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Dyes and Pigments 70 (2006) 71–75

DYES and PIGMENTS

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Synthesis and properties of new liquid crystalline compounds containing an alkoxyphenylazo group

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Received 19 November 2004; received in revised form 12 January 2005; accepted 8 April 2005
Available online 27 June 2005

Abstract

In the present study, a series of Schiff bases: 5-((4-^{n}hexadecyloxyphenyl)azo)-*N*-(4-^{n}alkoxyphenyl) salicylaldimine (^{n}alkoxy = octyloxy, dodecyloxy, hexadecyoxy) homologues have been synthesized and characterized by IR, NMR, mass spectroscopy and elemental analyses. The mesomorphic character of these compounds was studied by using differential scanning calorimetry (DSC) and polarizing microscope equipped with a heating and cooling stage. Octyloxy and dodecyloxy-containing compounds exhibit monotropic smectic A liquid crystalline behavior, but hexadecyloxy-containing compound shows enantiotropic smectic A mesophase.
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Keywords: Azo compounds; Schiff bases; Salicylaldimine; Smectic A

1. Introduction

Azo compounds are important due to their applications in dyes, pigments, and functional materials. For example, azo-containing photochromic organic compounds – specially with liquid crystalline character – and azo-conjugated metal complexes have been attracting much attentions recently because of their possible applications in the area of photon-mode high-density information storage, photo-switching devices and optical computing [1–4]. Development of these materials requires discovery of compounds that exhibit two distinct chemical or physical forms that are interconverted and detected by light without their destruction. Azobenzene is one of the representative photochromic molecules with two geometric isomers, a *trans* form and a *cis* form [5–9]. The *trans*-to-*cis* isomerization occurs by phtoirradiation with UV light and *cis*-to-*trans* isomerization proceeds with blue-light irradiation or by heating, because the *trans* form is thermodynamically more stable than the *cis* form. Incorporation of a photoresponsive component into a supramolecular structure can lead to artificial photoresponsive species that may be quite valuable as photochemical molecular devices [1–4,10].

Because of the importance of azo-containing liquid crystalline dyes and in continuance of our interest in syntheses of azo-based liquid crystalline compounds [11–14], we report herein the syntheses and study the liquid crystalline character of a series of azo-linked salicylidenic Schiff bases named 5-((4-^{n}hexadecyloxyphenyl) azo)-*N*-(4-^{n}alkoxy phenyl) salicylaldimine (^{n}alkoxy = octyloxy, dodecyloxy, hexadecyoxy) homologues (see Scheme 1).

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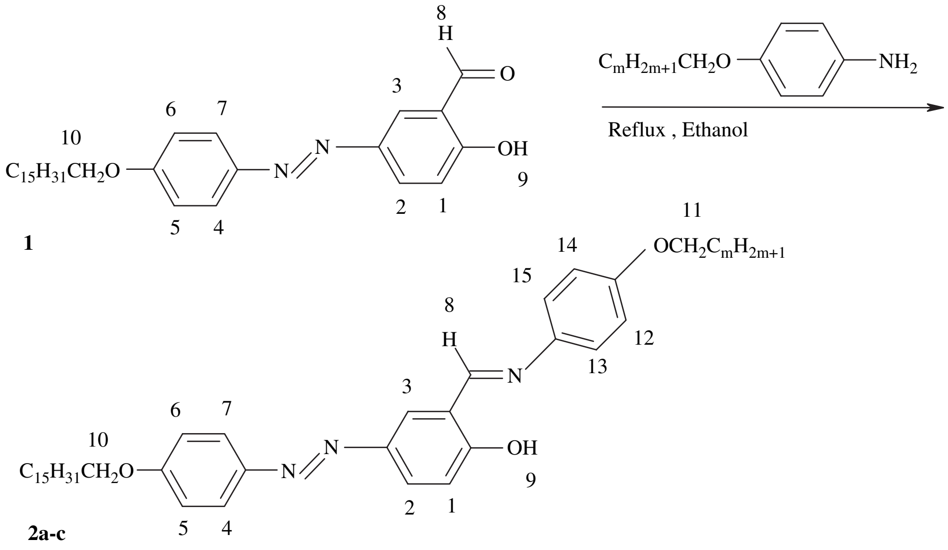
doi:10.1016/j.dyepig.2005.04.015



Compound no.	*n*
2a	7
2b	11
2c	15

Scheme 1.

2. Experimental

2.1. Reagents

All reagents and solvents were used as supplied by Merck chemical company and used without further purification. 4-Hexadecyloxynitrobenzene was obtained by reaction between 4-nitrophenol with 1-bromohexadecan in DMF as solvent and K_2CO_3 as base by refluxing for 3 h [15] and then crude 4-hexadecyloxynitrobenze was purified by recrystallization from ethanol. 4-Hexadecyloxyaniline was prepared by reducing the 4-hexadecyloxynitrobenzne as described in the literature [16].

2.2. Physical measurements

Elemental (C, H and N) analyses were carried out in a Perkin-Elmer automatic equipment model 240B. Electron impact (70 eV) mass spectra were recorded on a Finnegan-mat GC-MS-DS spectrometer model 8430. Infrared spectra were taken with an FT-IR Bruker vector 22 spectrometer using KBr pellets in the 400–4000 cm^{-1} range. The DSC thermograms of the compounds were obtained on a Mettler-Toledo DSC 822e module, which was calibrated with indium metal ($T = 156.6 \pm 0.3$, $\Delta H = 28.45 \pm 0.6\ J\,g^{-1}$). Samples of 2–5 mg in solid form were placed in aluminum pans (40 μl) with a pierced lid, and heated or cooled at a scan rate of 10 $°C\,min^{-1}$ under a nitrogen flow.

The optical observations were made with a Zeiss polarizing microscope equipped with a Linkam THMSG 600 heating and cooling stage and Linkam THMS 93 programmable temperature-controller. ^1H NMR spectra were obtained in deutrated chloroform as solvent on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in δ (ppm) relative to the tetramethylsilane as internal standard.

2.3. Materials

2.3.1. 5-(4-Hexadecyloxyphenylazo) salicylaldehyde (*1*)

This compound was prepared as described elsewhere [12]. Yellow, yield 60%. MS *m*/*z* (relative intensity): 467.6 (M + 1,12), 466.6 (M, 50), 241.4 ($M-C_{16}H_{33}$, 25), 121.5 ($M-C_{16}H_{33}OC_6H_4N_2$, 100). Anal. calc. for $C_{29}H_{42}N_2O_3$: C 74.64, H 9.00, N 6.00. Found: C 74.3, H 8.7, N 5.7. ^1H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, H-9), 10.02 (s, H-8), 8.15 (d, *J* 2.9 Hz, H-3), 8.12 (dd, *J* 3.0, 8.1 Hz, H-2), 7.88 (dd, *J* 3.0, 8.0 Hz, H-4, H-7), 7.10 (d, *J* 8.0 Hz, H-1), 7.00 (dd, *J* 3.0, 7.7 Hz, H-5, H-6), 4.04 (t, *J* 6.7 Hz, H-10), 1.84–0.87 (31H, alkyl chain).

2.3.2. Syntheses of *2a–c*

All homologue materials were prepared similarly. The related amine (4-alkoxyaniline, 0.026 mol) and 0.026 mol of 5-(4-^{n}hexadecyloxyphenylazo) salicylaldehyde were dissolved in 100 ml absolute ethanol with a few drops of glacial acetic acid as a catalyst. The solution was then refluxed for 1 h. The solution was left at room temperature and after cooling, the ligands were obtained as yellow micro-crystals. The micro-crystals were filtered off, washed with 15 ml of cold absolute ethanol and then recrystallized for several times from ethanol–chloroform (1:3, v/v).

2a. Yellow, yield 80%. MS *m*/*z* (relative intensity): 670.7 (M + 1,12), 669.7 (M, 55), 444.6 ($M-C_{16}H_{33}$, 30), 324.7 ($M-C_{16}H_{33}OC_6H_4N_2$, 100). Anal. calc. for $C_{43}H_{63}N_3-O_3$: C 77.11, H 9.41, N 6.27. Found: C76.8, H 9.0, N 6.1. ^{1}H NMR (400 MHz, $CDCl_3$). δ 14.00 (s, H-9), 8.73 (s, H-8), 7.98 (d, *J* 6.7 Hz, H-3), 7.95 (dd, *J* 3.1, 6.7 Hz H-2), 7.87(dd, *J* 3.1, 6.8 Hz, H-4, H-7), 7.30 (dd, *J* 3.0, 7.7 Hz, H-5, H-6), 7.11 (d, *J* 8.5 Hz, H-1), 6.99 (dd, *J* 2, 8.9 Hz, H-13, H-15), 6.95 (dd, 1.9, 8.8 Hz, H-12, H-14), 4.03 (t, *J* 6.5 Hz, H-10), 3.99 (t, *J* 6.5 Hz, H-11), 1.85–0.86 (46H, alkyl chain).

2b. Yellow, yield 75%. MS *m*/*z* (relative intensity): 726.7 (M + 1, 13), 725.7 (M, 100), 500.6 ($M-C_{16}H_{33}$, 25), 380.6 ($M-C_{16}H_{33}OC_6H_4N_2$, 80). Anal. calc. for $C_{47}H_{71}$. N_3O_3: C 74.10, H 8.98, N 9.60. Found: C 73.78, H 8.73, N 9.43. ^{1}H NMR (400 MHz, $CDCl_3$), δ 14.00 (s, H-9), 8.73 (s, H-8), 7.98 (d, *J* 6.7 Hz, H-3), 7.95 (dd, *J* 3.1, 6.7 Hz H-2),7.87 (dd, *J* 3.0, 6.8 Hz H-4, H-7), 7.31 (dd, *J* 3.0, 7.7 Hz, H-5, H-6), 7.11 (d, *J* 8.5 Hz, H-1), 6.99 (dd, *J* 2, 8.9 Hz, H-13, H-15), 6.96 (dd, 1.9, 8.8 Hz, H-12, H-14), 4.04 (t, *J* 6.5 Hz, H-10), 3.99 (t, *J* 6.5 Hz, H-11), 1.83–0.86 (54H, alkyl chain).

2c. Yellow, yield 70%, mp 77 °C. MS *m*/*z* (relative intensity): 782.7 (M + 1, 10), 781.7 (M, 100), 556.7 ($M-C_{16}H_{33}$, 30), 436.7 ($M-C_{16}H_{33}OC_6H_4N_2$, 65). Anal. calc. for $C_{51}H_{79}N_3O_3$: C 74.79, H 9.31, N 9.02. Found: C 74.44, H 9.04, N 8.69. ^{1}H NMR (400 MHz, $CDCl_3$), δ 14.00 (s, H-9), 8.73 (s, H-8), 7.98 (d, *J* 6.7 Hz, H-3), 7.96 (dd, *J* 3.0, 6.7 Hz H-2), 7.87 (dd, *J* 3.0, 6.8 Hz, H-4, H-7), 7.30 (dd, *J* 3.0, 7.6 Hz, H-5, H-6), 7.11 (d, *J* 8.4 Hz, H-1), 6.99 (dd, *J* 2.1, 8.5 Hz, H-13, H-15), 6.96 (dd, 2.0, 8.5 Hz, H-12, H-14), 4.04 (t, *J* 6.5 Hz, H-10), 3.99 (t, *J* 6.5 Hz, H-11), 1.83–0.86 (62H, alkyl chain).

3. Results and discussion

3.1. Synthesis

Schiff base dyes, **2a**–**2c**, were synthesized in a four-step process, in which the hydroxy group in 4-nitrophenol is first replaced by a hexadecyloxy chain followed by reductions of nitro group to amine. In the third step, salicylaldehyde coupled with the diazonium chloride obtained from the 4-hexadecyloxyaniline and finally the Schiff base dyes were obtained by reaction of 5-(4-hexadecyloxyphenylazo) salicylaldehyde (**1**) with an appropriate aromatic amine (Scheme 1) by refluxing in absolute ethanol using a few drops of acetic acid as catalyst. The Schiff bases, **2a**–**2c**, were purified by repeated crystallization in the ethanol/chloroform mixture.

The 5-(4-^{n}hexadecyloxyphenylazo) salicylaldehyde; **1** and Schiff base dyes, **2a**–**2c**, were characterized by IR, ^{1}H NMR, mass spectroscopy and elemental analyses. The IR spectral frequencies of synthesized compounds, **1** and **2a**–**2c** were carried out using KBr pellets as described in Section 2. In the compound **1**, the hydroxyl group was observed at 3190 cm^{-1} because the intramolecular hydrogen bonding between OH and formyl group in compound **1** leads to decrease in the stretching frequency of OH. In the compounds **2a**–**2c**, the OH group was formed at 3420–3450 cm^{-1} because of the poor intramolecular hydrogen bonding between OH and C=N [12–14]. The carbonyl group in the compound **1** was observed at 1666 cm^{-1}, but in the compounds **2a**–**2c** the C=O stretching disappeared and a sharp strong peak at 1632–1637 cm^{-1} due to C=N was appeared. Physical and characterization data for compounds **1** and **2a**–**c** are given in Section 2 and some selected IR data are given in Table 1.

3.2. Mesomorphism

The mesomorphic properties of 5-(4-^{n}hexadecyoxyphenylazo) salicylaldehyde homologues (**1**) and azo-linked schiff bases; **2a**–**2c** have been studied by polarizing optical microscopy observations using a heating–cooling stage and the phase transition temperature and enthalpy were obtained by differential scanning calorimetry (DSC). Phase transition temperatures along with the corresponding enthalpy values for all synthesized compounds are summarized in Table 2.

5-(4-^{n}Hexadecyoxyphenylazo) salicylaldehyde (**1**) did not show any liquid crystalline character on heating or cooling. In the heating cycle, the compound **1** clearly melted to isotropic liquid as seen optically. Under examination by polarizing microscopy in the cooling scan, the compound **1** was found to crystallize directly from the isotropic liquid. As can be seen from Table 2, in the first heating on the DSC measurement, the

Table 1
Selected IR data for compounds **1** and **2a**–**c**

Compound	ν/cm^{-1}						
	O–H	C–H (aromatic)	C–H (aliphatic)	C=N	N=N	C–O (etheric)	C=O
1	3190 (br, m)	3072–3075 (m)	2950–2850 (s)	–	1505 (s)	1241–1244 (s)	1666 (s)
2a–**c**	3420–3450 (br, m)	3052–3055 (m)	2950, 2865 (s)	1632–1637 (s)	1505 (s)	1250–1280 (s)	–

s: Strong, m: medium, br: broad.

Table 2
Transition temperatures and enthalpy changes of compounds **1** and **2a**–**2c**

Compound	Transition[a]	T^{b}/°C	ΔH^{b}/KJ mol^{-1}
1	K_1–K_2	84.2	1.3
	K_2–K_3	101.9	2.8
	K_3–I	122.0	38.2
2a	K_1–K_2	90.1	4.2
	K_2–I	115.1	34.7
	(I–S_A)[c]	113.2	1.8
2b	K_1–K_2	92.5	3.8
	K_2–I	112.2	35.2
	(I–S_A)[c]	109.7	2.0
2c	K_1–S_A	109.1	32.4
	S_A–I	119.3	2.3

[a] K: crystal, N: nematic, I: isotropic liquid.
[b] Data obtained from first DSC cycle.
[c] Monotropic transition.

compound **1** showed three endothermal peaks at 84.2 °C, 101.9 °C and 122.0 °C. The peak at 122.0 °C is attributed to melting, and other peaks are related to solid–solid phase transitions. The melting peak is narrow and the enthalpy of fusion amounts to 38.2 kJ mol^{-1} which is in agreement with the presence of a perfect crystalline State [17].

Compounds **2a** and **2b** show a monotropic liquid crystalline behavior on cooling from the isotropic liquid. Under the optical microscope with polarized light the texture organizes as Maltese crosses [17,18] at 113.2 °C for **2a** and 109.7 °C for **2b**. When the polarizer is rotated the cross-like arms turn in opposite direction. This mesophase is stable until the compounds **2a** and **2b** start to crystallize at 100 °C and 97.2 °C, respectively. Different sizes of "Maltese crosses" were observed on the mesophase. The enthalpy changes of 4.2 and 3.8 kJ mol^{-1} (for **2a** and **2b**, respectively) observed on cooling from isotropic liquid are in agreement with the formation of mesosphere [17].

Compound **2c** shows an enantiotropic liquid crystalline phase behavior. The polarizing microscopy study for **2c** showed liquid crystalline character on heating and cooling from the isotropic liquid. The texture of mesophase for **2c** is similar to those of the **2a** and **2b**. In addition, from the DSC thermogram obtained from **2c**, the mesomorphic behavior on the heating and cooling scan was confirmed. When a sample of **2c** was heated, two endothermic peaks at 109.1 °C and 119.3 °C due to crystal to mesophase and mesophase to isotropic liquid were observed. On cooling from the isotropic liquid, the mesophase was formed at 117.2 °C and crystallized at 105.3 °C. A representative optical polarized micrograph from mesophase for **2c** is illustrated in Fig. 1 and a microscopic picture from crystalline state of **2c** is shown in Fig. 2.

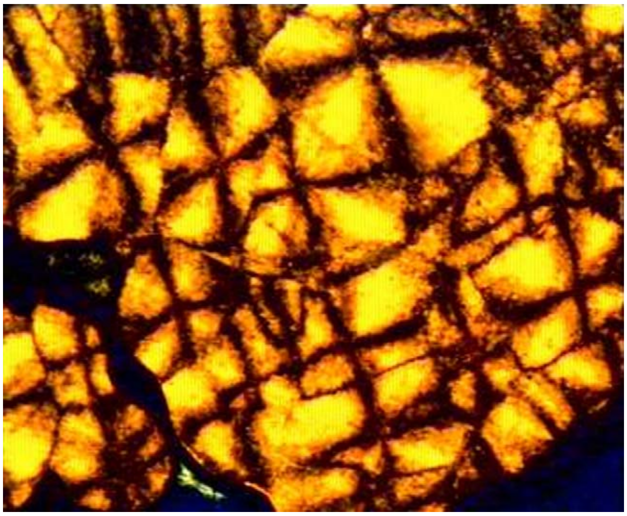


Fig. 1. Optical polarized micrograph of the texture exhibited by the S_A mesophase of **2c** at 115.0 °C on the cooling scan.

On the bases of optical observations and DSC data we concluded that the compounds **2a**–**2c** exhibit a smectic A mesophase. The textures exhibited by **2a**–**2c** are similar to that of the texture reported in previous literature [19].

4. Conclusion

In this work we have prepared a series 5-((4-hexadecyloxyphenyl) azo)-*N*-(4-^{n}alkoxyphenyl) salicylaldimine derived from 5-(4-hexadecyloxyphenylazo) salicylald-ehyde and 4-alkoxyanilines. The stability of mesophase was found to be controlled by alkyl length (*n*). The compound with long alkyl chain length (**2c**) exhibits enantiotropic mesophase which is thermodynamically stable, but compounds with short chain length exhibit monotropic phase (unstable) behavior.

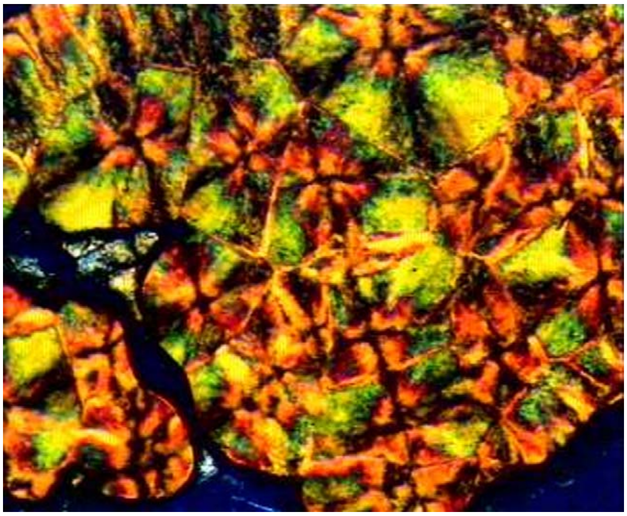


Fig. 2. Representative optical polarized micrograph of crystalline state of **2c** at 100 °C on the cooling scan.

Acknowledgment

Financial support from Azarbaijan University of Tarbiat Moallem Research Council greatly appreciated.

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