New thermotropic liquid crystals with benzoxazole core

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Abstract

New thermotropic liquid crystals containing benzoxazole core and alkanoyloxy chain at the end group of the molecules ($C_{n-1}H_{2n-1}COO$-, n = 14, 16, 18) was synthesized. The present compounds are enantiotropic smectic A liquid crystals. It was also found that the end groups of the molecules and polar chloro substituent at the benzoxazole fragment had effect on the mesomorphic properties.

Keywords: Schiff bases, Benzoxazoles, Mesomorphic, Smectic A, Structure-property relationship

INTRODUCTION

Study of mesomorphic heterocycles has received overwhelming attentions in the recent years due to their wider range of structural templates, as well as their optical and photochemical properties [1-3]. Heterocyclic structures generally incorporated unsaturated atoms, such as, O, N, S and/or others, and the presence of these electronegative atoms often resulted in a reduced symmetry for the overall molecules; and a stronger polar induction [1]. In addition, benzene-fused heterocycles has also become one of the popular mesogenic cores in liquid crystal research. Examples of heterocyclic fused-ring derivatives are benzothiazole [4], benzopyran-4-one [5], benzothiadiazole [6] and benzoxazole [7]. However, examples of benzoxazole-based liquid crystals are relatively rare [7]. Therefore, in the search of new benzoxazole liquid crystals, we describe here mesomorphic properties of 5-chloro-2-(4-alkanoyloxybenzylidenamino)benzoxazoles.

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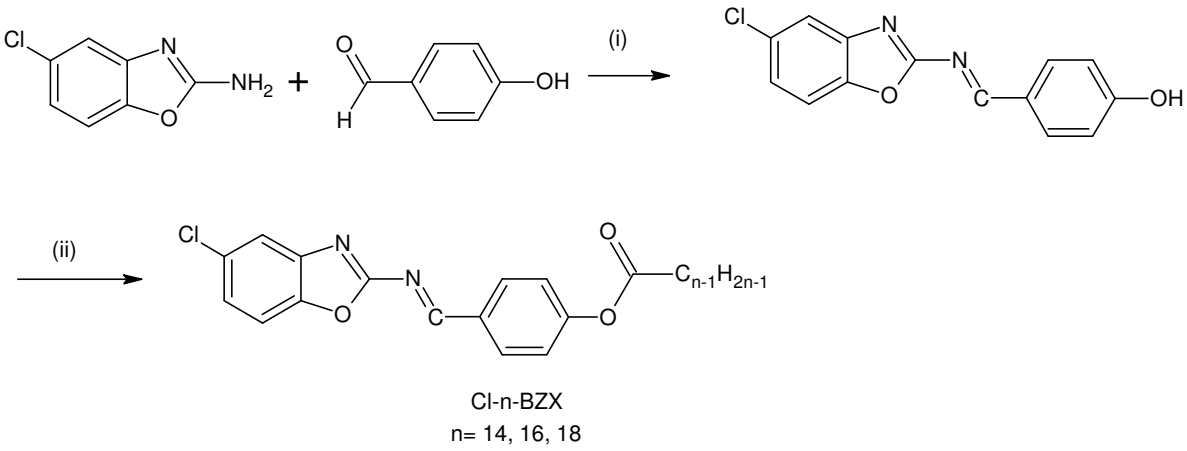
MATERIALS AND METHODS

The synthetic route is illustrated in Scheme 1.



Scheme 1. Synthetic route for the target compounds. (i) CH_2Cl_2 (ii) $C_{n-1}H_{2n-1}COOH$, DCC, DMAP, CH_2Cl_2, DMF.

RESULTS AND DISCUSSION

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

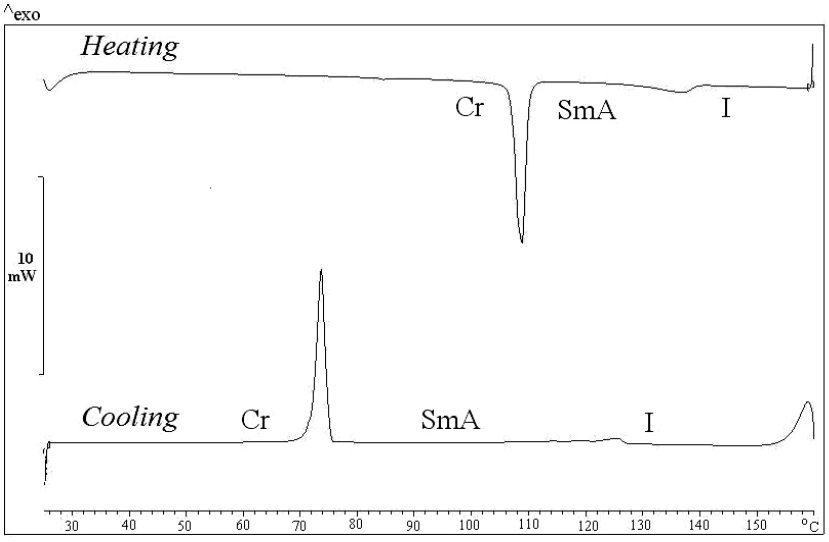


Fig. 1. DSC thermogram of Cl-16-BZX during heating and cooling cycles.

From Table 1, it is clearly noticed that the target compounds showing enantiotropic properties as the mesophase were observed during heating and cooling cycles [8]. Upon

cooling of the isotropic liquid, compound Cl-14-BZX exhibited filament textures which coalesce to form a focal-conic fan texture of smectic A phase on further cooling.

Table 1. Phase transition and transition enthalpy changes for Cl-n-BZX upon heating and cooling

Compound	Phase transition, ^{o}C (corresponding enthalpy changes, kJmol^{-1})	Heating *Cooling*
Cl-14-BZX	Cr 105.9 (47.4) SmA 143.0 (8.9) I	
	Cr 67.7 (51.1) SmA 134.9 (7.0) I	
Cl-16-BZX	Cr 108.5 (47.1) SmA 136.7 (7.7) I	
	Cr 74.0 (46.7) SmA 125.4 (2.8) I	
Cl-18-BZX	Cr 109.1 (44.9) SmA 130.3 (5.7) I	
	Cr 75.2 (43.4) SmA 118.9 (1.7) I	

Cr = crystal; SmA = Smectic A ; I = isotropic. Value in the bracket is enthalpy change.

Conjugative interaction over the entire molecule is better achieved between the polar (chloro) substituent and benzoxazole, and led to smectic property in Cl-*n*-BZX. This suggests that polar terminal substituent has substantial effect on influencing certain phase.

Clearing temperatures exhibited ascending trend as length of alkanoyloxy chain increased from *n*-tetradecanoyloxy to *n*-octadecanoyloxy. It was attributed to the increasing *van der Waals* forces between the alkyl chains [9]. Decrement of phase range was noticed as the chain length keeps increasing. Certain extent of flexibility is essential for promoting liquid crystal phase [10,11]. However, further increasing of the carbon chain of compound (from C14 to C16) will cause the molecule to be too flexible, hence, reducing the stability of mesophase (in term of phase range) [12,13].

CONCLUSIONS

All the target compounds exhibited enantiotropic smectic A phase. The length of the terminal alkanoyloxy chain (end molecule) affects the clearing temperatures and phase ranges. The polar (chloro) substituent at the benzoxazole moiety was among the factors influencing the formation of the smectic phase in the target compounds.

ACKNOWLEDGEMENTS

The authors would like to thank Universiti Tunku Abdul Rahman for the research facilities, and Malaysia Ministry of Higher Education (MOHE) for funding this project via LRGS scheme.

REFERENCES

[1] A. Seed, Chem. Soc. Rev. 36 (2007) 2046.

[2] V.V. Titov, A.I. Pavlyuchenko, Chemistry of Heterocyclic Compounds. 16 (1980) 1.

[3] M.P. Aldred, P. Vlachos, D. Dong, et al. Liq. Cryst. 32 (2005) 951.

[4] E. Meyer, C. Zucco, H. Gallardo, J. Mater. Chem. 8 (1998) 1351; P. Vlachos, B. Mansoor, M.P. Aldred, et al. Chem. Commun. (2005) 2921; M.P. Aldred, P. Vlachos, D. Dong, et al. Liq. Cryst. 32 (2005) 951; C. Zuniga, J. Belmar, M. Zarraga, et al. Bol. Soc. Chil. Quim. 41 (1996) 209; J. Belmar, M. Parra, C. Zuniga, C. Perez, C. Munoz, Liq. Cryst. 26 (1999) 389; M. Funahashi, J.I. Hanna, Phys. Rev. Lett. 78 (1997) 2184; A.K. Prajapati, N.L. Bonde, J. Chem. Sci. 118 (2006) 203; A.K. Prajapati, N.L. Bonde, Mol. Cryst. Liq. Cryst. 501 (2009) 72; S.T. Ha, T.M. Koh, G.Y. Yeap, et al. Mol. Cryst. Liq Cryst. 506 (2009) 56; S.T. Ha, T.M. Koh, H.C. Lin, et al. Liq. Cryst. 36 (2009) 917.

[5] J. Belmar, M. Parra, C. Zuniga, C. Perez, C. Munoz, Liq. Cryst. 26 (1999) 75; J. Alderete, J. Belmar, M. Parra, C. Zuniga, Liq. Cryst. 30 (2003) 1319; G.Y. Yeap, W.S. Yam, D. Takeuchi, et al. Liq. Cryst. 35 (2008) 315; G.Y. Yeap, W.S. Yam, D. Takeuchi, et al. Mol. Cryst. Liq. Cryst. 482 (2008) 87; G.Y. Yeap, W.S. Yam, M.M. Ito, et al. Liq. Cryst. 34 (2007) 649.

[6] A.A. Vieira, R. Cristiano, A.J. Bortoluzzi, H. Garllardo, J. Mol. Struc. 875 (2008) 364.

[7] C. S. Wang, I.W. Wang, K.L. Cheng, C.K. Lai, Tetrahedron. 62 (2006) 9383; C.K. Lai, H.C. Liu, F.J. Li, et al. Liq. Cryst. 32 (2005) 85; C.C. Liao, C.S. Wang, H.S. Sheu, C.K. Lai, Tetrahedron. 64 (2008) 7977; H.C. Wang, Y.J. Wang, H.M. Hu, et al. Tetrahedron. 64 (2008) 4939; S. Kim, S.Y. Park, Mol. Cryst. Liq. Cryst. 337 (1999) 405.

[8] S. Kumar, Liquid Crystals Experimental Study of Physical Properties and Phase Transitions, Cambridge University Press, 2001.

[9] G.W. Gray, Molecular Structure and Properties of Liquid Crystals, Academic Press, London, 1962.

[10] X.G. Li, M.R. Huang, Polym. Plast. Technol. Eng. 39 (2000) 317.

[11] X.G. Li, M.R. Huang, Polym. Test. 19 (2000) 385.

[12] M. Koden, T. Yagyu, S. Takenaka, S. Kusabayashi, J. Phys. Chem. 87 (1983) 4730.

[13] X.G. Li, M.R. Huang, Polym. Test. 19 (2000) 373.