Mesomorphic Properties of Biphenyl Derivatives with Cholesteryl Moiety

Sie-Tiong Ha[1,*], Guan-Yeow Yeap[2] and Peng-Lim Boey[2]

[1]Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Jln Universiti, Bandar Barat, Kampar, 31900 Perak, Malaysia.

[2]Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia.

*Corresponding Author. Email: hast@utar.edu.my or hast_utar@yahoo.com

ABSTRACT

A series of cholesteryl 4'-alkyloxybiphenyl-4-carboxylates ($C_nH_{2n+1}OC_6H_4$ C_6H_4COOCh, where Ch = cholesteryl) possessing different length of alkyl chain (n = 6, 8, 10, 12, 14, 16, 18) were synthesized and their molecular structures were proposed via physical measurement and spectroscopic techniques. Phase transition temperatures and thermal parameters were obtained from differential scanning calorimetry. Observation under polarizing optical microscope revealed all the members of the series exhibiting fan-shaped texture which can be assigned to the SmA phase. Additional mesophase was observed for lower members whereby C6-14 derivatives displayed fan-shaped and oily streaks textures of cholesteric phase. The influence of structural changes (core structure and terminal chain) on the mesomorphic properties is discussed.

Keywords: *cholesteryl ether, biphenyl, cholesteric, smectic A*

INTRODUCTION

Cholesterol is one of the famous natural products and possesses multiple chiral carbon atoms which are prerequisites for chiral recognition (Kyba et al., 1973). Its derivatives exist in several unique aggregates such as liquid crystals, organic gels and monolayers (Elser et al., 1970; Koden et al., 1982; Shinkai & Murata, 1998). In 1888, the Austrian botanist Reinitzer discovered the first liquid crystal known as cholesteryl benzoate. Later, Dave and Vora (1970) made an expansion of cholesteryl benzoate through the preparation of cholesteryl 4-*n*-alkyloxybenzoates ($C_nH_{2n+1}OC_6H_4COOCh$, **nOACh** where Ch represents the cholesteryl moiety). Dave and Vora (1970) also reported the mesomorphic properties of these compounds.

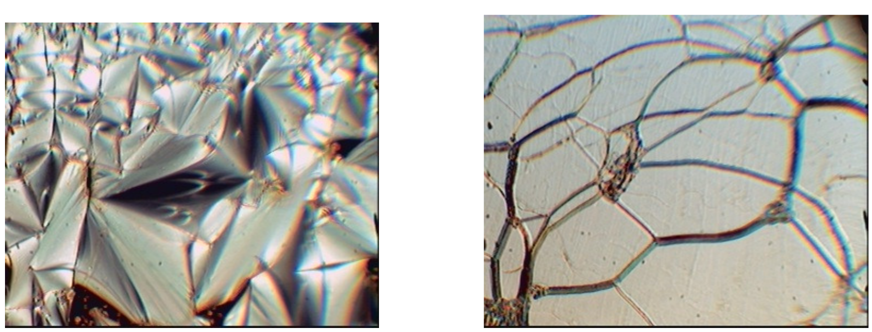
As the continuation of our effort to further investigate the properties of the cholesteryl liquid crystals (Yeap et al., 2004), an aromatic ring was introduced into the existing core system with the aim of enhancing the length-breadth ratio of the molecule. The molecular structure and synthetic method of the present compounds, cholesteryl 4'-alkyloxybiphenyl-4-carboxylates is shown in the synthetic scheme.

RESULTS AND DISCUSSION

Optical and Thermal Studies

Upon heating, optical microscopy studies reveal that compounds **nOBPCh** (where n = 6, 8, 10, 12 and 14) exhibit SmA and N* phases at different transition temperatures. As for compounds **16OBPCh** and **18OBPCh**, only SmA phase is observed. The smectic and chiral nematic characters of these compounds conform to that reported in literature (Demus and Richter, 1978 and Kelker and Hatz, 1980 and Neubert, 2001). Figure 1a shows the representative optical photomicrograph of compound **10OBPCh** exhibiting SmA phase. The SmA phase is identified based on the microscopic observation of characteristic fan-shaped textures using homogenously aligned slides.

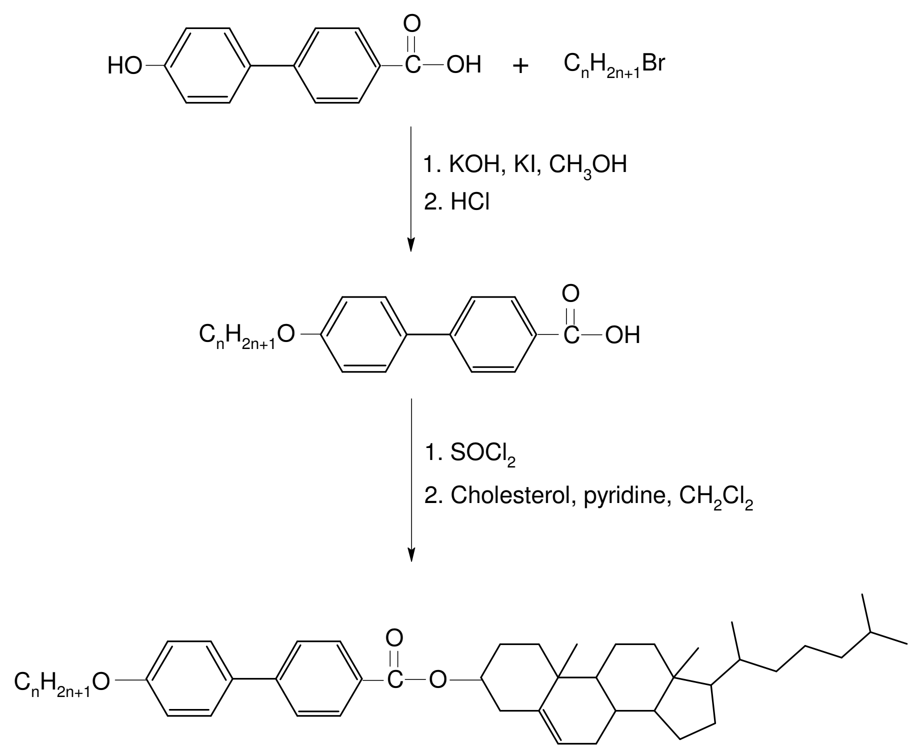
Observation under the crossed polarizers showed that the N* phase exhibited characteristic fan-shaped and oily streak textures in the homogenously and homeotropically aligned slides, respectively. As the representative illustration, Figure 1b show the optical photomicrographs of respective compound **8OBPCh** exhibiting N* phase with oily streak texture.



(a) (b)

Figure 1. (a) Optical photomicrograph of **10OBPCh** exhibiting SmA phase with fan-shaped textures. ((c) Optical photomicrograph of compound **8OBPCh** exhibiting cholesteric (N*) phase with oily streak textures.

SYNTHETIC SCHEME



nOBPCh

where n = 6, 8, 10, 12, 14, 16, 18

Influence of Structural Changes on Mesomorphic Properties

The transition temperatures of the compounds **nOBPCh** are plotted in Figure 2 as a function of the number of carbons in the *n*-alkoxy chain. As can be seen from the graph, the clearing temperatures fall smoothly as the series ascends. This falling curve is attributed to the dilution of the core structure as the length of the terminal alkoxy chain increases (Berdague et al., 1993). The melting temperatures are found to decrease when the length of the alkoxy chain increases from n = 6 to n = 18. The similar characteristic was also observed for the analogous compounds **nOACh** except that the melting temperature of the homologous series **nOBPCh** falls in a zig-zag manner. Another similar feature is the SmA-N* transition temperatures rise to a maximum at the dodecyloxy derivative and then fall steadily as the alkoxy chain length increases to the octadecyloxy derivative.

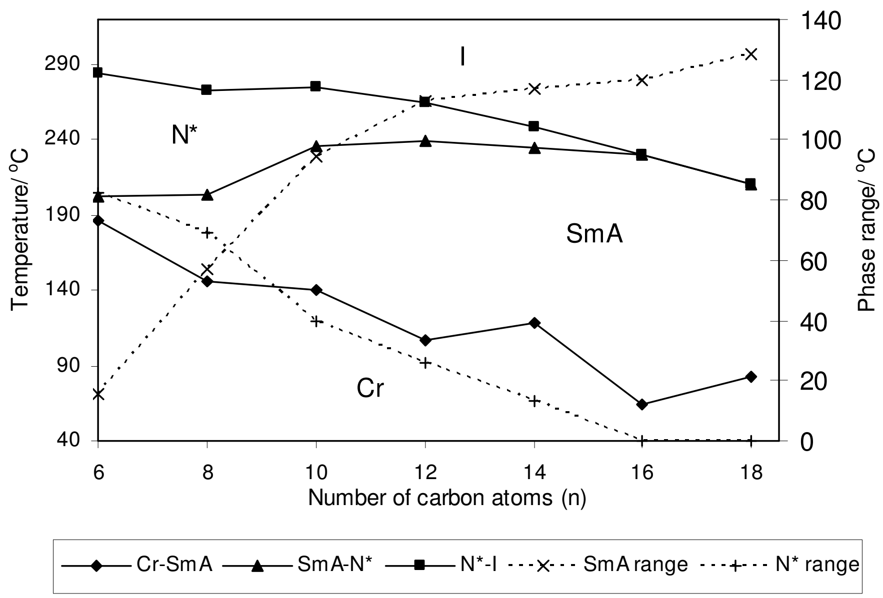


Figure 2. Plot of the transition temperatures and phase (SmA and N*) range upon heating cycle of compounds **nOBPCh** as a function of the number of carbons in the *n*-alkoxy chain.

From the graph, the SmA phase range increases at the cost of the N* phase when the series ascends. This observation is in accordance with the phenomenon reported for the analogous compounds **nOACh**. In the graph, the SmA-N* transition temperature curve is found to coincide with the falling N*-I curve at n = 16 and this gives rise to direct SmA-I transition for the longer chain esters with n = 16 and 18 which is the case in *p*-n-alkoxybenzylidene-*p*-alkoxyanilines (Dave and Patel, 1966). Therefore, the higher members of the series (n = 16 and 18) do not exhibit the N* phase.

CONCLUSIONS

A homologous series of cholesteryl 4'-alkyloxybiphenyl-4-carboxylates were prepared and found to possess mesomorphic properties. Lower members (C6-C14 derivatives) exhibited both smectic A and cholesteric phases. As the alkyloxy chain length increased to C16 and C18, the cholesteric phase was diminished and only smectic A phase was observed.

ACKNOWLEDGEMENT

The authors would like to thank Universiti Tunku Abdul Rahman and Universiti Sains Malaysia for the research facilities and financial supports.

REFERENCES

Berdague, P., Bayle, J. P., Ho, M. S. & Fung, B. M. (1993). New laterally aromatic branched liquid crystal materials with large nematic ranges. Liq. Cryst. 14: 667-674.

Dave, J. S. & Patel, P. R. (1966). Influence of molecular structure on liquid crystalline properties and phase transitions in these structures, Part 1. Mol. Cryst. 2: 103.

Dave, J. S. & Vora, R. A. (1970). Mesomorphic behaviour of the cholesteryl esters-I: *p-n*-alkoxybenzoates of cholesterol In: Liquid crystals and ordered fluids (Johnson, J. F. and Porter, R.S., eds.). Plenum Press, New York, 477.

Demus, D & Richter, L. (1978). Textures of Liquid Crystals, Verlag Chemie, New York.

Elser, W. & Ennulat, R.D. (1970). The mesomorphic behavior of cholesteryl S-alkyl thiocarbonates. J. Phys. Chem. 74: 1545-1551.

Kelker, H. & Hatz, R. (1980). Handbook of liquid crystals. Verlag Chemie, Weinheim.

Koden, M., Takenaka, S. & Kusabayashi, S. (1982). Substituents effects on the mesophase stability for cholesteryl benzoylbenzoates. Bull. Chem. Soc. Jpn. 55: 2460-2463.

Kyba, E.B., Koga, K., Sousa, L.R., Siegel, M.G. & Cram, D.J. (1973). Chiral recognition in molecular complexing. J. Am. Chem. Soc. 95: 2692-2693.

Neubert, M. E. (2001). Liquid Crystals: experimental study of physical properties and phase transitions (Kumar, S., ed). Cambridge University Press, United Kingdom.

Shinkai, S. & Murata, K. (1998). Cholesteryl-based functional tectons as versatile building-blocks for liquid crystals, organic gels and monolayers. J. Mater. Chem. 8: 485-495.

Yeap, G.Y., Ha, S.T., Nakamura, Y., Boey, P.L., Mahmood, W.A.K., Ito, M.M., Nakai, H. & Yamaki, M. (2004). Fourier transform infrared and conformational analysis of cholesteryl 4-n-alkoxybenzoates in solution. Spectrosc. Lett. 37: 319-336.