Cryst.*, **25,** 165; (*b*) Gray, G. W., 1962, *Molecular Structure and Properties of Liquid Crystals* (New York: Academic Press).

[6] Lai, L. L., and Lin, H.-C., 2000, *Liq. Cryst.* (in the press).

[7] (*a*) Lin, W., Lin, W., Wong, G. K., and Marks, T. J., 1996, *J. Am. chem. Soc.*, **118,** 8034; (*b*) Gao, L. H., Wang, K. Z., Huang, C. H., Zhao, X. S., Xia, X. H., Li, T. K., and Xu, J. M., 1995, *Chem. Mater.*, **7,** 1048; (*c*) Kalatzis, E., 1967, *J. chem. Soc. B*, 273.

[8] Lai, L.-L., Wang, E., Lee, L.-J., Chen, J.-J., and Wang, D.-W., *Liq. Cryst.* (to be published).

[9] (*a*) Lin, H.-C., Ko, C. W., Guo, K., and Cheng, T. W., 1999, *Liq. Cryst.*, **26,** 613; (*b*) Lin, H.-C., Lin, Y. S., Cheng, Y. T., Chao, I., and Li, T. W., 1998, *Macromolecules*, **31,** 7298; (*c*) Kurihara, S., Mori, T., and Nonaka, T., 1998, *Macromolecules*, **31,** 5940; (*d*) Kresse, H., 1998, *Liq. Cryst.*, **25,** 437; (*e*) Mallia, V. A., George, M., and Das, S., 1999, *Chem. Mater.*, **11,** 207.

[10] Gray, G. W., and Jones, B., 1953, *J. Chem. Soc.*, 4179.