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Mesomorphic behaviour of new azomethine liquid crystals having terminal bromo substituent

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Abstract

A homologous series of azomethine esters, 4-*n*-alkanoyloxybenzylidene-4′-bromoanilines possessing even number of carbon atoms at the terminal alkanoyloxy chain ($C_{n-1}H_{2n-1}COO$–, n = 8, 10, 12, 14, 16, 18) was synthesized and characterized. Whilst *n*-octanoyloxy to *n*-dodecanoyloxy derivatives exhibited enantiotropic smectic A and smectic B phases, *n*-tetradecanoyloxy to *n*-octadecanoyloxy derivatives possessed enantiotropic smectic A and monotropic smectic B properties. *n*-Decanoyloxy derivatives demonstrated the optimum exhibition for both smectic A and smectic B phases. It was found that the length of terminal alkanoyloxy chain has an influence on mesomorphic properties.

Keywords: Liquid crystals; Schiff base ester; Enantiotropic; Smectic A; Smectic B

Mesomorphic materials, either low molar mass or polymeric in nature, having an azo group in the mesogenic core, are often studied owing to their interesting oxygen-enriching ability, enhanced air-separation performance and optical properties, which enable applications in, for example, optical switching, holography and optical storage devices [1]. Dyes containing azo group are also being used in liquid crystal display (LCD) devices for the guest–host interaction [2].

Low-mass molecules compounds containing as simple as two unsaturated (aromatic) rings with one or multiple terminal substituents are capable of exhibiting mesomorphic properties [3]. Some studies showed that the influence of a terminal alkyl chain upon the liquid crystalline properties [4] and the possibility of enhancing the rigidity of core system of azo compounds through metal complexes formation [5,6] have been claimed as two of the favourable pathways to improve mesogenic properties.

In our previous studies, the results revealed that azomethine and ester are useful linking units for generating mesomorphism in two and three aromatic rings compounds. The presence of different polarity of terminal substituents has been well reported that will either promote or suppress the mesomorphic properties [7–11].

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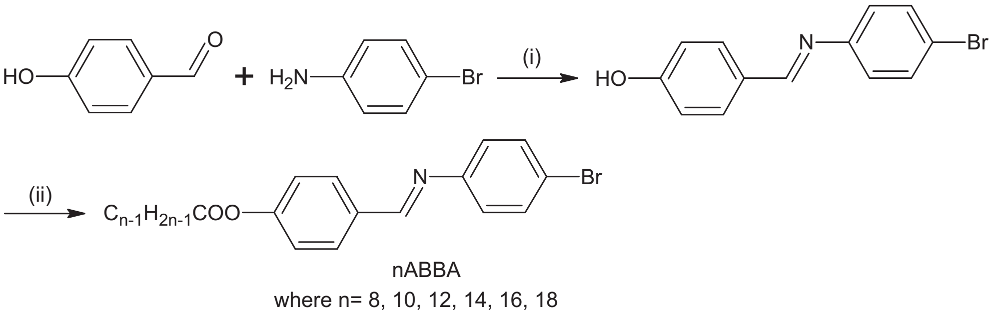

Scheme 1. Synthetic route of nABBA. (i) CH_3OH, reflux, 3 h (ii) $C_{n-1}H_{2n-1}COOH$, DCC, DMAP, THF, r.t., 6 h.

In order to accomplish the research on mesomorphic properties of two aromatic rings Schiff base ester, we reported another homologous series of liquid crystal, 4-*n*-alkanoyloxybenzylidene-4′-bromoanilines (*n*ABBA) and its synthetic route is shown in Scheme 1. 4-Bromoaniline was condensed with 4-hydroxybenzaldehyde upon refluxing in methanol for an hour [12]. Then, the Schiff base intermediate was subjected to Steglich esterification with fatty acids in the presence of DCC and DMAP [13]. All the crude products were purified by repeated recrystallization using ethanol and hexane until constant melting points were obtained. Molecular structure of *n*ABBA was confirmed by elemental analysis and spectroscopic techniques including FT-IR, ^{1}H and ^{13}C NMR and EI-MS [14].

The mesophase textures of the products were examined under a polarizing optical microscope equipped with a Linkam hotstage and temperature regulator. Phase identification was made by comparing the observed textures with those reported in the literature [15,16]. Transition temperatures and enthalpy changes were determined using a differential scanning calorimeter. The results are summarized in Table 1.

All synthesized compounds showed liquid crystal characteristics based on the endotherms appeared in the DSC thermograms (Fig. 1) which can be attributed to the crystal-mesophase and mesophase-isotropic transitions.

Based on DSC data, *n*-octanoyloxy to *n*-dodecanoyloxy derivatives exhibited enantiotropic smectic A and smectic B phases whilst *n*-tetradecanoyloxy to *n*-octadecanoyloxy derivatives displayed enantiotropic smectic A and monotropic B phases. For enantiotropic compounds, similar mesophases were observed during heating and cooling cycles. Upon cooling of 8ABBA from isotropic liquid, homogenous focal-conic texture of smectic A phase (Fig. 2a) was first observed followed by temporary transition bars which indicate transition phase from smectic A to smectic B phase (Fig. 2b).

A plot of phase transition temperatures against number of carbon atoms (*n*) in alkanoyloxy chain during cooling scan is shown in Fig. 2c. Based on the plot, it can be deduced that length of terminal alkanoyloxy chain influenced the

Table 1
Phase transition temperatures and enthalpy changes of nABBA upon heating and cooling.

Compound	Phase transition temperature, °C (enthalpy change, kJ mol^{-1})
8ABBA	Cr 89.62 (25.09) SmB 94.40 (2.27) SmA 110.55 (6.39) I (heating) I 106.78 (6.53) SmA 91.03 (3.02) SmB 46.16 (10.64) Cr (cooling)
10ABBA	Cr 86.70 (26.28) SmB 96.17 (2.78) SmA 113.55 (8.16) I (heating) I 108.44 (8.65) SmA 92.33 (3.27) SmB 40.48 (28.73) Cr (cooling)
12ABBA	Cr 90.95 (31.54) SmB 96.50 (3.09) SmA 115.08 (8.16) I (heating) I 108.82 (7.46) SmA 90.83 (3.20) SmB 53.47 (31.75) Cr (cooling)
14ABBA	Cr 91.26 (41.08) SmA 110.55 (8.08) I (heating) I 105.72 (8.00) SmA 84.83 (3.25) SmB 54.15 (36.98) Cr (cooling)
16ABBA	Cr 94.35 (53.70) SmA 107.13 (9.27) I (heating) I 102.16 (10.45) SmA 84.13 (3.79) SmB 70.74 (50.79) Cr (cooling)
18ABBA	Cr 97.11 (73.88) SmA 105.50 (11.44) I (heating) I 102.39 (11.93) SmA 83.92 (4.52) SmB 74.26 (69.16) Cr (cooling)

Note: Cr = crystal; SmB = smectic B; SmA = smectic A; I = isotropic.

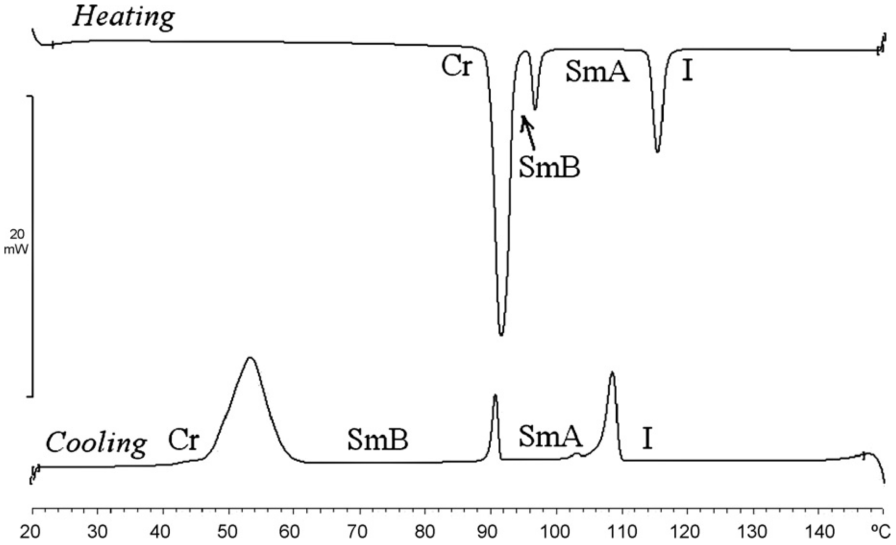

Fig. 1. DSC thermogram of 12ABBA.

mesomorphic properties. With the increasing length of terminal chain, the phase changed from enantiotropic to monotropic smectic B phase. From the graph, it is apparent that mesophase range increased from *n*-octanoyloxy to *n*-decanoyloxy members. This is because the increase of length of terminal alkanoyloxy chain led to the enhancement of the smectic properties. However, the mesophase range of *n*-dodecanoyloxy till *n*-octadecanoyloxy decreased due to the dilution of mesogenic core [17,18]. Amongst all, *n*-decanoyloxy derivatives demonstrated the optimum exhibition (largest mesophase range) for both smectic A and smectic B phase.

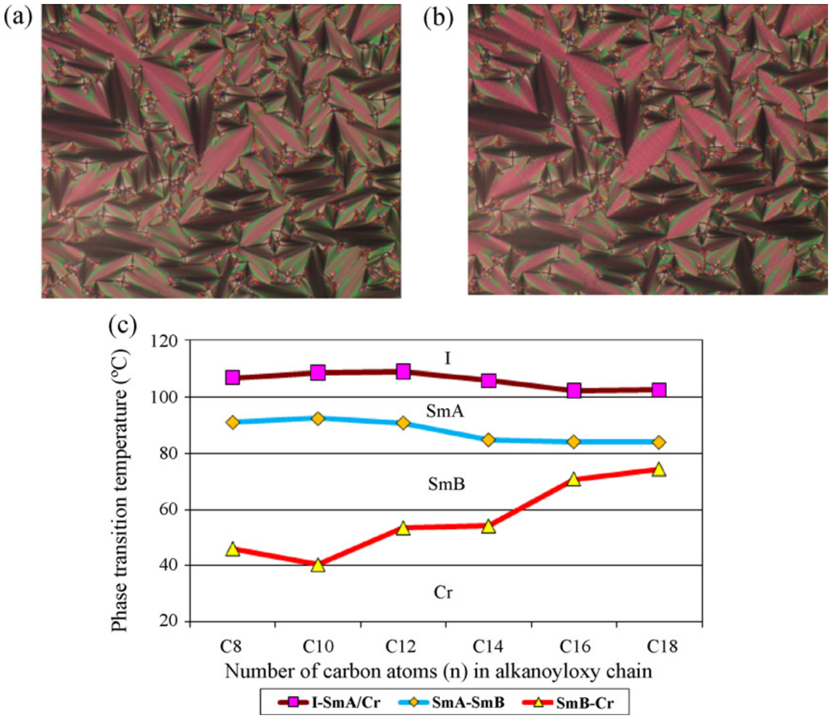

Fig. 2. Liquid crystals textures of 8ABBA upon cooling. Homogenous focal-conic textures of smectic A phase (a) and temporary transition bars (b) when changing from smectic A to smectic B phase. (c) Plot of phase transition temperatures against number of carbon atoms (*n*) in alkanoyloxy chain during cooling scan.

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References

[1] (a) C. Ruslim, K. Ichimura, J. Mater. Chem. 9 (1999) 673;
  (b) J. Belmar, M. Parra, C. Zuniga, et al. Liq. Cryst. 26 (1999) 389;
  (c) L.L. Lai, E. Wang, Y.H. Liu, Y. Wang, Liq. Cryst. 29 (2002) 871;
  (d) A.K. Prajapati, Mol. Cryst. Liq. Cryst. 364 (2001) 769;
  (e) L. Komitov, K. Ichimura, A. Strigazzi, Liq. Cryst. 27 (2000) 51;
  (f) L. Komitov, C. Ruslim, Y. Matsuzawa, K. Ichimura, Liq. Cryst. 27 (2000) 1011;
  (g) X.G. Li, M.R. Huang, G. Lin, J. Membr. Sci. 116 (1996) 143;
  (h) M.R. Huang, X.G. Li, G. Lin, Sep. Sci. Technol. 30 (1995) 449;
  (i) X.G. Li, M.R. Huang, G. Lin, P.C. Yang, Colloid Polym. Sci. 273 (1995) 772;
  (j) X.G. Li, M.R. Huang, Angew. Macromol. Chem. 220 (1994) 151.
[2] M. Matsui, Y.H. Nakagaway, B. Joglekary, et al. Liq. Cryst. 21 (1996) 669.
[3] A. Jacobi, W. Weissflog, Liq. Cryst. 22 (1997) 107.
[4] (a) J.S. Dave, G. Kurian, Mol. Cryst. Liq. Cryst. 42 (1977) 175;
  (b) Z.Y. Cheng, B.Y. Ren, S.Y. He, et al. Chin. Chem. Lett. 22 (2011) 1375;
  (c) X.D. Li, M.S. Zhan, K. Wang, Chin. Chem. Lett. 22 (2011) 1111.
[5] N. Hoshino, K. Takashi, T. Sekuchi, et al. Inorg. Chem. 37 (1998) 882.
[6] Y. Tian, F. Su, P. Xing, et al. Liq. Cryst. 20 (1996) 139.
[7] G.Y. Yeap, S.T. Ha, P.L. Lim, et al. Mol. Cryst. Liq. Cryst. 423 (2004) 73.
[8] G.Y. Yeap, S.T. Ha, P.L. Lim, et al. Mol. Cryst. Liq. Cryst. 452 (2006) 63.
[9] G.Y. Yeap, S.T. Ha, P.L. Boey, et al. Mol. Cryst. Liq. Cryst. 452 (2006) 73.
[10] G.Y. Yeap, S.T. Ha, P.L. Lim, et al. Liq. Cryst. 33 (2006) 205.
[11] S.T. Ha, T.L. Lee, G.Y. Yeap, et al. Chin. Chem. Lett. 21 (2010) 637.
[12] A.A. Jarrahpour, M. Zarei, Molbank (2004) M352.
[13] S.T. Ha, L.K. Ong, Y.F. Win, et al. Molbank 3 (2008) M582.
[14] Analytical and spectroscopic data for the representative compound 18ABBA: Yield 60.86%, EI-MS *m/z* (rel. int. %): 541.3 (5.34) [M$^+$], 275.0 (100.00), IR $\nu_{\max}$ (KBr, cm^{-1}): 2951, 2919, 2850 (C–H aliphatic); 1749 (C═O ester); 1619 (C═N); 1211, 1100 (C–O ester), ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.899 (t, 3H, J = 6.6 Hz, CH_3–), 1.279 (m, 28H, CH_3–$(CH_2)_{14}$–), 1.785 (qt, 2H, J = 7.5 Hz, –CH_2–CH_2–COO–), 2.597 (t, 2H, J = 7.5 Hz, –CH_2–COO–), 7.098 (d, 2H, J = 8.7 Hz, Ar–H), 7.223 (d, J = 8.4 Hz, 2H, Ar–H), 7.522 (d, J = 8.7 Hz, 2H, Ar–H), 7.930 (d, J = 8.4 Hz, 2H, Ar–H), 8.423 (s, 1H, –CH═N–), ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.091 (CH_3–), 22.675 (CH_3CH_2–), 24.881 ($CH_3CH_2CH_2$–), 29.096, 29.238, 29.346, 29.443, 29.584, 29.648, 29.685 for methylene carbons ($CH_3CH_2CH_2$–$(CH_2)_{14}$–), 31.917 (–CH_2CH_2COO–), 34.429 (–CH_2COO–), 119.369, 122.098, 122.559, 130.048, 132.203, 133.529, 150.880, 153.363 for aromatic carbons, 159.445 (–CH═N–), 171.874 (–COO–), anal. calcd. for $C_{31}H_{44}BrNO_2$: C, 68.62%, H, 8.17%, N, 2.58%; found: C, 68.93%, H, 8.41%, N, 2.48%.
[15] D. Demus, L. Richter, Textures of Liquid Crystals, Verlag Chemie, New York, 1978.
[16] I. Dierking, Textures of Liquid Crystals, Wiley-VCH, Weinheim, 2003.
[17] G.W. Gray, Molecular Structure and Properties of Liquid Crystals, Academic Press, London, 1962.
[18] P. Berdague, J.P. Bayle, M.S. Ho, B.M. Fung, Liq. Cryst. 14 (1993) 667.