



Mesomorphic behavior of new benzothiazole liquid crystals having Schiff base linker and terminal methyl group

Sie Tiong Ha^{a,*}, Kok Leei Foo^a, Hong Cheu Lin^b, Masato M. Ito^c,
Kazuma Abe^c, Kenji Kunbo^c, S. Sreehari Sastry^d

^a Department of Chemical Science, Faculty of Science, Centre for Biodiversity Research, Universiti Tunku Abdul Rahman, Jln Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

^b Department of Material Science & Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, China

^c Faculty of Engineering, Soka University, 1-236 Tangi-cho, Hachioji, Tokyo 192-8577, Japan

^d Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar 522 510, India

Received 15 February 2012

Available online 9 June 2012

Abstract

A homologous series of heterocycles, 6-methyl-2-(4-alkoxybenzylidenamino)benzothiazoles, were synthesized and characterized using FT-IR, ¹H and ¹³C NMR and mass spectrometric analysis. Enantiotropic nematic phase was observed for shorter members. Smectic A phase only emerged from octyloxy derivative onwards. The terminal methyl group at the benzothiazole fragment and the Schiff base linkage influenced the mesomorphic behavior of the present series.

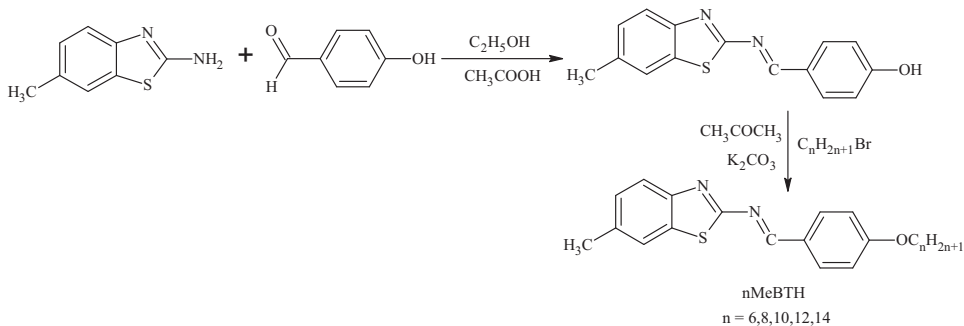
© 2012 Sie Tiong Ha. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Schiff bases; Benzothiazole; Liquid crystal; Smectic A; Nematic

Over the past thirty years, liquid crystals have become the quintessential molecular electronic materials of our present day era. Their applications encompass research activities in the field of surfactant and detergents, membrane for air separation, high strength polymers, heat resistant materials, photonic, thin films, semiconductors *etc.* [1]. Heterocycles are of great importance as core units in thermotropic liquid crystals due to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape [2]. A great deal of mesomorphic compounds containing heterocyclic units have been synthesized, and interest in such structures is constantly growing [2,3]. However, only scant information on the inclusion of benzothiazole core into liquid crystal system is available [4–6]. Funahashi and Hanna have reported the fast hole transport property of the photoconductive calamitic liquid crystal, 2-(4-heptyloxyphenyl)-6-dodecylthiobenzothiazole [7]. A benzothiazole ring containing the electron-rich sulphur atom can contribute to a low ionization potential and also induce a smectic phase. The flat molecular shape with little interannular twisting in fused heterocyclic rings may also facilitate a high degree of overlapping molecular wave function for an efficient hopping mechanism of charge transport [8]. Benzothiazole unit was also found in fluorescent compounds, which is useful in applications as a result of high fluorescence quantum yields in the presence

* Corresponding author.

E-mail addresses: hast_utar@yahoo.com, hast@utar.edu.my (S.T. Ha).



Scheme 1. Synthetic route for the target compounds.

of the rigid core structure [9]. Recently, benzothiazole derivatives have been continuously investigated for application in thin-film, organic field-effect transistors [10].

In order to further explore benzothiazole as a mesogenic core in Schiff base liquid crystals, here, we reported a new homologous series of 6-methyl-2-(4-alkoxybenzylideneamino)benzothiazoles. The synthetic route for the benzothiazole derivatives is illustrated in Scheme 1. 2-Amino-6-methylbenzothiazole and 2, 4-dihydroxybenzaldehyde were coupled by reflux in ethanol for three hours, following which the Schiff base intermediate was subjected to Williamson etherification with the appropriate bromoalkanes in the presence of potassium carbonate anhydrous. The crude products were purified upon repeated recrystallization using ethanol and their structures were elucidated *via* elemental analysis, FT-IR, NMR and EI-MS spectroscopic techniques [11].

The liquid crystalline textures of the products were observed under a polarizing optical microscope equipped with a hotstage and temperature regulator. Phase identification was made by comparing the observed textures with those reported in the literature [12,13]. Transition temperatures and associated enthalpy changes were determined using a differential scanning calorimeter. The results are summarized in Table 1.

Under the polarizing microscope, shortest member of the series, 6MeBTH exhibited nematic phase. The mesophase was identified by the nematic droplets texture. Brownian flashes, a feature of the nematic phase were also observed before recrystallization [14]. By referring to the chemical constitution of the present series, the nematic phase which was observed could have resulted from the terminal methyl group at the sixth position which disrupted the lamellar arrangement of the smectic phase. The similar phenomenon was also reported for a homologous series of azo liquid crystals with a benzothiazole core [5]. Furthermore, the Schiff base (CH=N) linker which conferred a step like structure resulted in the thickening effect which in turn enhanced the nematic phase stability [15].

An interesting phenomenon was observed for 8MeBTH where an additional phase with fan-shaped texture assigned as smectic A (SmA) phase (Fig. 1b) was observed after the formation of the nematic droplets (Fig. 1a) on the cooling run. SmA phase emerged as monotropic phase (metastable) in 8MeBTH. From C10 derivative onwards, SmA phase

Table 1
Phase transition and transition enthalpy for nMeBTH upon heating and cooling cycle.

Compound	Phase transition, °C (corresponding enthalpy changes, kJ mol ⁻¹)	Heating Cooling
6MeBTH	Cr 105.5 (39.83) N 119.5 (1.03) I Cr 83.3 (35.60) N 119.4 (1.47) I	
8MeBTH	Cr 108.2 (49.10) N 118.3 (1.33) I Cr 70.4 (33.94) SmA 96.2 (1.43) N 118.2 (1.84) I	
10MeBTH	Cr 99.0 (49.84) SmA 110.7 (3.41) N 118.4 (1.79) I Cr 61.1 (37.42) SmA 110.8 (3.13) N 118.1 (1.94) I	
12MeBTH	Cr 81.6 (44.98) SmA 116.1 (8.25) I Cr 68.9 (41.13) SmA 116.7 (8.90) I	
14MeBTH	Cr 83.2 (48.79) SmA 113.6 (8.6) I Cr 69.7 (47.86) SmA 115.1 (8.97) I	

Cr = crystal; N = nematic; SmA = smectic A; I = isotropic.

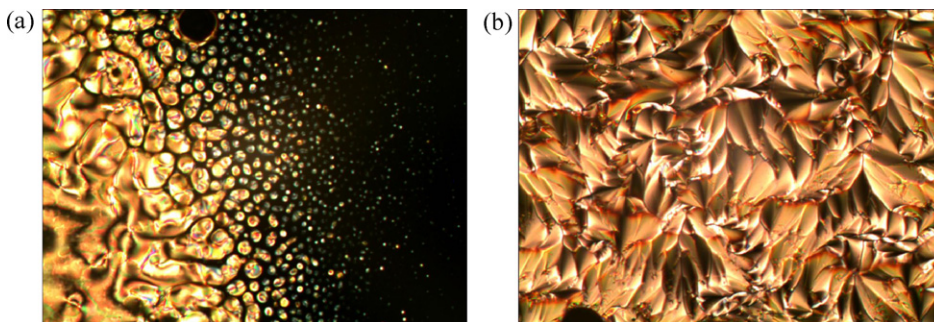


Fig. 1. Optical photomicrographs of 8MeBTH upon cooling. Formation of nematic droplets (a) cooled from isotropic and upon further cooling, Smectic A phase with focal conic texture (b) was observed.

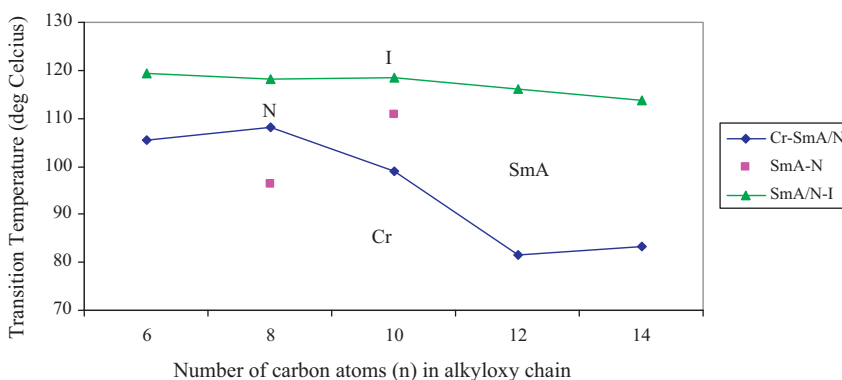


Fig. 2. Plot of transition temperature *versus* the number of carbon (n) in the alkyloxy chain during heating cycle.

exists as enantiotropic phase (stable) and persists to C14 derivative. Higher members of the series (C12 and C14) displayed only smectic phase. This suggested that with increasing the length of the terminal chain, the nematic properties decreased and led to the emergence of the smectic phase. This is due to attraction between the long alkyloxy chains leading to their intertwining, which facilitates the lamellar packing and is vital for the smectic phase [14]. It can therefore be proposed that in order to generate the enantiotropic (stable) smectic phase in the analogous substituted $C_7H_5SNCH=NC_6H_5$ compounds, the number of carbons in the alkyl chain must be at least 10 ($n \geq 10$) [16].

A plot of the transition temperature against the number of carbons in the alkyloxy chain during the heating scan is depicted in Fig. 2. The melting temperature was considerably reduced by the increase in the length of the chain owing to the increase in its flexibility [15]. As for clearing temperature, it descended as the number of carbon atoms increased, resulting from the dilution of the core induced by the increase in the length of the terminal chain [17]. Furthermore, the nematic phase range is reduced and the SmA phase range is increased as the alkyl chain length ascended. The increasing van der Waals forces tend to stabilize the SmA phase by favoring the lamellar packing, on the other hand, suppressed the nematic phase range.

In conclusion, all the synthesized compounds exhibited mesomorphic properties whereby nematic phase exists for the shorter members and SmA phase emerged from the C8 derivatives onwards. The presence of the ordered smectic structure in the title compounds becomes potential interest in electrical studies for device application.

Acknowledgment

The author (S.T. Ha) would like to thank Universiti Tunku Abdul Rahman and Ministry of Higher Education (MOHE) for the financial supports *via* LRGS (No. LR003-2011A) and research facilities.

References

- [1] (a) J.W. Goodby, Chem. Soc. Rev. 36 (2007) 1855;
(b) M.R. Huang, X.G. Li, J. Appl. Polym. Sci. 54 (1994) 463;
(c) X.G. Li, M.R. Huang, Sep. Sci. Technol. 29 (1994) 1905;
(d) X.G. Li, M.R. Huang, G. Lin, P.C. Yang, Sep. Sci. Technol. 29 (1994) 671;
(e) X.G. Li, M.R. Huang, J. Macromol. Sci. Pure Appl. Chem. A36 (1999) 859;
(f) X.G. Li, Polym. Test. 19 (2000) 43.
- [2] A. Seed, Chem. Soc. Rev. 36 (2007) 2046.
- [3] (a) A.S. Matharu, D. Chambers-Asman, Liq. Cryst. 34 (2007) 1317;
(b) H. Gallardo, R.F. Magnago, A.J. Bortoluzzi, Liq. Cryst. 28 (2001) 1343;
(c) L.L. Lai, C.H. Wang, W.P. Hsien, H.C. Lin, Mol. Cryst. Liq. Cryst. 287 (1996) 177;
(d) V.F. Petrov, A.I. Pavluchenko, N.I. Smirnova, Mol. Cryst. Liq. Cryst. 265 (1995) 47;
(e) N.L. Campbell, W.L. Duffy, G.I. Thomas, et al. J. Mater. Chem. 12 (2002) 2706;
(f) S.T. Ha, K.L. Foo, R.T. Subramaniam, et al. Chin. Chem. Lett. 22 (2011) 1191;
(g) G.Y. Yeap, T.N. Chan, W.S. Yam, et al. Chin. Chem. Lett. 22 (2011) 947;
(h) W.S. Yam, G.Y. Yeap, Chin. Chem. Lett. 22 (2011) 229.
- [4] (a) A.I. Pavluchenko, N.I. Smirnova, V.V. Titov, et al. Mol. Cryst. Liq. Cryst. 37 (1976) 35;
(b) J. Belmar, M. Parra, C. Zuniga, et al. Liq. Cryst. 26 (1999) 389;
(c) M. Matsui, Y. Kamino, M. Hayashi, et al. Liq. Cryst. 25 (1998) 235;
(d) M.P. Aldred, P. Vlachos, D. Dong, et al. Liq. Cryst. 32 (2005) 951;
(e) C. Sekine, N. Konya, M. Minai, K. Fujisawa, Liq. Cryst. 28 (2001) 1361.
- [5] (a) A.K. Prajapati, N.L. Bonde, J. Chem. Sci. 118 (2006) 203;
(b) A.K. Prajapati, N.L. Bonde, Mol. Cryst. Liq. Cryst. 501 (2009) 72.
- [6] S.T. Ha, T.M. Koh, G.Y. Yeap, H.C. Lin, et al. Mol. Cryst. Liq. Cryst. 506 (2009) 56.
- [7] (a) M. Funahashi, J. Hanna, Jpn. J. Appl. Phys. 35 (1996) L703;
(b) M. Funahashi, J. Hanna Phys. Rev. Lett. 78 (1997) 2184.
- [8] P. Vlachos, B. Mansoor, M.P. Aldred, et al. Chem. Commun. (2005) 2921.
- [9] B.M. Krasovitski, B.M. Bolotin, Organic Luminescent Materials, VCH, Weinheim, 1988.
- [10] G.K. Dutta, S. Guha, S. Patil, Org. Electron. 11 (2010) 1.
- [11] Analytical and spectroscopic data for the representative compound 12MeBTH: Yield 65%; IR ν_{\max} (KBr, cm^{-1}): 3053 (C–H aromatic), 2919, 2849 (C–H aliphatic), 1597 (C=N Schiff base), 1567 (C=N thiazole), 1286 (C–O aromatic ether); ^1H NMR (400 MHz, CDCl_3): δ 0.90 (t, 3H, $J = 6.9\text{Hz}$, CH_3 –), 1.27–1.49 (m, 18H, CH_3 – $(\text{CH}_2)_9$ –), 1.80 (p, 2H, $J = 6.9\text{Hz}$, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 2.48 (s, 3H, CH_3 –), 4.03 (t, 2H, $J = 6.6\text{Hz}$, $-\text{CH}_2-\text{O}-\text{Ar}-$), 6.99 (d, 2H, $J = 8.7\text{Hz}$, Ar–H), 7.27 (d, 1H, $J = 8.1\text{Hz}$), 7.61 (s, 1H, Ar–H), 7.83 (d, 1H, $J = 8.1\text{Hz}$, Ar–H), 7.96 (d, 2H, $J = 8.7\text{Hz}$, Ar–H), 8.94 (s, 1H $-\text{N}=\text{CH}-$). ^{13}C NMR (100 MHz, CDCl_3): δ 164.93 (CH=N), 163.51, 149.84, 134.97, 134.49, 132.24, 127.84, 127.56, 122.40, 121.42, 114.99 for aromatic carbons, 68.39 (Ar–O– CH_2 –), 31.92 (Ar–O– CH_2 – CH_2 –), 29.65, 29.63, 29.58, 29.55, 29.35, 29.11, 25.98, 22.68, 21.56 for methylene carbons [$\text{CH}_3(\text{CH}_2)_9\text{O}$], 14.10 (CH_3).
- [12] (a) D. Demus, L. Richter, Textures of Liquid Crystals, Verlag Chemie, New York, 1978;
(b) I. Dierking, Textures of Liquid Crystals, Wiley-VCH, Weinheim, 2003.
- [13] Z.Q. Yu, C.Z. Zhu, Z. Zhang, J.H. Liu, J.W.Y. Lam, B.Z. Tang, Chin. Chem. Lett. 22 (2011) 1355.
- [14] S. Singh, D.A. Dunmur, Liquid Crystals: Fundamentals, World Scientific Publishing Co. Pte. Ltd., London, 2002.
- [15] P.J. Collings, M. Hird, Introduction of Liquid Crystals: Chemistry and Physics, Taylor & Francis Ltd., London, 1998.
- [16] G.Y. Yeap, S.T. Ha, P.L. Lim, et al. Liq. Cryst. 33 (2006) 205.
- [17] P. Berdague, J.P. Bayle, M.S. Ho, B.M. Fung, Liq. Cryst. 14 (1993) 667.