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Full Length Research Paper

Mesomorphic properties of biphenyl derivatives with cholesteryl moiety

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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.

Key words: 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; Pochan et al., 1973; Koden et al., 1982; Shinkai et al., 1998). Chirality has become one of the most important and complex topics of liquid crystal research today (Collings and Hird, 1998; Goodby, 1999; Collings, 2005). Interest in chiral mesogens increased dramatically since the discovery of the first ferroelectric liquid crystal, 2-methylbutyl 4-(4-n-decyloxybenzylideneamino) cinnamate (DOBAMBC) (Meyer et al., 1975).

Many of the cholesterol derivatives possessed cholesteric mesophases since the existence of cholesteryl fragment in the molecular structure is one of the requirements towards the formation of mesophase (Collings and Hird, 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 ($C_nH_{2n+1}OC_6H_4COOCh$ or nOACh where Ch represents the cholesteryl moiety). Dave and Vora (1970) also reported the mesomorphic properties of these compounds. Later, a Russian research group carried out X-ray diffraction analysis on these compounds (Polishchuk et al., 1985a, 1985b, 1986, 1988, 1990). In addition, Yakubov (1999) also studied the structure of nOACh in solid state by using infrared spectroscopy.

Still on 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 (nOBPCh, where n = 6, 8, 10, 12, 14, 16, 18) is shown in Scheme 1.

MATERIALS AND METHODS

Materials

4-Hydroxybiphenyl-4'-carboxylic acid was obtained from TCI

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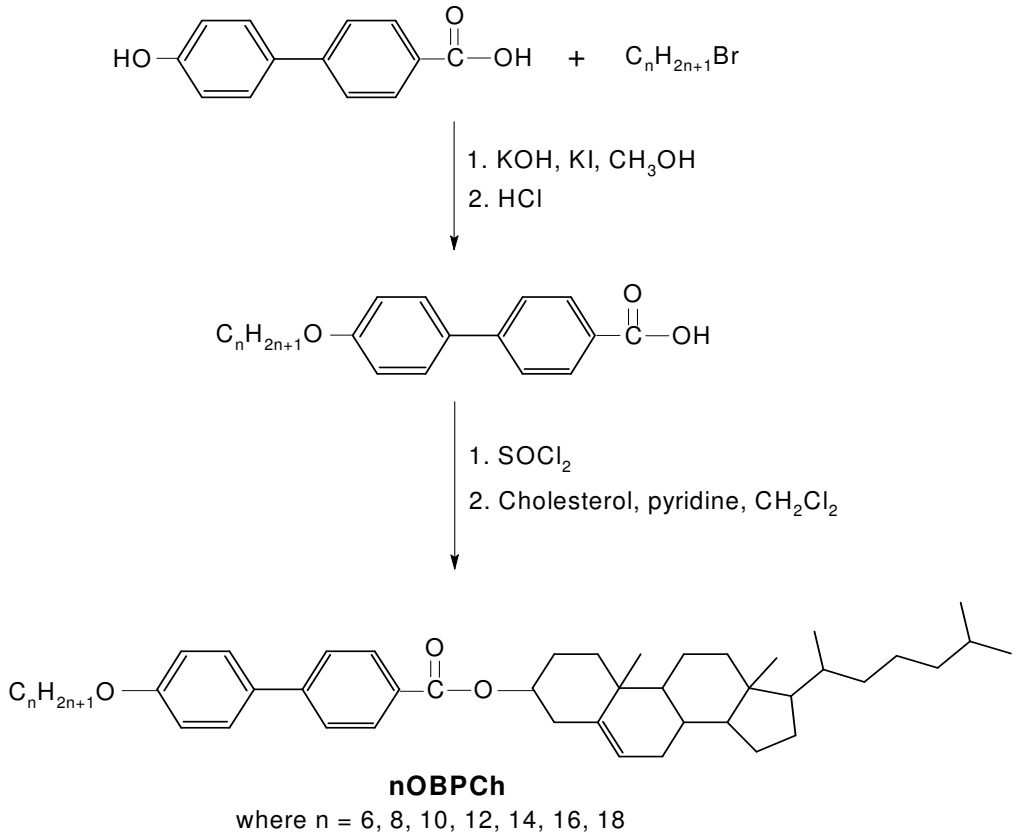

Scheme 1. Synthetic routes towards the formation of intermediate and target compounds nOBPCh.

chemical company (Japan). Whilst cholesterol was purchased from Acros Organics (USA), 1-bromoalkanes were obtained from Aldrich chemical company (USA).

Characterization techniques

Elemental analyses were performed on a Perkin Elmer 2400 LS series CHNS/O analyzer. Infrared spectra were recorded with a Perkin Elmer 2000-FTIR spectrophotometer in the frequency range of 4000-650 cm^{-1} with samples sandwiched between two zinc selenide windows. NMR spectra were recorded in $CDCl_3$ at 298 K on a Bruker of 400 MHz ultrashield spectrometer. The complete ^1H and ^{13}C NMR assignments of the representative compound were obtained and were substantiated by means of ^1H-^1H COSY, ^{13}C-^1H HMQC and ^{13}C-^1H HMBC correlation spectroscopic measurements. Standard Bruker pulse programs were used throughout the entire experiment. Thin layer chromatography analyses were performed using aluminium backed silica gel plates (Merck 60 F254) and were examined under short wave UV light.

The textures of the mesophases were studied with a Carl Zeiss polarizing optical microscope (POM) equipped with a Mettler FP52 hot stage. A video camera (Video Master coomo20P), installed on the polarizing microscope was coupled with a video capture card (Video Master coomo600), allowing real time video capture and image saving. The phase transition temperatures were determined by polarizing microscope and by differential scanning calorimetry (DSC) under a flow of dry nitrogen using a Shimadzu DSC-50 apparatus. The thermal behaviour of the title compounds was studied via the enthalpy values expresses in kJ/mol at a heating and cooling rate of 2°C/min. Phase identification was made by comparison of the observed texture with those reported in the literature (Demus and Richter, 1978; Neubert, 2001).

Synthesis

Synthesis of 4-(4-n-alkyloxyphenyl) benzoic acids, nOBP (where n = 6, 8, 10, 12, 14, 16, 18)

These intermediate compounds were prepared according to a previously described method (Nishiyama and Goodby, 1993; Jin et al., 1997; Nishiyama et al., 2002). Potassium hydroxide (KOH) (0.56 g, 10 mmol) and catalytic amount of potassium iodide (KI) (0.83 g, 5 mmol) were added to 4-(4-hydroxyphenyl) benzoic acid (2.14 g, 10 mmol) dissolved in methanol (80 mL). The mixture was heated under reflux for an hour in the presence of nitrogen atmosphere. Then, 1-bromoalkane ($C_nH_{2n+1}Br$, where n = 6, 8, 10, 12, 14, 16, 18) (10 mmol) in methanol (10 mL) was added to the reaction mixture. The mixture was further heated for 12 h. White precipitate was formed upon cooling the resultant solution. 4-(4-n-Alkoxyphenyl) benzoic acid thus obtained was filtered and washed several times with dilute hydrochloric acid.

Synthesis cholesteryl 4'-alkyloxybiphenyl-4-carboxylates, nOBPCh (where n = 6, 8, 10, 12, 14, 16, 18)

4-(4-n-Alkyloxyphenyl) benzoic acid (2 mmol) was dissolved in thionyl chloride (25 mL) and the mixture was refluxed for 4 h upon

Table 1. The yields, analytical data of the compounds studied and their IR frequencies.

Compound	Yield, %	% Experimental (% calculated)		IR (cm^{-1})					
		C	H	*v* (C-H aliphatic)	*v* (C=O)	*v* (CH_2)[a]	*v* (C_{29}-C_{28}-O)	*v* (C_{36}-O)	*v* (aromatic)[b]
6OABCh	7	82.87 (82.83)	9.92 (9.97)	2932, 2868	1709	1467	1287	1257	828
8OABCh	15	83.00 (82.94)	10.09 (10.15)	2930, 2868	1706	1467	1286	1256	827
10OABCh	18	83.08 (83.05)	10.27 (10.31)	2926, 2852	1706	1467	1286	1256	828
12OABCh	6	83.09 (83.14)	10.55 (10.47)	2923, 2852	1705	1467	1285	1258	827
14OABCh	11	83.19 (83.23)	10.63 (10.61)	2923, 2852	1704	1467	1287	1258	827
16OABCh	12	83.35 (83.32)	10.71 (10.74)	2923, 2852	1703	1469	1287	1257	830
18OABCh	8	83.47 (83.39)	10.81 (10.86)	2918, 2850	1711	1469	1290	1255	828

[a]methylene groups in cholesteryl fragment, [b] 1,4-disubstituted aromatic ring.

stirring. The remaining thionyl chloride in the reaction mixture was removed by vacuum distillation. The acid chloride produced was then dissolved in 50 mL of CH_2Cl_2 and esterified with cholesterol (0.77 g, 2 mmol) in the presence of pyridine (0.60 mL). The mixture was refluxed under nitrogen atmosphere for 17 h. The pyridinium choride (white solid) produced from the reaction was filtered away. The filtrate thus obtained was evaporated until dryness with mild heating. The resultant solid was recrystallized with petroleum ether, 60 to 80°C. The product was further purified by column chromatography over Silica gel 60 and was eluted with chloroform: n-hexane (2:1). The TLC (Silica gel 60 F_{254}, chloroform: n-hexane = 2:1) profile was checked before and after these compounds were separated from the side products and starting materials using column chromatography. The yield, elemental data and IR data of all the title compounds are given in Table 1. While the representative ^1H and ^{13}C NMR spectra of 10OBPCh are depicted in the respective Figures 1 and 2, the NMR data of 10OBPCh is summarized as follows:

Cholesteryl 4'-decyloxybiphenyl-4-carboxylate, 10OBPCh

The ^1H and ^{13}C NMR spectral data were assigned based on the numbering scheme as shown in Figures 1 and 2, respectively. Abbreviation: s = singlet, d = doublet, t = triplet, dd = double of doublets, m = multiplet. ^1H NMR (400 MHz, $CDCl_3$): δ 2.50 (d, 2H, H4), 4.03 (t, 2H, H41), 4.90 (m, 1H, H3), 5.46 (d, 1H, H6), 7.01 (dd, 2H, H35 and H37), 7.58 (d, 2H, H34 and H38), 7.63 (d, 2H, H31 and H39), 8.10 (dd, 2H, H30 and H40). ^{13}C NMR (100 MHz, $CDCl_3$): 37.47 (C1), 29.97 (C2), 74.92 (C3), 38.67 (C4), 140.13 (C5), 123.16 (C6), 32.35 (C7), 32.31 (C8), 50.47 (C9), 37.07 (C10), 21.46 (C11), 40.16 (C12), 42.74 (C13), 57.12 (C14), 24.71 (C15), 28.65 (C16), 56.56 (C17), 12.27 (C18), 19.80 (C19), 36.21 (C20), 19.13 (C21), 36.60 (C22), 24.25 (C23), 39.93 (C24), 28.43 (C25), 22.97 (C26), 23.23 (C27), 166.38 (C28), 129.33 (C29), 132.66 (C32), 145.52 (C33), 159.81 (C36), 130.46 (C30 and C40), 128.71 (C34 and C38), 126.75 (C31 and C39), 115.33 (C35 and C37), 68.56 (C41), 23.08-29.99 (C42-C49), 14.52 (C50).

The ^1H and ^{13}C NMR spectral data of the remaining members (nOBPCh, where n = 6, 8, 12, 14, 16 and 18) are given as follows:

Cholesteryl 4'-hexyloxybiphenyl-4-carboxylate, 6OBPCh

^1H NMR (400 MHz, $CDCl_3$): δ 2.51 (d, 2H, H4), 4.03 (t, 2H, H41), 4.90 (m, 1H, H3), 5.45 (d, 1H, H6), 7.00 (dd, 2H, H35 and H37), 7.58 (d, 2H, H34 and H38), 7.63 (d, 2H, H31 and H39), 8.10 (dd, 2H, H30 and H40). ^{13}C NMR (100 MHz, $CDCl_3$): 37.48 (C1), 29.98 (C2), 74.92 (C3), 38.68 (C4), 140.11 (C5), 123.15 (C6), 32.36 (C7), 32.31 (C8), 50.48 (C9), 37.08 (C10), 21.48 (C11), 40.17 (C12), 42.74 (C13), 57.12 (C14), 24.71 (C15), 28.65 (C16), 56.59 (C17), 12.28 (C18), 19.79 (C19), 36.22 (C20), 19.14 (C21), 36.62 (C22), 24.28 (C23), 39.94 (C24), 28.43 (C25), 22.98 (C26), 23.23 (C27), 166.34 (C28), 129.31 (C29), 132.64 (C32), 145.49 (C33), 159.81 (C36), 130.46 (C30 and C40), 128.69 (C34 and C38), 126.78 (C31 and C39), 115.33 (C35 and C37), 68.56 (C41), 23.02-32.01 (C42-C45), 14.43 (C46).

Cholesteryl 4'-octyloxybiphenyl-4-carboxylate, 8OBPCh

^1H NMR (400 MHz, $CDCl_3$): δ 2.50 (d, 2H, H4), 4.03 (t, 2H, H41), 4.90 (m, 1H, H3), 5.45 (d, 1H, H6), 7.01 (dd, 2H, H35 and H37), 7.59 (d, 2H, H34 and H38), 7.63 (d, 2H, H31 and H39), 8.10 (dd, 2H, H30 and H40). ^{13}C NMR (100 MHz, $CDCl_3$): 37.46 (C1), 29.97 (C2), 74.92 (C3), 38.67 (C4), 140.11 (C5), 123.18 (C6), 32.25 (C7), 32.29 (C8), 50.45 (C9), 37.07 (C10), 21.47 (C11), 40.15 (C12), 42.73 (C13), 57.10 (C14), 24.72 (C15), 28.66 (C16), 56.54 (C17), 12.28 (C18), 19.81 (C19), 36.23 (C20), 19.14 (C21), 36.60 (C22), 24.26 (C23), 39.93 (C24), 28.44 (C25), 22.99 (C26), 23.26 (C27), 166.39 (C28), 129.32 (C29), 132.63 (C32), 145.50 (C33), 159.79 (C36), 130.47 (C30 and C40), 128.71 (C34 and C38), 126.79 (C31 and C39), 115.31 (C35 and C37), 68.54 (C41), 23.09-32.24 (C42-C47), 14.54 (C48).

Cholesteryl 4'-dodecyloxybiphenyl-4-carboxylate, 12OBPCh

^1H NMR (400 MHz, $CDCl_3$): δ 2.51 (d, 2H, H4), 4.03 (t, 2H, H41), 4.90 (m, 1H, H3), 5.46 (d, 1H, H6), 7.00 (dd, 2H, H35 and H37), 7.58 (d, 2H, H34 and H38), 7.63 (d, 2H, H31 and H39), 8.10 (dd, 2H, H30 and H40). ^{13}C NMR (100 MHz, $CDCl_3$): 37.46 (C1), 29.98 (C2), 74.92 (C3), 38.67 (C4), 140.10 (C5), 123.17 (C6), 32.34 (C7), 32.29 (C8), 50.45 (C9), 37.07 (C10), 21.47 (C11), 40.15 (C12), 42.73 (C13), 57.10 (C14), 24.71 (C15), 28.66 (C16), 56.54 (C17), 12.28 (C18), 19.81 (C19), 36.22 (C20), 19.14 (C21), 36.60 (C22), 24.25 (C23), 39.93 (C24), 28.43 (C25), 22.99 (C26), 23.25 (C27), 166.38 (C28), 129.31 (C29), 132.62 (C32), 145.50 (C33), 159.79 (C36), 130.46 (C30 and C40), 128.71 (C34 and C38), 126.79 (C31 and C39), 115.31 (C35 and C37), 68.54 (C41), 23.11-32.28 (C42-C51), 14.55 (C52).

Cholesteryl 4'-tetradecyloxybiphenyl-4-carboxylate, 14OBPCh

^1H NMR (400 MHz, $CDCl_3$): δ 2.51 (d, 2H, H4), 4.02 (t, 2H, H41), 4.90 (m, 1H, H3), 5.45 (d, 1H, H6), 7.00 (dd, 2H, H35 and H37), 7.58 (d, 2H, H34 and H38), 7.63 (d, 2H, H31 and H39), 8.10 (dd,

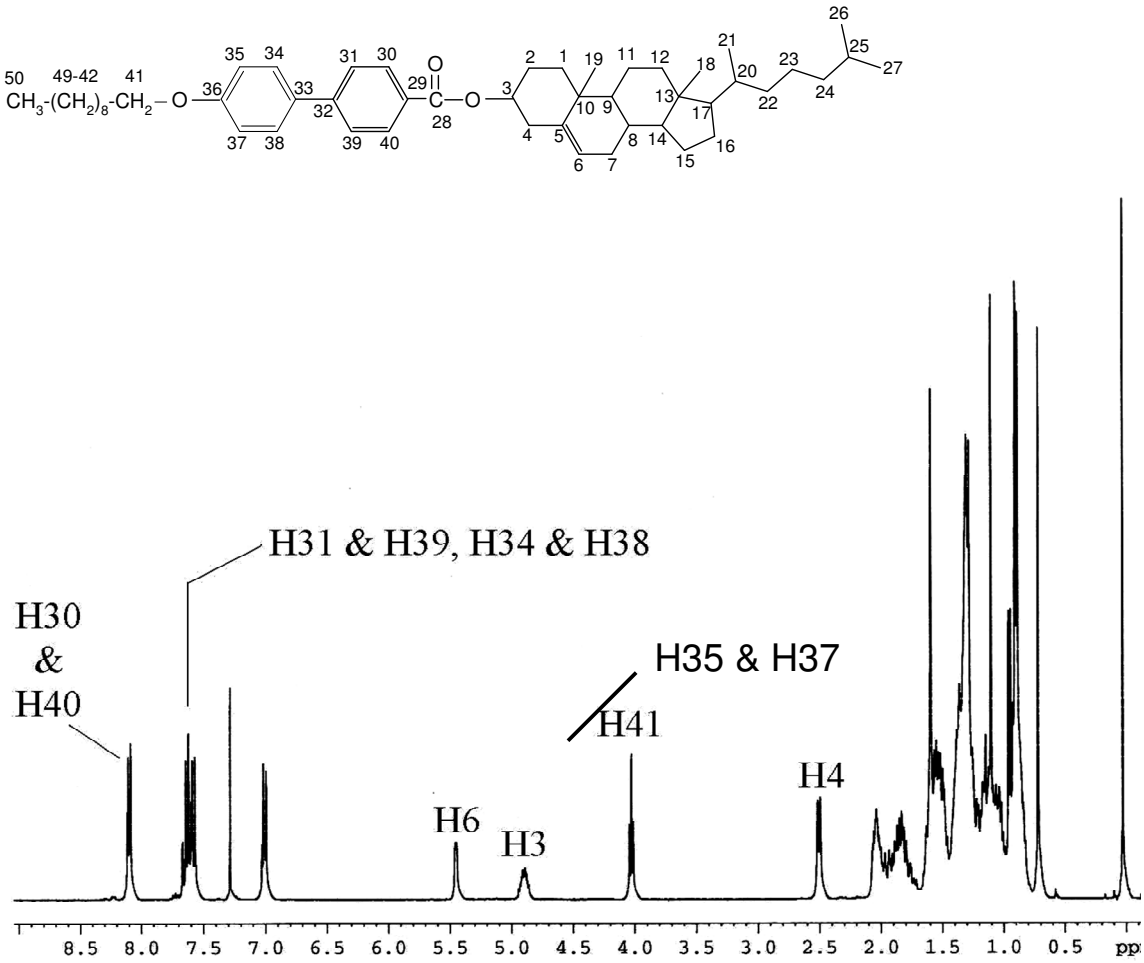

Figure 1. ^{1}H NMR spectrum of cholesteryl 4'-decyloxybiphenyl-4-carboxylate.

2H, H30 and H40). ^{13}C NMR (100 MHz, $CDCl_3$): 37.48 (C1), 29.98 (C2), 74.91 (C3), 38.68 (C4), 140.10 (C5), 123.16 (C6), 32.35 (C7), 32.30 (C8), 50.48 (C9), 37.07 (C10), 21.48 (C11), 40.17 (C12), 42.74 (C13), 57.11 (C14), 24.72 (C15), 28.66 (C16), 56.57 (C17), 12.28 (C18), 19.80 (C19), 36.23 (C20), 19.14 (C21), 36.62 (C22), 24.28 (C23), 39.95 (C24), 28.43 (C25), 22.99 (C26), 23.24 (C27), 166.34 (C28), 129.27 (C29), 132.63 (C32), 145.49 (C33), 159.81 (C36), 130.46 (C30 and C40), 128.69 (C34 and C38), 126.73 (C31 and C39), 115.32 (C35 and C37), 68.54 (C41), 23.11-32.30 (C42-C53), 14.55 (C54).

Cholesteryl 4'-hexadecyloxybiphenyl-4-carboxylate, 16OBPCh

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (d, 2H, H4), 4.03 (t, 2H, H41), 4.88 (m, 1H, H3), 5.46 (d, 1H, H6), 7.01 (dd, 2H, H35 and H37), 7.57 (d, 2H, H34 and H38), 7.65 (d, 2H, H31 and H39), 8.10 (dd, 2H, H30 and H40). ^{13}C NMR (100 MHz, $CDCl_3$): 37.47 (C1), 29.96 (C2), 74.92 (C3), 38.67 (C4), 140.12 (C5), 123.16 (C6), 32.35 (C7), 32.31 (C8), 50.47 (C9), 37.08 (C10), 21.46 (C11), 40.16 (C12), 42.74 (C13), 57.11 (C14), 24.71 (C15), 28.65 (C16), 56.56 (C17), 12.28 (C18), 19.80 (C19), 36.22 (C20), 19.14 (C21), 36.60 (C22), 24.25 (C23), 39.93 (C24), 28.43 (C25), 22.97 (C26), 23.23 (C27), 166.32 (C28), 129.32 (C29), 132.65 (C32), 145.51 (C33), 159.81 (C36), 130.46 (C30 and C40), 128.70 (C34 and C38), 126.75 (C31 and C39), 115.33 (C35 and C37), 68.55 (C41), 23.10-32.34 (C42-C55), 14.53 (C56).

Cholesteryl 4'-octadecyloxybiphenyl-4-carboxylate, 18OBPCh

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (d, 2H, H4), 4.03 (t, 2H, H41), 4.90 (m, 1H, H3), 5.46 (d, 1H, H6), 7.01 (dd, 2H, H35 and H37), 7.58 (d, 2H, H34 and H38), 7.64 (d, 2H, H31 and H39), 8.10 (dd, 2H, H30 and H40). ^{13}C NMR (100 MHz, $CDCl_3$): 37.45 (C1), 29.97 (C2), 74.91 (C3), 38.66 (C4), 140.13 (C5), 123.17 (C6), 32.36 (C7), 32.30 (C8), 50.47 (C9), 37.08 (C10), 21.45 (C11), 40.17 (C12), 42.74 (C13), 57.11 (C14), 24.73 (C15), 28.68 (C16), 56.56 (C17), 12.29 (C18), 19.79 (C19), 36.22 (C20), 19.15 (C21), 36.61 (C22), 24.25 (C23), 39.93 (C24), 28.44 (C25), 22.98 (C26), 23.23 (C27), 166.36 (C28), 129.32 (C29), 132.63 (C32), 145.50 (C33), 159.80 (C36), 130.45 (C30 and C40), 128.71 (C34 and C38), 126.76 (C31 and C39), 115.35 (C35 and C37), 68.54 (C41), 23.12-32.41 (C42-C57), 14.50 (C58).

RESULTS AND DISCUSSION

The structural analogy of the title compounds is evident from the elemental analysis, IR, ^{1}H and ^{13}C NMR. The elemental analyses of all the compounds were found to

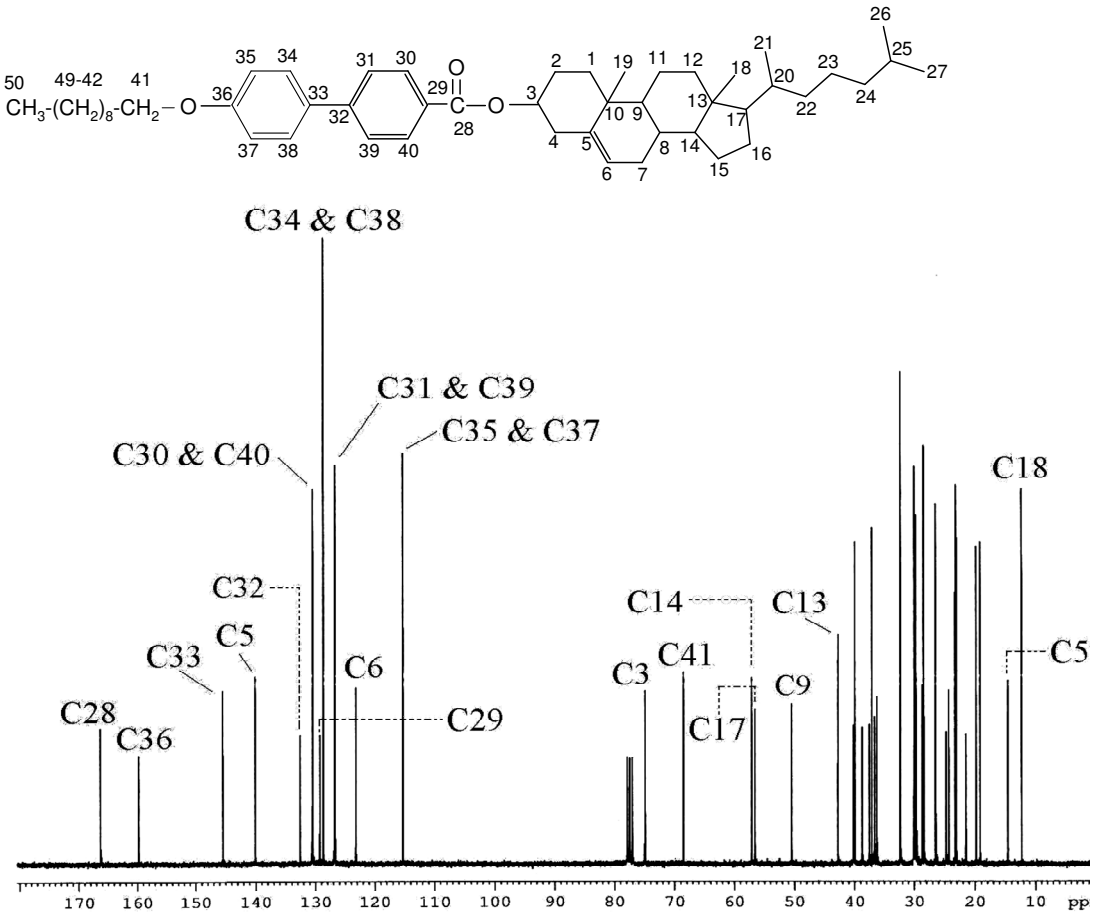

Figure 2. ^{13}C NMR spectrum of cholesteryl 4'-decyloxybiphenyl-4-carboxylat

be satisfactory and have been depicted in Table 1. The IR spectrum of 10OBPCh showed that the characteristics bands at 1469 cm^{-1} are assignable to the methylene groups of the cholesterol fragment (Parker, 1971). A strong band at 1287 cm^{-1} can be attributed to the stretching of the C_{29}-C_{28}-O bond (Smith, 1999). The 1,4-disubstituted aromatic rings attached to the cholesteryl fragment can also be assigned from the diagnostic band observed at 830 cm^{-1}.

The ^{1}H and ^{13}C NMR assignments of the representative compound 10OBPCh as listed in the materials and methods section were obtained with the aid of ^{1}H-^{1}H COSY, ^{13}C-^{1}H HMQC and ^{13}C-^{1}H HMBC correlations. The representative ^{1}H and ^{13}C NMR spectra of 10OBPCh are shown in Figures 1 and 2, respectively. The other homologues show similar IR and NMR characteristics as that discussed for compound 10OBPCh.

Optical and thermal studies

All the synthesized compounds exhibited characteristics of the crystal-mesophase and mesophase-isotropic transitions at a temperature higher than the melting temperature. These compounds have been characterized by DSC and POM methods. The phase transition temperatures and associated enthalpy changes (ΔH) are tabulated in Table 2. Figure 3 shows the representative DSC trace upon the heating scan of compound 10OBPCh. The representative optical photomicrographs are depicted in Figure 4(a)-(c).

Upon heating, optical microscopy studies reveal that compounds nOBPCh (where n = 6, 8, 10, 12 and 14) exhibited SmA and N* phases at different transition temperatures (Table 2). As for compounds 16OBPCh and 18OBPCh, only SmA phase was observed. The smectic and chiral nematic characters of these compounds conform to that reported in literature (Demus and Richter, 1978; Kelker and Hatz, 1980; Neubert, 2001). Figure 4a shows the representative optical photomicrograph of compound 10OBPCh exhibiting SmA phase. The SmA phase was identified based on the microscopic observation of characteristic fan-shaped textures using homogenously aligned slides. Observation under the crossed polarizers show that the N* phase exhibited characteristic fan-shaped (Figure 4b), and oily streak

Table 2. Phase transition temperatures and enthalpy changes of the compounds studied.

Compound	Phase Transitions/ °C corresponding enthalpy change/ kJ mol^{-1})
6OBPCh	Cr_1 88.0(8.5) Cr_2 186.5 (16.5) SmA 202.1(0.7) N* 284.3(0.5) I
8OBPCh	Cr 146.3(22.3) SmA 203.5(0.4) N* 272.4(0.4) I
10OBPCh	Cr_1 79.7(4.3) Cr_2 140.8(16.8) SmA 235.5(0.6) N* 275.1(0.5) I
12OBPCh	Cr 107.3(21.5) SmA 239.1(1.3) N* 264.9(0.5) I
14OBPCh	Cr_1 76.4(3.5) Cr_2 102.5(12.1) Cr_3 118.3(7.3) SmA 235.2(0.7) N* 248.5 (0.4) I
16OBPCh	Cr_1 64.6(4.9) Cr_2 110.4(11.6) SmA 230.4(2.3) I
18OBPCh	Cr 82.1(21.8) SmA 210.5(2.5) I

Cr_1, Cr_2, Cr_3, crystal; SmA, smectic A; N*, chiral nematic (or cholesteric); I, isotropic.

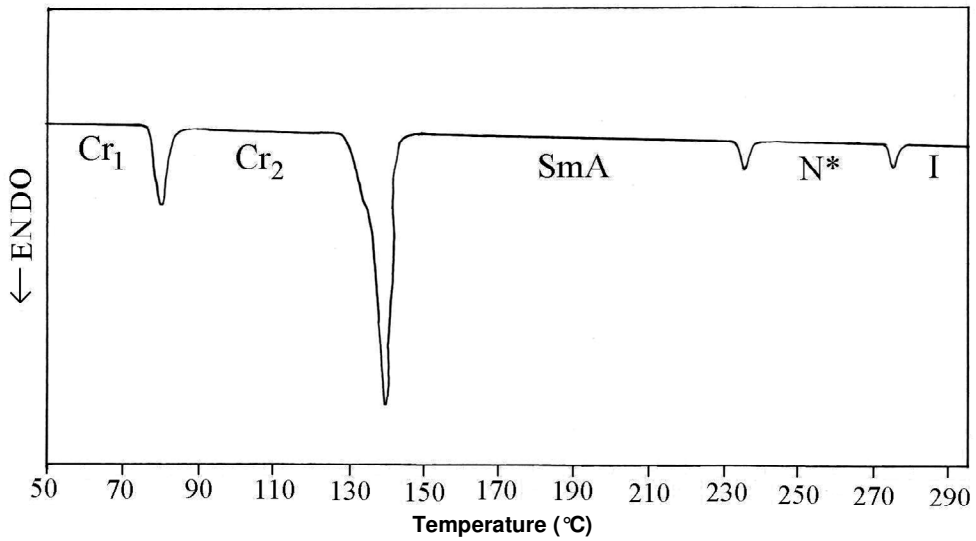

Figure 3. DSC trace of cholesteryl 4'-decyloxybiphenyl-4-carboxylate during heating scan.

(Figure 4c) textures in the homogenously and homeotropically aligned slides, respectively. From the illustration, Figure 4(b)-(c) shows the optical photomicrographs of respective compounds 6OBPCh and 8OBPCh exhibiting N* phase.

Except for compounds 8OBPCh, 12OBPCh and 18OBPCh, the rest of the homologues show an endotherm in the DSC data before the crystal-to-smectic A transition. The texture observed under POM is indicative of the presence of sub phases as those phenomena observed for the analogous compounds, cholesteryl 4-n-alkoxybenzoates (nOACh) (Ha, 2006).

Influence of structural changes on mesomorphic properties

The mesomorphic properties of compounds nOBPCh were compared to the analogous compounds nOACh (Ha, 2006), in which n = 6, 8, 10, 12, 14, 16 and 18. Compounds nOBPCh were different from those analogous compounds nOACh owing to the presence of an additional aromatic ring joined to the cholesteryl core system. Thus, it has been presumed to increase the molecular length with little or no change in the width. This factor allows an increase in the anisotropy of the molecule. As such, the polarizability of the molecules in the nOBPCh series is expected to rise (Gray, 1962). As a consequence, the clearing temperature (T_c) of nOBPCh (where n = 6, 8, 10, 12, 14, 16 and 18) was comparatively higher than those reported for the analogous compounds nOACh (where n = 6, 8, 10, 12, 14, 16 and 18), respectively, and is represented in Figure 5.

The transition temperatures of the compounds nOBPCh are plotted in Figure 6 as a function of the number of carbons in the n-alkoxy chain. The influence of the terminal alkyl chain length on the clearing temperature (or N*-I transition temperature) for this series of compounds in general followed that, characteristically seen for calamitic systems. As can be seen from the graph, the clearing temperatures fall smoothly as the series ascends. The clearing temperature (T_c) decreased following the order: 6OBPCh: T_c = 284.3°C < 8OBPCh: T_c = 272.4°C ≈ 10OBPCh: T_c = 275.1°C < 12OBPCh: T_c =

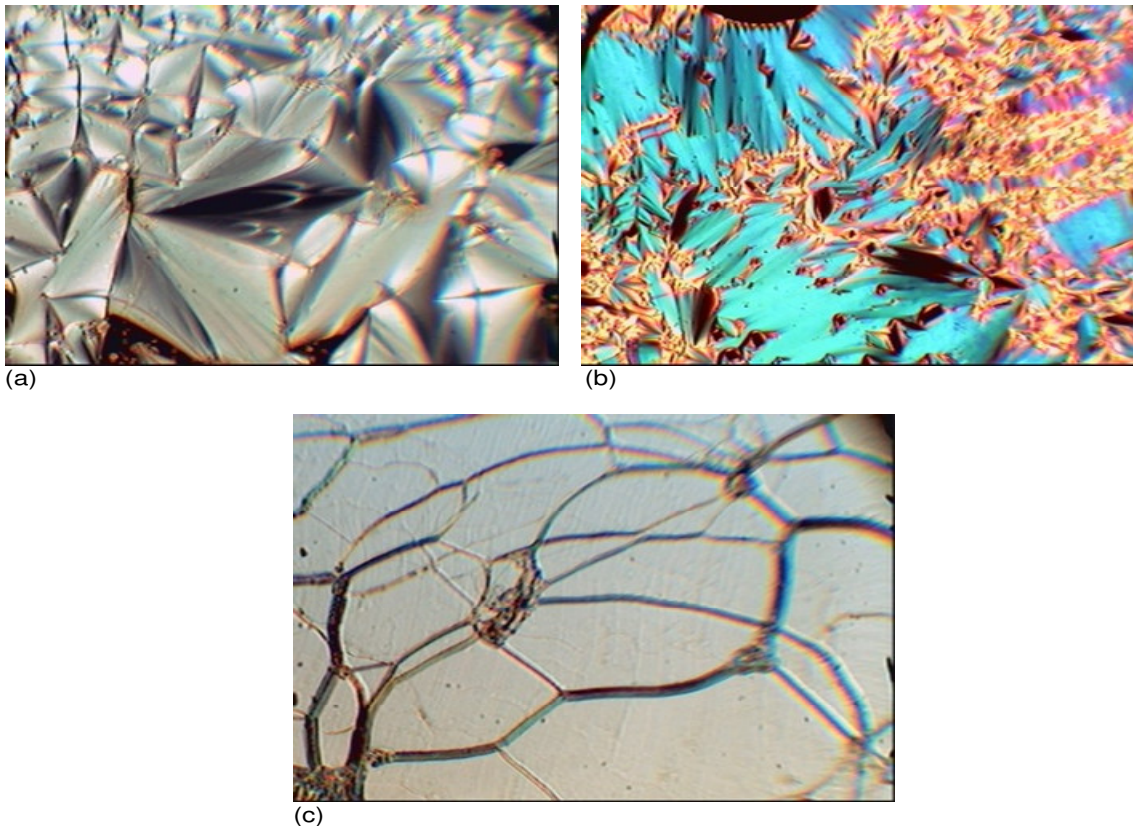

Figure 4. (a) Optical photomicrograph of 10OBPCh exhibiting SmA phase with fan-shaped textures. (b) Optical photomicrograph of 6OBPCh exhibiting cholesteric (N*) phase with fan-shaped textures. (c) Optical photomicrograph of compound 8OBPCh exhibiting cholesteric (N*) phase with oily streak textures.

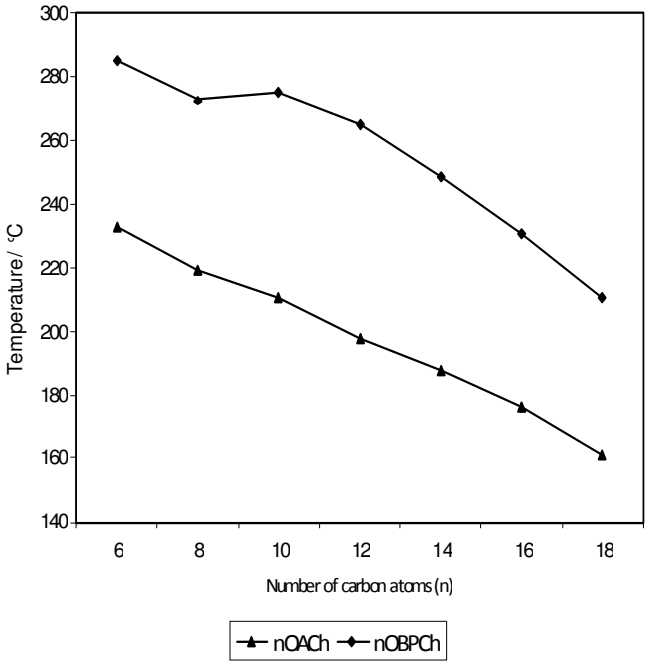

Figure 5. Plot of the clearing temperatures (T_c) of compounds nOACh and nOBPCh as a function of the number of carbons in the *n*-alkoxy chain.

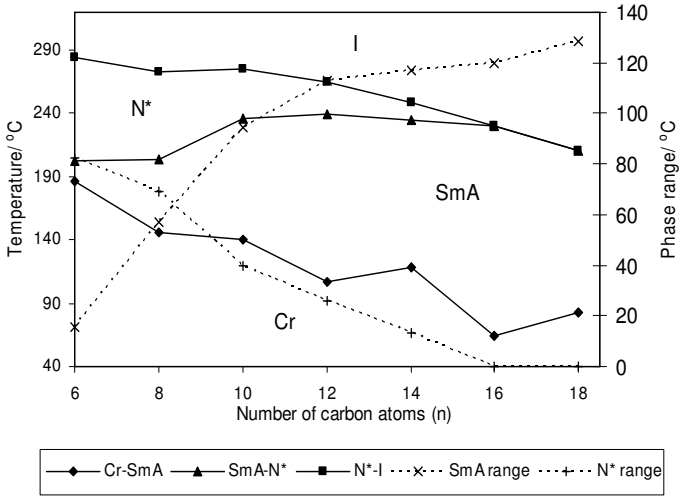

Figure 6. Plot of the transition temperatures and phase (SmA and N*) range upon heating cycle of compounds nOBPCh as a function of the number of carbons in the *n*-alkoxy chain.

264.9°C < 14OBPCh: T_c = 248.5°C < 16OBPCh: T_c = 230.4°C < 18OBPCh: T_c = 210.5°C. This falling curve was attributed to the dilution of the core structure as the

length of the terminal alkoxy chain increased (Berdague et al., 1993). The melting temperatures were found to decrease when the length of the alkoxy chain increased 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 fell in a zigzag 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.

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.

Conclusion

A 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.

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