

Synthesis and Characterization of New Thermotropic Liquid Crystals Derived from 4-Hydroxybenzaldehyde

Sie-Tiong Ha,* Teck-Leong Lee, Yip-Foo Win, Siew-Ling Lee and Guan-Yeow Yeap

Abstract—A homologous series of aromatic esters, 4-*n*-alkanoyloxybenzylidene-4'-bromoanilines, **nABBA**, consisting of two 1,4-disubstituted phenyl cores and a Schiff base central linkage was synthesized. All the members can be differed by the number of carbon atoms at terminal alkanoyloxy chain ($C_{n-1}H_{2n-1}COO-$, $n = 2, 6, 18$). The molecular structure of **nABBA** was confirmed with infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and electron-ionization mass (EI-MS) spectrometry. Mesomorphic properties were studied using differential scanning calorimetry and polarizing optical microscopy.

Keywords—Liquid Crystals, Schiff base, Smectic, Mesomorphic

I. INTRODUCTION

Liquid crystals had become quintessential advanced materials in our daily life today for more than a century of studies. Its applications were developed in various areas such as advanced technological devices, prototypical self-organizing molecular materials, smart biological and pharmacological uses [1]. Selection of mesogenic core, terminal groups and suitable length of flexible chain are among the essential criteria in designing new thermotropic liquid crystals [2]. Low mass molecules compounds containing two unsaturated rings with one or multiple terminal substituents are capable of exhibiting mesomorphic properties [3]. 1,4-Disubstituted phenyl ring often serves as an important core unit which ensures that molecules possess structural linearity and large molecular polarisability, thus consequently enables them to exhibit mesophase in low molar mass

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mesogen systems [4].

Schiff base, also known as imine ($CH=N$), is a linking group used to connect between core groups. It provides a stepped core structure but still maintained the molecular linearity in order to exhibit higher stability and form mesophases [4,5]. Extensive studies of Schiff base core system had been conducted ever since discovery of MBBA showing nematic phase at room temperature [6]. Nowadays, a lot of studies have been conducted on the Schiff base possessing ester chain or called Schiff base esters owing to their interesting properties and considerable temperature range [7-13].

In order to accomplish research of Schiff base ester mesogens, we report another homologous series of Schiff base ester, 4-*n*-alkanoyloxybenzylidene-4'-bromoanilines, **nABBA**, consisting of two 1,4-disubstituted phenyl core, a Schiff base central linkage and an even number of carbon atoms of terminal alkanoyloxy chain ($C_{n-1}H_{2n-1}COO-$, $n = 2, 6, 18$). Bromo group was served as terminal substituent while no lateral substituent is present in this series.

II. EXPERIMENTAL

A. Materials and Methods

4-Dimethylaminopyridine (DMAP), fatty acids ($C_{n-1}H_{2n-1}COOH$ where $n = 2, 6, 18$) and 4-hydroxybenzaldehyde and were purchased from Merck (Germany). *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-bromoaniline were purchased from Acros Organics (USA). All solvents and reagents were purchased commercially and used without any further purification.

IR spectra were recorded using Perkin-Elmer System 2000 FT-IR Spectrometer via KBr disc procedure. 1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ using Bruker Avance 400 MHz Spectrometer in the Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia. EI-MS (70 eV) were measured with Mass Spectrometer Finnigan MAT95XL-T at source temperature of 200 °C.

Phase-transition temperatures and enthalpy changes were measured using Differential Scanning Calorimeter Mettler Toledo DSC823° at heating and cooling rates of 10 °C/min and -10 °C/min, respectively. Polarizing optical microscope (Carl Zeiss) equipped with Linkam heating stage was used for temperature dependent studies of the liquid crystal textures. Phase identification was made by comparing the observed textures with those reported in the literature [14,15].

B. Synthesis of Schiff Base Liquid Crystals

nABBA were synthesized via modification of previously reported methods [16, 17]. The synthetic route of **nABBA** is illustrated in Fig. 1. 4-Hydroxybenzaldehyde (0.61 g, 5 mmol) and 4-bromoaniline (0.86 g, 5 mmol) were condensed upon stirring at room temperature for three hours in appropriate amount of methanol. Precipitate formed, **HBBA** was separated by suction filtration and washed several times with methanol.

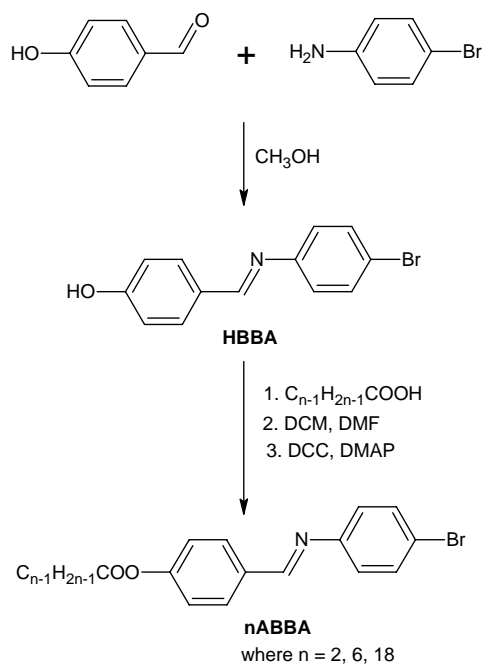


Fig. 1 Synthetic route of **nABBA**

HBBA (0.2433 g, 4 mmol), 3 mmol of fatty acids ($C_nH_{2n-1}COOH$, $n = 2, 6, 18$), DMAP (0.0244 g, 0.6 mmol) and DCC (0.2063 g, 3 mmol) were mixed and stirred at room temperature for six hours in appropriate amount of THF. Solvent of reaction mixture was removed by evaporation till dryness. Precipitate obtained was recrystallized several times with hexane and methanol whereupon pure compound was isolated. The FTIR, 1H NMR, ^{13}C NMR and mass spectral data for the representative compound, **18ABBA**, are summarized as follows.

(18ABBA). IR (KBr) ν_{max} cm^{-1} 2951 (C-H aromatic), 2919, 2850 (C-H aliphatic), 1749 (C=O ester), 1619 (C=N), 1211, 1100 (C-O ester). 1H NMR (300 MHz, $CDCl_3$, δ ppm): 0.90 (t, 3H, CH_3 -), 1.28-1.46 (m, 28H, $CH_3-(CH_2)_{14}$ -), 1.79 (quint, 2H, $-CH_2-CH_2-COO-$), 2.60 (t, 2H, $-CH_2-COO-$), 7.10 (d, 2H, Ar-H), 7.22 (d, 2H, Ar-H), 7.52 (d, 2H, Ar-H), 7.93 (d, 2H, Ar-H), 8.42 (s, 1H, $-CH=N-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.09 (CH_3 -), 22.68 (CH_3CH_2 -), 24.88 ($CH_3CH_2CH_2$ -), 29.10, 29.24, 29.35, 29.44, 29.58, 29.65, 29.69 for methylene carbons ($CH_3CH_2CH_2-(CH_2)_{14}$ -), 31.92 ($-CH_2CH_2COO-$), 34.43 ($-CH_2COO-$), 119.37, 122.10, 122.56, 130.05, 132.20, 133.53, 150.88, 153.36 for aromatic carbons,

159.45 ($-CH=N-$), 171.87 ($-COO-$). EI-MS m/z (rel. int. %): 543.3(5.51) [$M^+ + 2$], 541.3(5.34) [M^+], 277.0(97.94), 275.0(100.00).

III. RESULTS AND DISCUSSION

A. Synthesis and Spectral Studies

Structure elucidation of compounds **nABBA** was ascertained by using mass spectrometry and spectroscopic methods (FT-IR and NMR). The molecular ion peak at $m/z = 541.3$ in the mass spectrum of the representative compound **18ABBA** (Fig. 2) suggested that **18ABBA** with a molecular formula of ($C_{31}H_{44}BrNO_2$) was successfully synthesized.

The 1H NMR spectrum of **18ABBA** (Fig. 3) further supported its structure. The two triplets at $\delta = 0.90$ ppm and $\delta = 2.60$ ppm, were respectively ascribed to the methyl and methylene protons ($-CH_2COO-Ar$), while the multiplet between $\delta = 1.28-1.46$ ppm was assigned to the methylene protons of the long alkyl chain $\{-(CH_2)_{14}-\}$. The four distinct doublets between $\delta = 7.10-7.93$ ppm were indicative of the aromatic protons. The singlet observed at the most downfield region, $\delta = 8.42$ ppm, supported the presence of the imine linking group [18].

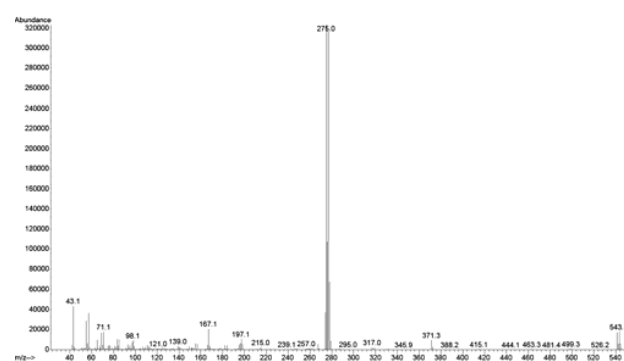


Fig. 2 EI-MS spectrum of **18ABBA**

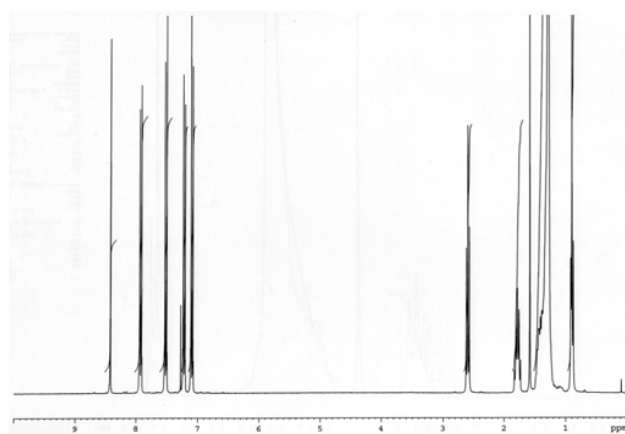


Fig. 3 1H NMR spectrum of **18ABBA**

The molecular structure of **16CIAB** was further verified by using ^{13}C NMR spectroscopy (Fig. 4). The peak at $\delta = 14.09$ ppm was attributed to the methyl carbon while the peaks between $\delta = 22.68$ - 34.43 ppm represented the methylene carbons of the long alkyl chain. Twelve aromatic carbons in **18ABBA** is resonated between $\delta = 119.37$ - 153.36 ppm. The peak at $\delta = 159.45$ ppm and $\delta = 171.87$ ppm confirmed the presence of the azomethine carbon and the carbonyl group in the molecule.

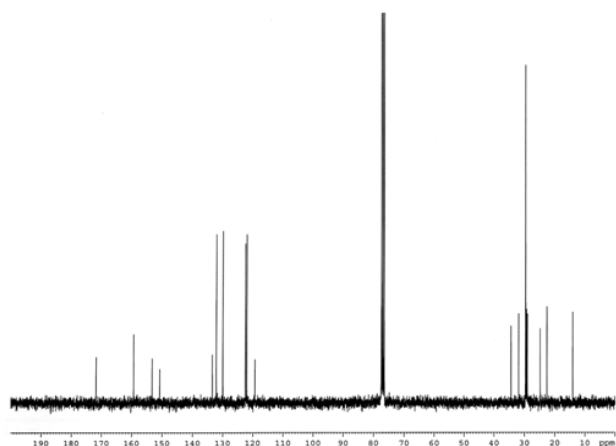


Fig. 4 ^{13}C NMR spectrum of **18ABBA**

B. Phase Transition Behavior and Liquid Crystallinity

6ABBA exhibited interesting thermotropic properties and its melting behavior was carefully monitored by POM during both heating and cooling scans. Optical photomicrographs of **6ABBA** are shown in Fig. 5 as the representative illustration. The results from the POM observation were verified by the DSC measurements (Fig. 6). The transition temperatures, enthalpy changes, and phase sequences are summarized in Table 1. Phase identification was based on the optical textures, and the magnitude of isotropization on enthalpies is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus [19] and Gray and Goodby [20].

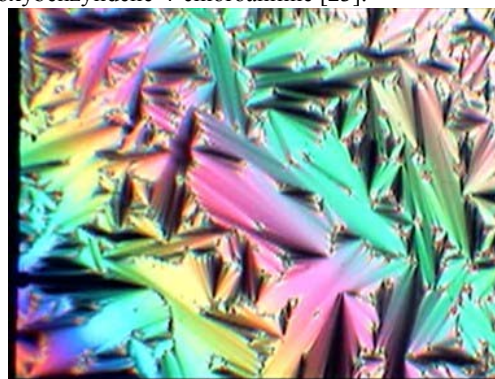
TABLE I

PHASE TRANSITION TEMPERATURES AND ENTHALPY CHANGES OF **NABBA**

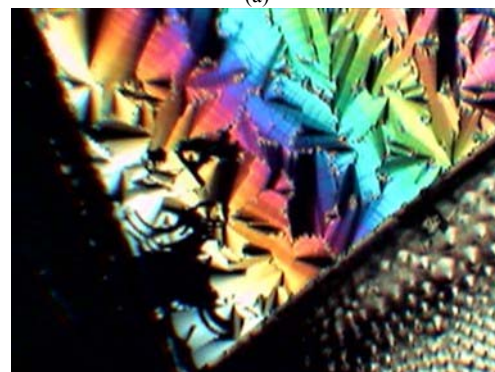
Compound	Phase transition temperature, $^{\circ}\text{C}$ (enthalpy change, kJ mol^{-1})
2ABBA	Cr 97.2 (24.8) I <i>I 60.8 (16.5) Cr</i>
6ABBA	Cr 102.9 (39.8) I <i>I 99.6 (6.3) SmA 88.3 (3.4) SmB 39.4 (24.8) Cr</i>
18ABBA	Cr 97.1 (73.9) SmA 105.5 (11.4) I <i>I 102.4 (11.9) SmA 83.9 (4.5) SmB 74.3 (69.2) Cr</i>

Note: Cr= crystal; SmB= smectic B; SmA= smectic A; I= isotropic. Cooling data is presented in *italics*.

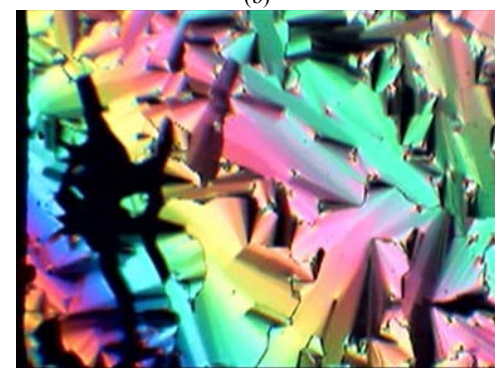
Under polarizing optical microscope (POM), focal conic fan-shaped textures of a smectic A phase was observed during the cooling cycle (Fig. 5a). Upon further cooling, the back of the fan-shaped domains developed a series of dark-lines, which is transitory in nature (Fig. 5b) [5,21]. When further cooled, the bands expanded, met and eventually coalesce to produce a polygonal-like texture (Fig. 5c) [22]. This phase is identified as a smectic B phase. This similar behavior was also reported for a closely-related compound, 4-butylxybenzylidene-4-chloroaniline [23].



(a)

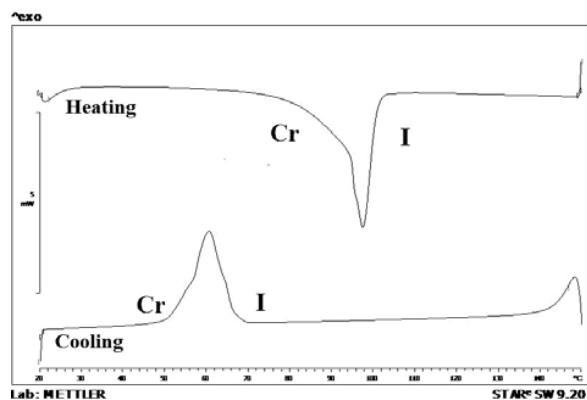


(b)

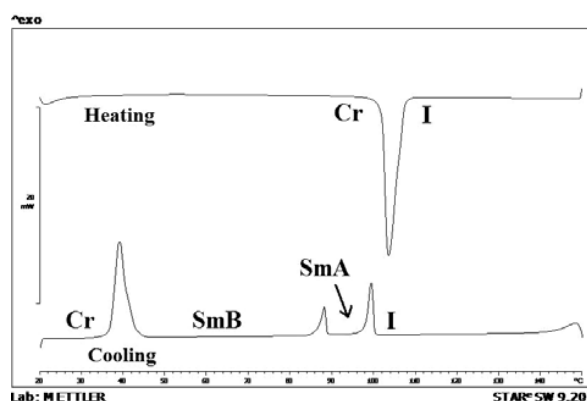


(c)

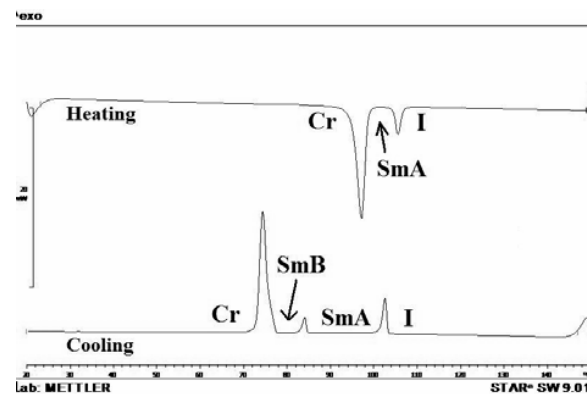
Fig. 5 Liquid crystals textures (100x) of **6ABBA** upon cooling. (a) Optical photomicrograph of homogenous focal-conic texture of smectic A phase, (b) optical photomicrograph of temporary transition bars which indicate transition phase from smectic A to smectic B phase, (c) optical photomicrograph of well formed smectic B phase were observed.



(a)



(b)



(c)

Fig. 6 DSC thermograms of (a) **2ABBA**, (b) **6ABBA** and (c) **18ABBA** during heating and cooling cycles

The shortest member of this series, **2ABBA** is a non-mesogenic compound. In the DSC thermogram of **2ABBA** (Fig. 6a), it showed an endotherm and exotherm, respectively during both heating and cooling cycles. This observation indicates direct melting of the crystal phase to the isotropic liquid phase and vice versa. Under POM observation, crystal changed to dark region isotropic during heating run. **2ABBA** is not mesogenic due to incorporation of high rigid core

system with short alkanoyloxy chain which resulting in high melting point and suppressing liquid crystals phase [4]. However, two additional peaks of low enthalpy changes (Fig. 6b) were observed on the medium member of the series, **6ABBA** upon cooling scan. This indicated the exhibition of monotropic smectic phase on this compound. In monotropic mesogens, the melting points were always equal to or higher than the clearing points, hence exhibiting supercooling properties [24]. As for the highest member of the series, **18ABBA** exhibited enantiotropic property whereby smectic A phase was observed during heating scan. The better mesophase stability of **18ABBA** was due to enhancement of flexibility resulted by longer terminal alkanoyloxy which contributed to the suitable harmonizing of rigidity and flexibility of these compounds and subsequently promotes the exhibition of enantiotropic smectic A phase [14].

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