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N,N-Disubstituted-4-aminophenylazostyrylformate derivatives: their synthesis, mesogenic behaviour and photostability

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N,N-Disubstituted-4-aminophenylazostyrylformate derivatives: their synthesis, mesogenic behaviour and photostability

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A series of new azo dye liquid crystals was prepared by the reaction of the *N,N*-disubstituted-4-aminophenylazobenzaldehydes with butyl cyanoacetate in the presence of piperidine in refluxing ethanol. The new azo dye liquid crystals possess a SmA phase, and representative samples were found to be reasonably photostable.

1. Introduction

In recent years, azo dyes have been extensively studied because of their ready availability and applications potential [1, 2]. For example, a polarizer with better reflectance can be obtained by dissolving a dichroic azo dye in a liquid crystal [3]. In particular, azo dyes have a useful dichroic ratio and are used in low power consumption reflective liquid crystal devices. A three-layered guest–host (G-H) system from these dyes, with subtractive colour mixing of yellow, magenta, and cyan is expected to be used for developing full colour reflective displays [4]. In additional, a combination of the materials with chiral nematic liquid crystals has been demonstrated as a replacement for the polarizer in display devices [4*d*]. Although the potential uses of azo dye materials have been well explored, the phase transition temperatures and solubility of azo dye in G-H systems present serious problems in applications. For example, clearing temperatures vary with the components of the G-H systems, and the addition of non-mesogenic dyes often causes instability of the liquid crystalline phase [5], although dyes which are themselves mesogenic minimize this effect.

We have previously synthesized and studied a series of *N,N*-disubstituted-4-aminophenylazobenzaldehydes **3a**–**3d** together with other azo dye liquid crystal derivatives [6]. We have now prepared a series of new azo dye liquid crystals **4a**–**4d** from the reaction of compounds **3a**–**3d** with butyl cyanoacetate in the presence of piperidine in refluxing ethanol [7]. As the photostability of the azo dye materials is an important characteristic in relation LCD application, the decay rate of representative samples of **4a** and **4c** in toluene under UV radiation was also studied.

2. Experimental

Commercial grades of chemicals were used without further purification. The dichroic dye SI-426 were purchased from Mitsui. Mesogenic behaviour and phase transitions were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (Perkin-Elmer DSC 6). Powder X-ray diffraction (XRD) patterns were obtained from a Siemens D-5000 X-ray diffractometer equipped with a TTK 450 temperature controller and using Cu radiation with the wavelength $\lambda = 1.5406$. The absorbance of azo dyes in toluene was recorded with a Jasco-V530 spectrometer.

2.1. *Synthesis of compounds* ***4a***–***4d***

Compound **3a** (0.20 g, 0.5 mmol), prepared according to our previous procedure [6*f*, 6*j*], and butyl cyanoacetate (0.07 ml, 0.5 mmol) were dissolved in ethanol (30 ml) (see the scheme). A few drops of piperidine were then added, and the resulting solution was heated under reflux for 2 h. Water (30 ml) was added and the mixture extracted with CH_2Cl_2 (50 ml). After removing solvent under reduced pressure, the crude product was dissolved in a small amount of CH_2Cl_2 and the desired azo dye **4a** (62.8%; 160 mg) was precipitated by the addition of acetone (30 ml). This product was pure enough for physical measurements. Compounds **4b**–**4d** were prepared similarly in comparable yields and characterized

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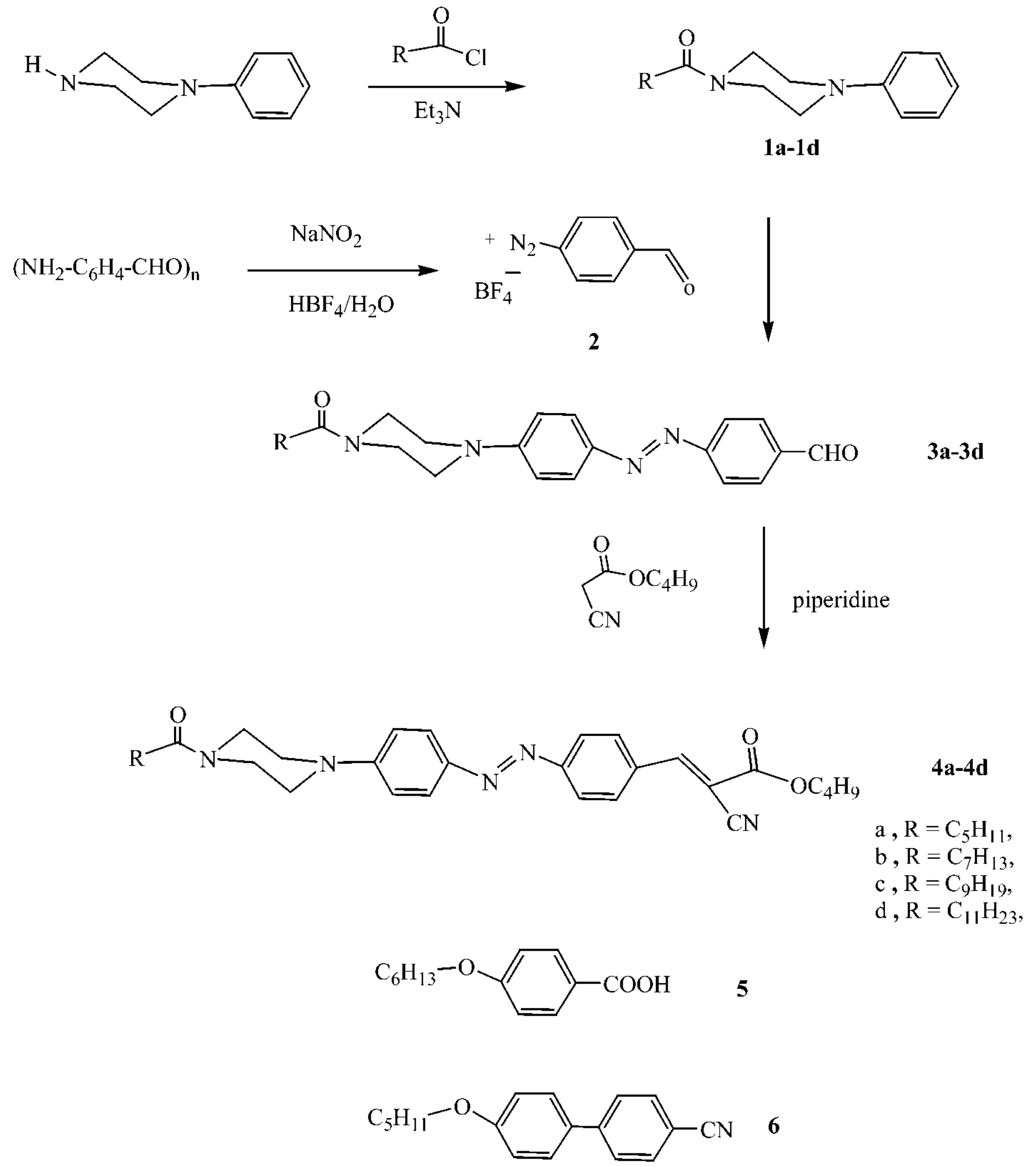


Scheme.

by ^{1}H NMR (Varian 300 MHz FT NMR spectrometer) at room temperature, using $CDCl_3$ (7.24 ppm) as internal standard; high resolution mass spectra (VG70-250; EI, 70ev); and elemental analysis (Heraeus). **4a**: ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, $J = 6.9$, CH_3), 0.99 (t, 3H, $J = 6.9$, CH_3), 1.30–1.76 (m, 10H, $5CH_2$), 2.36 (t, 2H, $J = 6.3$, CH_2), 3.40 (Br. s, 4H, $2CH_2$), 3.66 (Br. s, 2H, CH_2), 3.80 (Br. s, 2H, CH_2), 4.33 (t, 2H, $J = 6.3$, CH_2), 6.96 (d, 2H, $J = 9.0$, 2Ar–H), 7.90, 7,93, 7.95 (mix of 2d, 4H, 4Ar–H), 8.11 (d, 2H, $J = 8.7$, 2Ar–H), 8.27 (s, 1H, CH). HRMS for $C_{30}H_{37}N_5O_3$: 515.2896; found: 515.2896. Analytical data for $C_{30}H_{37}N_5O_3$ C 69.80, H 7.18, N 13.57; found C 69.70, H 7.16, N 13.67%. **4b**: ^{1}H NMR ($CDCl_3$): δ 0.87 (t, 3H, $J=6.9$, CH_3), 0.97 (t, 3H, $J=6.9$, CH_3), 1.27–1.76 (m, 14H, $7CH_2$), 2.33 (t, 2H, $J=6.3$, CH_2), 3.40 (Br. s, 4H, $2CH_2$), 3.66 (Br. s, 2H, CH_2), 3.80 (Br. s, 2H, CH_2), 4.32 (t, 2H, $J=6.3$, CH_2), 6.95 (d, 2H, $J=9.0$, 2Ar–H), 7.90, 7.92, 7,93, 7.94 (mix of 2d, 4H, 4Ar–H), 8.11 (d, 2H, $J=8.7$, 2Ar–H), 8.26 (s, 1H, CH). HRMS for $C_{32}H_{41}N_5O_3$: 543.3209; found: 543.3209. Analytical data for $C_{32}H_{41}N_5O_3$ C 70.06, H 7.54, N 12.87; found C, 70.28, H 7.49, N 13.06%. **4c**: ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, $J=6.9$, CH_3), 0.97 (t, 3H, $J=6.9$, CH_3), 1.26–1.77 (m, 18H, $9CH_2$), 2.34 (t, 2H, $J=6.3$, CH_2), 3.40 (Br. s, 4H, $2CH_2$), 3.66 (Br. s, 2H, CH_2), 3.80 (Br. s, 2H, CH_2), 4.32 (t, 2H, $J=6.3$, CH_2), 6.96 (d, 2H, $J=9.0$, 2Ar–H), 7.89, 7,93, 7.94 (mix of 2d, 4H, 4Ar–H), 8.12 (d, 2H, $J=8.7$, 2Ar–H), 8.26 (s, 1H, CH). HRMS for $C_{34}H_{45}N_5O_3$: 571.3523; found: 571.3523. Analytical data for $C_{34}H_{45}N_5O_3$ C 71.36, H 7.87, N 12.24; found C 71.30, H 7.92, N 12.24%. **4d**: ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, $J=6.9$, CH_3), 0.97 (t, 3H, $J=6.9$, CH_3), 1.24–1.80 (m, 22H, $11CH_2$), 2.35 (t, 2H, $J=6.3$, CH_2), 3.41 (Br. s, 4H, $2CH_2$), 3.66 (Br. s, 2H, CH_2), 3.79 (Br. s, 2H, CH_2), 4.32 (t, 2H, $J=6.3$, CH_2), 6.96 (d, 2H, $J=9.0$, 2Ar–H), 7.90, 7,93, 7.94 (mix of 2d, 4H, 4Ar–H), 8.12 (d, 2H, $J=8.7$, 2Ar–H), 8.26 (s, 1H, CH). HRMS for $C_{36}H_{49}N_5O_3$: 599.3836; found: 599.3838. Analytical data for $C_{36}H_{49}N_5O_3$ C 72.00, H 8.20, N 11.67; found C 71.87, H 8.12, N 11.85%.

2.2. *Study of photostability*

The photostability of compounds **4a** and **4c** ($\lambda_{max}=450$ nm) and SI-426 ($\lambda_{max}=500$ nm) were investigated in a RPR-100 photochemical reactor equipped with eight 3500 Å lamps (24 W × 8), using the following standard process. The azo dye compound was dissolved in toluene (5×10^{-5} g ml^{-1}) and divided into two quartz UV cuvettes. One was kept in the dark for reference and the other was exposed continuously to light in the photochemical reactor. To measure the percentage of decomposition of the azo dyes after exposure, the exposed and reference cuvettes were investigated on the UV-Vis spectrometer simultaneously. The absorption of the exposed cuvette was corrected from the reference and then recorded. The decay rate of each azo dye versus the exposure time was thus obtained, as shown in figure 1.

3. Results and discussion

3.1. *Synthesis*

Based on our previous experience on synthesizing azo dye liquid crystals [6], compounds **4a**–**4b** were successfully and conveniently prepared according to the scheme. The salt **2**, prepared from poly(aminobenzaldehyde), was allowed to react with phenylpiperazines **1a**–**1d** to give compounds **3a**–**3d**, respectively. The desired azo dyes **4a**–**4d** were obtained, respective from the further reaction of compounds **3a**–**3d** with butyl cyanoacetate in the presence of piperidine in refluxing ethanol [7]. The crude compounds **1**–**3** conld be used directly for subsequent reactions without further purification, and

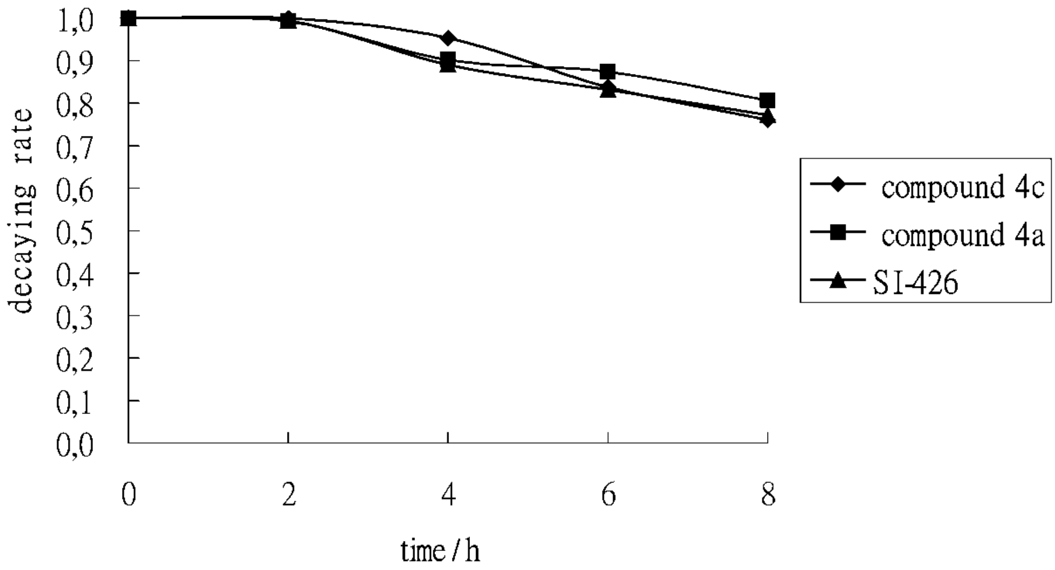


Figure 1. The photostabilities of compounds **4c** and **4a** and SI-426; the error percentage was estimated as within 3% on the basis of repeated experiments (three).

compounds **4a**–**4d**, crystallized from acetone, were identified as pure by thin layer chromatography together with ^{1}H NMR, high resolution mass spectroscopy, and elemental analysis.

The advantage of this preparation is that no complicated purification is needed for each procedural step. Also, the introduction of the piperazine moiety into the target molecules is noteworthy, because one of nitrogen atoms in the cyclic ring of compounds **4a**–**4d** plays the electron-donating role and, to some extent, decreases the HOMO–LUMO energy gap of the chromophore. The other nitrogen atom keeps the molecule **4** in a linear molecular shape and thus contributes the formation of the liquid crystalline phase.

3.2. *Mesogenic behaviour and photostability*

The phase transition temperature and corresponding enthalpies of compounds **4a**–**4d** were characterized by DSC and POM, and are shown in the table. The compounds show a SmA phase on heating, characterized by a typical focal-conic texture and low viscosity. Except for **4a**, the SmA range is about 20°C on heating and 40°C on cooling. To confirm further the SmA phase of compounds **4a**–**4d**, a representative sample of **4a** was further studied by powder XRD and molecular modelling. The *d*-spacing (the *Z* component of an extended molecular length) from the XRD study in the SmA phase at 175 and 180°C were both measured at 30.36 Å during cooling. As the molecular axis of a liquid crystal in the SmA phase is directed along the *Z* axis, the *d*-spacings of the molecules may not vary at different temperatures in this range.

For further confirmation, the length of the extended molecule **4a** was calculated. To obtain a reasonable calculation result, the starting conformation of molecule **4a** was first established on the basis of crystallographic data of compound **3b** [6*b*], modified, and then extended by connecting a C–C bond with butyl cyanoacetate in its *E* form (figure 2). Molecule **4a** was then optimized by the Cache program (version 4.1)

Table. Phase transition temperature (°C) and corresponding enthalpies (J g^{-1}) of compounds **4a**–**4d**, **5** and **6** together with mixtures **I**, **II**, and **III**. [**I** = **4a**/**5** (1/9); **II** = **4c**/**5** (1/9); **III** = **4a**/**6** (1/9) molar ratios]. Cr = crystalline, SmA = smectic A phase, N = nematic phase, I = isotropic liquid. r. t. = room temperature.

Compound **4a**	Cr	$\xrightleftharpoons[170.0(44.5)]{186.7(45.8)}$	SmA	$\xrightleftharpoons[181.3(1.5)]{212^{a}}$	I
Compound **4b**	Cr	$\xrightleftharpoons[164.7(30.0)]{183.1(33.3)}$	SmA	$\xrightleftharpoons[202.3(3.7)]{206.7(4.5)}$	I
Compound **4c**	Cr	$\xrightleftharpoons[162.1(28.8)]{180.7(30.8)}$	SmA	$\xrightleftharpoons[203.0(5.6)]{206.7(6.2)}$	I
Compound **4d**	Cr	$\xrightleftharpoons[145.7(26.0)]{170.4(25.4)}$	SmA	$\xrightleftharpoons[190.6(2.9)]{199.4(2.7)}$	I
Compound **5**	Cr	$\xrightleftharpoons[89.5(53.1)]{104.5(54.5)}$	N	$\xrightleftharpoons[145.1(8.6)]{148.6(9.7)}$	I
Compound **6**	Cr	$\xrightleftharpoons[30.1^{a}]{52.3(134.9)}$	N	$\xrightleftharpoons[67.0(2.3)]{68.0(1.5)}$	I
Mixture **I**	Cr	$\xrightleftharpoons[90.8(24.6)]{104.1(25.7)}$	N	$\xrightleftharpoons[143.9(3.4)]{148.1(2.6)}$	I
Mixture **II**	Cr	$\xrightleftharpoons[90.7(50.5)]{102.7(16.8)}$	N	$\xrightleftharpoons[145.4^{a}]{151.7^{a}}$	I
Mixture **III**	Cr	$\xrightleftharpoons[\text{r. t.}^{a}]{\text{r. t.}^{a}}$	N[b]	$\xrightleftharpoons[142.7(5.4)]{143.5(6.5)}$	I

[a] Determined by POM.

[b] Phase separation observed under POM during the nematic range.

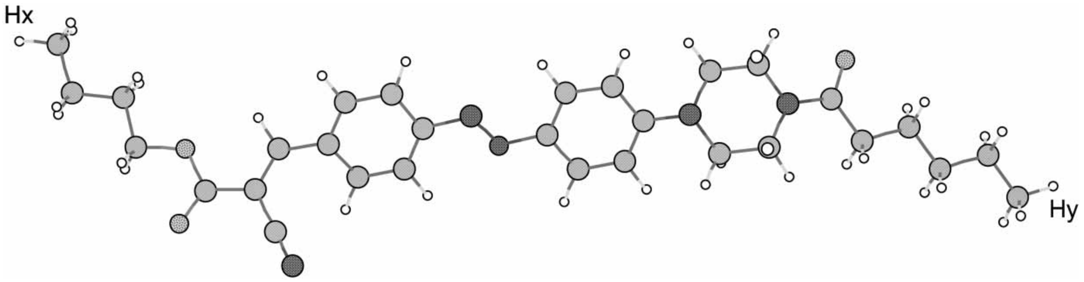
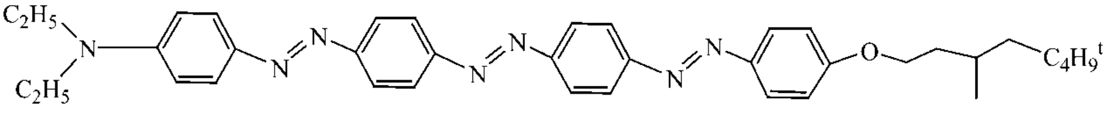


Figure 2. The optimized conformation of azo dye **4a** by Cache 4.1 using the AM1 model; the distance from Hx to Hy is calculated to be 30.57 Å.



SI-426

Figure 3. The structure of SI-426.

using the AM1 model; after optimization, the length of the extended molecule **4a** was calculated to be 30.57 Å (from Hx to Hy in figure 2), which is very close to the *d*-spacings obtained from the XRD study.

To investigate the miscibility of compound **4** in a host liquid crystal, compound **5**, prepared according to the literature [8*a*], was mixed with representative samples of **4a** and **4c** (9/1, molar ratio) to give mixtures **I** and **II**; their mesogenic behaviour is shown in the table. Compound **5** and mixtures **I** and **II** all show a nematic phase which was characterized by its schlieren texture, with droplets at the clearing point and four brushes at the lower temperature. The nematic ranges for compound **5** and mixtures **I** and **II** are at 40–50°. The nematic ranges of mixtures **I** and **II** are very similar, although the length of alkyl chain is different by four carbons. Also, no phase separation was observed for mixtures **I** and **II** under POM in the nematic range.

Compound **4a** was further mixed with compound **6**, prepared according to the literature [8*b*], in a similar molar ratio (9/1) to give mixture **III**. However, phase separation of the mixture **III** was observed under POM. The miscibility of compound **4a** with compound **5** is better than that of compound **4a** with compound **6**. This may arise from the slight basicity of the nitrogen atoms in the azo dye **4a**, as compound **5**, containing a carboxylic acid, is more acidic than compound **6**. Although the enthalpy changes of compounds **4a–4d** between the SmA and isotropic phases are variable, the variation is not significant and may arise from different molecular stacking in the solid state, resulting from the different length alkyl chain [6*i*, 6*j*].

Since the photostability of azo dyes is an important physical property in photo-optical applications, the representative azo dyes **4a** and **4c** were investigated under UV radiation. To realize the application potential of these dyes, their decay rates were compared with that of SI-426 (figure 3), a commercial dichroic dye from Mitsui, reasonably photostable and conventionally used in related LCD industry.† Surprisingly, the photostabilities of the azo dyes **4a** and **4c** are comparable with this commercial product. Apparently, the lengths of alkyl chain in azo dyes **4a** and **4c** do not significantly influence their photosatbilities. According to the Jones and Reeve [9], the instability of azo dyes arises from the hydrogen abstraction of the aryl group to the N–N moiety, thus the fading effect is accelerated by the electron-withdrawing group in the phenyl ring. Surprisingly, azo dyes **4a** and **4c**, both containing the electron-withdrawing groups CN and COOR, do not comply and possess good photostability. This will be studied further, especially since the structure of azo dyes **4a** and **4c** is different from those studied in [10].

4. Conclusions

We have successfully prepared by a convenient method a series of new azo dye liquid crystals which possess a SmA phase. These azo dye liquid crystals are

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†Sample SI-426 was purified by chromatography before measuring its photo-stability. ^{1}H NMR ($CDCl_3$): 0.90 (s, 9H, $3CH_3$), 1.00 (d, $J=6.0$, 3H, CH_3), 1.27 (t, 6H, $2CH_3$), 1.54–1.90 (m, 5H, $2CH_2$ +CH), 3.46 (quart, 4H, $2CH_2$), 4.06 (t, 2H, CH_2), 6.73 (d, 2H, $J=8.8$, 2Ar–H), 7.00 (d, 2H, $J=8.8$, 2Ar–H), 7.87–8.094 (mix of 6d, 12H, 12Ar–H). M^+ for $C_{37}H_{45}N_7O$: 604; found: 604.

reasonably photostable when compared with SI-426, on studying their decay rate under UV radiation, and this may increase their LCD applications potential. Although the introduction of the C–C–CN unit in azo dye liquid crystals **4a**–**4d** increases the size of the LC rigid core, and may reduce their solubility in host materials, this has been overcome experimentally in the presence of the slightly acidic compound **5**.

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