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Synthesis and mesomorphic properties of 4-(4-bromopropyloxy)-4'-(4-alkyloxybenzylidene)anilines

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Abstract

This article describes the preparation and liquid crystalline properties of a new homologous series of 4-(4-bromopropyloxy)-4'-(4-alkyloxybenzylidene)anilines in which the phenyl ring is armed by a bromopropyloxy chain. The thermal behavior and mesomorphic properties of the synthesized compounds were studied with particular attention given to the correlation between their phase transition temperatures and anisotropic change influenced by molecular structure. All the members displayed enantiotropic smectic phase except for the homologue with the longest alkyloxy chain ($\mathbf{R} = C_{18}H_{37}$), exhibiting only monotropic characteristic. The presence of bromine atom from the propyloxy side chain is found to be capable of altering and influencing the mesomorphic properties.

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Apart from the utilization in display and imaging, liquid crystal also plays an important role in the other fields of science. For instance, liquid crystal incorporating cellulose fragment have recently been used to study the air-separation performance owing to its potential application in membrane separation [1,2]. In addition, liquid crystalline polymers can also serve as thermotropic liquid crystals particularly in the preparation of high strength, good mechanical and heat-resistance materials [3,4]. One of the essential parts in these liquid crystals is made up by Schiff base.

Schiff base is a very interesting organic precursor for material science particularly in the preparation of liquid crystalline substance, thermochromic as well as photochromic material which may possess potential application in the measurement of radiation intensity and in optical display system [5]. Thus, their properties can be varied by appropriate molecular design. The aromatic imine compounds with rod-like structure are well known for their ability to exhibit liquid crystalline behaviours resulted from their high shape anisotropy and the presence of terminal halogen atom which help to increase the molecular polarizability [6–15]. The synthesis of 4-methoxybenzylidene-4'-butylaniline by Kelker and Scheurle [16] yielded the first thermotropic liquid crystal which showed nematic phase at room temperature. In view of the interesting mesomorphism of these imines, the exhaustic liquid crystalline series of 4-alkyloxybenzylidene-4'- alkyloxybenzylidene-4'- alkyloxybenzylidene have subsequently been studied [17–22]. Early findings revealed that this type of compound was nematognic and also exhibited a rich smectic polymorphism such as SmA, SmB, SmC as well as

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Scheme 1. Synthetic pathway towards the title compounds. Reagent and reaction condition: (i) K_2CO_3 (3 equiv.), 1-bromoalkane (1.2 equiv.), heat in DMF, 80 °C, 4 h; (ii) 4-aminophenol (1.0 equiv.), 3 drops glacial acetic acid, reflux in ethanol, 3 h; (iii) K_2CO_3 (3 equiv.), 1,3-dibromopropane (4 equiv.), reflux in acetone, 8 h.

the rare SmI phases. Hence, in order to further investigate the factors which govern the thermal behavior of the aromatic imines and their relationship with its molecular structures, we report herein the effect of terminal bromine atom from the propyloxy side chain upon the mesomorphic properties of newly derived imines containing ω -brominated alkyloxy side chain, 4-(4-bromopropyloxy)-4'-(4-alkyloxybenzylidene)-anilines **1a**–**1f**.

Scheme 1 outlined the synthetic pathway towards the formation of all intermediates and title compounds. 4-Alkyloxybenzaldehyde was prepared following the method described previously by Catanescu et al. [23] where 4hydroxybenzaldehyde was reacted through Williamson etherification with various bromoalkane, RBr (where $R = C_8H_{17}$, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ and $C_{18}H_{37}$) of even parity. The intermediate underwent condensation with 4-aminophenol under reflux for 3 h in ethanol with a catalytic amount of glacial acetic acid. Finally, the imine thus obtained was reacted with an excess of 1,3-dibromopropane to yield compounds **1a–1f**. Their molecular structures were elucidated by elemental analysis, FT-IR and FT-NMR spectroscopic techniques [24]. All phase transition temperatures and associated enthalpy changes of compounds **1a–1f** were determined by DSC with the heating and cooling rates of ± 2 °C. The results were summarized in Table 1. Polarizing optical microscope equipped with a hot stage and temperature controller was used for the texture observation,.

Optical microscopy studies reveal that all the title compounds 1a-1f exhibit liquid crystalline properties. All of them were enantiotropic except for compound 1f (R = C₁₈H₃₇). Upon heating, 1a-1d show three endothermic peaks. The first peak at lower temperature corresponds to the Cr₁-Cr₂ transition. The second peak which occurs at higher temperature and possesses small enthalpy change in comparison to the first peak can be ascribed to the transition from crystal to mesophase. Upon heating, the focal conic fan-shaped texture characteristics of SmA phase can be observed prior to isotropization. Compound 1e (R = C₁₆H₃₃) exhibits two endothermic peaks wherein the first and second peaks can be ascribed to the phase transitions of Cr–SmA and SmA–I, respectively. As for compound 1f which possesses the longest alkyl chain (R = C₁₈H₃₇), only one endotherm corresponding to direct melting of the crystal to isotropic transition was

Phase transition temperatures (°C) and transition enthalpy changes for compounds 1a-1f upon heating and cooling.

Compound	Phase transition, °C (enthalpy change, kJ mol ⁻¹)
1a (R = C ₈ H ₁₇)	Heating Cr 69.9 (35.4) Cr ₂ 98.3 (3.9) SmA 109.0 (7.2) I
	Cooling I 105.3 (4.8) SmA 88.5 (5.2) SmC 47.8 (21.2) Cr
1b (R = $C_{10}H_{21}$)	Heating Cr 78.8 (41.2) Cr ₂ 99.4 (4) 99.4 (4.0) SmA 111.6 (8.6) I
	Cooling I 107.3 (6.4) SmA 91.1 (3.0) SmC 63.6 (31.6) Cr
$1c \ (R = C_{12}H_{25})$	Heating Cr 82.1 (51.8) Cr ₂ 98.5 (4.4) SmA 112.8 (9.4) I
	Cooling I 109.0 (9.0) SmA 91.4 (3.5) SmC 73.6 (43.2) Cr
$1d \ (R = C_{14}H_{29})$	Heating Cr 88.9 (55.2) Cr ₂ 96.2 (4.0) SmA 111.6 (10.0) I
	Cooling I 108.5 (9.0) SmA 90.2 (3.5) SmC 78.5 (51.8) Cr
$1e \ (R = C_{16}H_{33})$	Heating Cr 93.3 (67.0) SmA 110.0 (11.6) I
	Cooling I 107.2 (9.9) SmA 89.8 (3.4) SmC 83.8 (58.7) Cr
1f ($\mathbf{R} = C1_8H_{37}$)	Heating Cr 95.5 (69.8) I
	Cooling I 94.7 (4.9) SmA 87.5 (42.9) Cr

Note: Cr, crystal; SmA, smectic A; SmC, smectic C; I, isotropic.

Table 1



Fig. 1. The photomicrographs of compound **1c** upon cooling. (a) The formation of batonets from isotropic. (b) The focal conic fan-shaped texture of SmA phase. (c) The appearance of broken fan-shaped texture characteristics of the SmC phase.

observed as it has a large enthalpy value. Upon cooling from isotropic phase, all the compounds show SmA phase which can be characterized by the formation of batonets that coalesce to form a focal conic fan-shaped texture as displayed in Fig. 1a and b. On further cooling, the broken fan-shaped texture typical of a SmC phase can be observed (Fig. 1c). In contrary to compound **1f**, the SmC phase is absent on cooling from the SmA phase as it undergoes direct crystallization at 87.5 °C. Overall, these data indicate that compounds **1a–1d** are enantiotropic smectogens while compound **1f** is monotropic smectogen of which the SmA phase is observed only in cooling cycle (Figs. 2 and 3).

A comparison between the present ω -brominated alkoxy imines **1a–1f** with the homologous series **I** [21] and **II** [19] prepared by Godzwon et al. shows that the difference lies on the presence of brominated propyloxy at one of the terminals lying along the long molecular axis. Inspection from the result shows that the present compounds display SmA and SmC phases only while the earlier reported analogues exhibited a nematic phase as well as a rich smectic mesomorphic behaviour such as SmA, SmB, SmC and SmI. Hence, it can be presumed that the introduction of polarizable Br atom in the alkoxy chain for these aromatic imines compounds will suppress the formation of nematic phase wherein the molecule will tend to self-assembly into smectic and tilted smectic arrangement. Thus, the presence of polarizable Br atom from the alkoxy side chain at one end is found to be capable of altering the mesomorphic properties as it increases the overall intermolecular attraction which can facilitate lamellar packing of molecules leading to the formation of smectic A and tilted arrangement of smectic C [25,26]. In addition, the thermal stability of the present series is quite similar to that in series **I** and **II**. The clearing temperature for compounds in both series is less than 120 °C regardless of the presence of Br atom in the molecular structure.

In conclusion, all the title compounds exhibit liquid crystal properties. The all the members in this series are enantiotropic while the higher member ($R = C_{18}H_{37}$) exhibits monotropic behaviour only. The tendency of forming only smectic phase can be attributed to the presence of polarizable Br atom.



Fig. 2. DSC thermograms of compound 1c (R = $C_{12}H_{25}$).



Fig. 3. Comparison between the molecular structures of title compounds 1a-1f and their reported analogues (I and II).

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- [24] Analytical and spectroscopic data for the representative compound le (R = C₁₆H₃₃): Yield 80%, Appearance white precipitate, IR v_{max} (KBr, cm(1)): 2918, 2850 (C–H apliphatic), 1608–1622 (C=N azomethine), 1251 (C–O ether), ¹H NMR (300 MHz, CDCl₃): δ 0.90 (t, 3H, J = 6.6 Hz, CH₃), 1.28–1.51 (m, 26H, CH₂), 1.78–1.87 (m, 2H, CH₂), 2.30–2.39 (m, 2H, CH₂), 3.64 (t, 2H, J = 6.5 Hz, BrCH₂), 4.03 (t, 2H, J = 6.6 Hz, OCH₂), 4.14 (t, 2H, J = 5.7 Hz, OCH₂), 6.94 (d, 2H, J = 9.0 Hz, Ar), 6.98 (d, 2H, J = 8.7 Hz, Ar), 7.21 (d, 2H, J = 8.4 Hz, Ar), 7.83 (d, 2H, J = 8.7 Hz, Ar), 8.41 (s, 1H, CH=N), ¹³C NMR (75 MHz, CDCl₃): δ 158.10 (C=N), 161.69, 157.02, 145.67, 130.25, 129.27, 122.08, 115.07, 114.70 (Caromatic), 68.22, 65.68 (OCH₂), 32.47 (BrCH₂), 22.69–31.92 (CH₂), 14.10 (CH₃). Anal. calcd. for C₃₂H₄₈NO₂Br: C 68.80, H 8.66, N 2.51, found, C 68.94, H 8.70, N 2.55.
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