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

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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.

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 photo-responsive species that may be quite valuable as photo-chemical 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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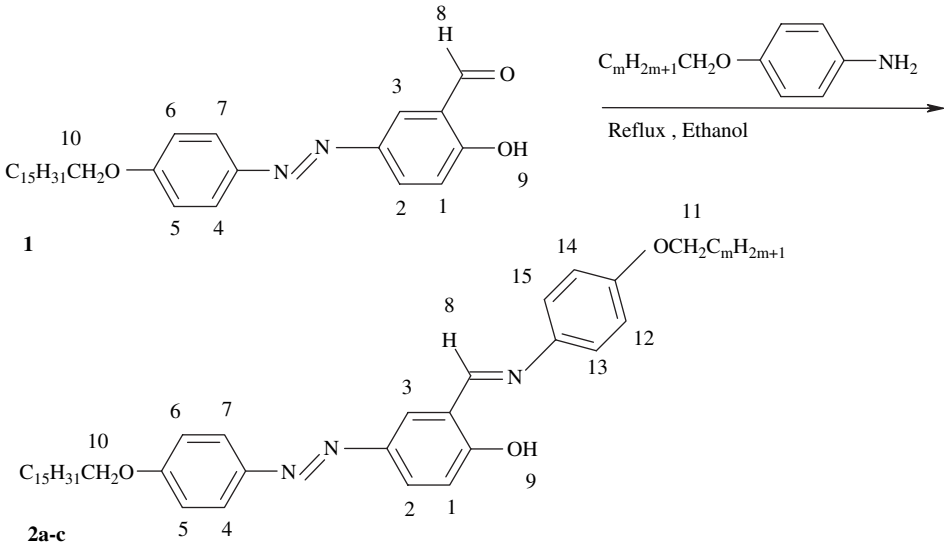

Compound no.	*n*
2a	7
2b	11
2c	15

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. ^{1}H 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. ^{1}H 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