

Full Length Research Paper

Synthesis and smectogenic A and C* properties of (S)-(-)-2-Methylbutyl 4'-(4''-n-alkanoyloxybenzoyloxy) biphenyl-4-carboxylates

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A series of chiral ester (S)-(-)-2-methylbutyl 4'-(4''-n-alkanoyloxybenzoyloxy)biphenyl-4-carboxylates possessing different length of alkyl chain have been isolated and their molecular structures were proposed via physical measurement and spectroscopy 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 and helical line textures which can be assigned to the SmA and tilted SmC* phases, respectively. The influence of structural changes (core structure and terminal chain) on the mesomorphic properties is discussed.

Key words: Chiral liquid crystals, smectic A, smectic C*, structure-property relationship.

INTRODUCTION

Chirality has become one of the most important and complex topics of liquid crystal research today (Collings and Hird, 1998; Goodby, 1999; Collings, 2005). The early discovery of chiral nematic phase can be dated back to end of the 1960s (Sackmann et al., 1967). Interest in chiral mesogens increased dramatically since the discovery of the first ferroelectric liquid crystal (FLC) 2-methylbutyl 4-(4-n-decyloxybenzylideneamino) cinnamate (DOBAMBC) (Meyer et al., 1975). Ferroelectricity has generally been ascribed to the presence of a tilted smectic phase comprising chiral molecules which reduce the overall symmetry of the liquid crystal (Meyer, 1977). FLCs exhibit polarization bistability and fast electro-optic response in the range of microseconds, therefore, these materials have been of great interest in the use of optical switches, light valves, display and storage devices and other electro-optic device applications. In view of the great applications of the chiral liquid crystals, thus, there has been continuous interest in developing new materials

or in modifying existing FLCs.

The chiral centre in FLCs can be generated from the readily available precursors such as alkan-2-ols (Eagle et al., 1998; Xu et al., 2002), D-(+)-glucose (Ho et al., 1995) and α -halohydrins derived from amino acids (Schacht et al., 1998). The well-known precursor, 2-methylbutanol has been used since the synthesis of the first FLC, DOBAMBC. An example of chiral liquid crystals comprising the 2-methylbutyl fragment are (S)-(-)-2-methylbutyl 4'-(4''-alkanoyloxyphenyl) benzoates (Goodby et al., 1987). Further study on this type of material has been carried out wherein the chemical and physical properties of the analogue compounds (S)-(-)-2-methylbutyl 4-[4-(d_n)-alkyloxyphenyl] benzoates which contained deuterated alkoxy chains (C_nD_{2n+1}O) as the achiral substituents were studied (Yeap et al., 2000a, 2000b).

In this continuation work, 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, (S)-(-)-2-methylbutyl 4'-(4''-n-alkanoyloxybenzoyloxy)-biphenyl-4-carboxylates (S-MB-nB - BC, where n = 12, 14, 16 and 18) is shown in

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

Compound	Yield (%)	Empirical Formula	% C		% H		IR (cm ⁻¹)		
			Calculated	Found	Calculated	Found	ν (C-H aliphatic)	ν (C=O)	ν (C=C aromatic)
S-MB-12B-BC	18	C ₃₇ H ₄₆ O ₆	75.74	75.61	7.90	7.96	2958, 2918, 2849	1752, 1732, 1713	1605
S-MB-14B-BC	22	C ₃₉ H ₅₀ O ₆	76.19	76.24	8.20	8.13	2958, 2918, 2849	1751, 1733, 1713	1604
S-MB-16B-BC	15	C ₄₁ H ₅₄ O ₆	76.60	76.75	8.47	8.38	2958, 2918, 2849	1750, 1733, 1714	1604
S-MB-18B-BC	17	C ₄₃ H ₅₈ O ₆	76.98	77.11	8.71	8.64	2957, 2917, 2849	1749, 1733, 1713	1603

Scheme 1.

MATERIALS AND METHODS

Materials

Lauroyl chloride, myristoyl chloride, palmitoyl chloride, 4-hydroxybenzoic acid and 4-dimethylaminopyridine (DMAP) were obtained from Merck (Germany). 4-Hydroxybiphenyl-4'-carboxylic acid was purchased from TCI Chemical Company (Japan). While dicyclohexylcarbodiimide (DCC) was obtained from Acros Organics (USA), stearoyl chloride, triethylamine and (*S*)-(-)-2-methylbutanol were purchased from Fluka Chemie (Switzerland). Sulphuric acid was obtained from System (Malaysia).

Characterization techniques

Elemental analyses were performed on a Perkin Elmer 2400 LS series CHNS/O analyzer. Infrared spectra were taken with a Perkin Elmer 2000-FTIR spectrophotometer in the frequency range 4000 - 650 cm⁻¹ with samples sandwiched between two zinc selenide windows. NMR spectra were recorded in CDCl₃ at 298 K on a Bruker 400 MHz Ultrashield Spectrometer. Standard Bruker pulse programs were used throughout the entire experiment. The complete ¹H and ¹³C NMR assignments of the representative compound were obtained and were substantiated by means of ¹H-¹H COSY, ¹³C-¹H HMQC and ¹³C-¹H HMBC correlation spectroscopic measurements. 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 Seiko DSC6200R 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-n-alkanoyloxybenzoic acid, nBA (where n = 12, 14, 16 and 18)

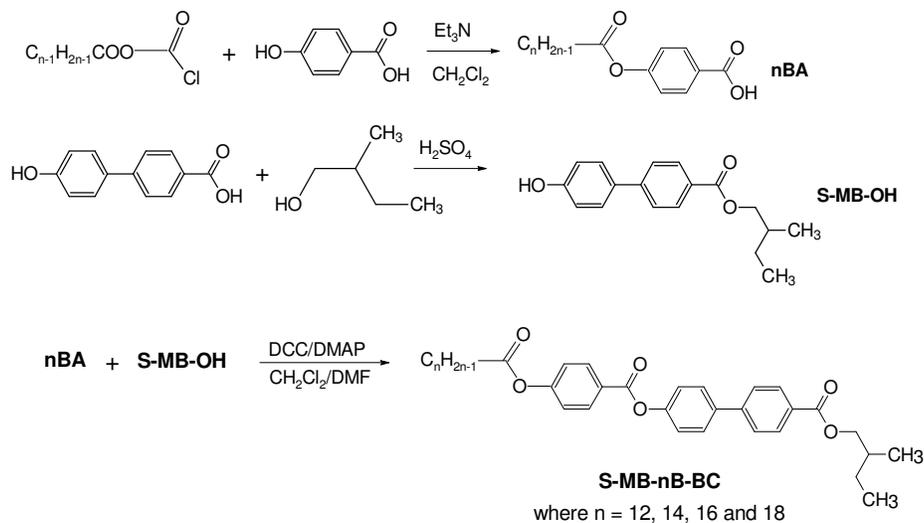
The 4-n-alkanoyloxybenzoic acids were prepared according to a previously described method (Yeap et al., 2006a). 4-Hydroxybenzoic acid (10 mmole) and 5 ml triethylamine (Et₃N) were added into 50 ml dichloromethane (DCM) and the solution was heated until all substances were completely dissolved. To this solution, 13 mmole of alkanoyl chloride (C_{n-1}H_{2n-1}COCl, where n = 12, 14, 16 and 18) were added and refluxed upon stirring for five hours. The reaction was performed under a constant flow of nitrogen gas. Finally, the reaction mixture was filtered and DCM was removed from the filtrate by evaporation. The white solid thus obtained was recrystallized twice with chloroform.

Synthesis of (S)-(-)-2-methylbutyl 4'-(4''-hydroxyphenyl) benzoate, S-MB-OH [Yeap et al., 2000]

4-Hydroxybiphenyl-4'-carboxylic acid (10 mmole) was added to 15 ml of (*S*)-(-)-2-methylbutanol which also served as the reaction medium. The mixture was then refluxed for 24 h in the presence of 1 ml sulphuric acid at 120°C. The mixture was cooled to room temperature before washing with 5% sodium hydrogen carbonate (5 x 20 ml) followed by distilled water (2 x 10 ml). The organic layer thus obtained was dried overnight with anhydrous sodium sulfate (Na₂SO₄). The final solution was further concentrated to yield white precipitate which was recrystallized from chloroform.

Synthesis of (S)-2-methylbutyl 4'-(4''-n-alkanoyloxybenzoxyloxy) biphenyl-4-carboxylates, S-MB-nB-BC (where n = 12, 14, 16 and 18)

4-n-Alkanoyloxybenzoic acid (nBA, where n = 12, 14, 16 or 18) (1.2 mmole), S-MB-OH (1 mmole) and DMAP (0.1 mmole) were dissolved in a mixture of DCM (50 ml) and dimethylformamide (DMF) (2 ml) and stirred at 0°C. To this solution, 1 mmole of DCC dissolved in 10 ml DCM was added dropwise and stirred at 0°C for an hour and then stirred at room temperature for 24 h. Finally, the reaction mixture was filtered and the DCM was removed from the filtrate by evaporation. The white solid thus obtained was recrystallized twice with chloroform. Then, the purification of the product was followed by column chromatography over Silica gel 60 (230 - 400 mesh) using chloroform as the eluent. The yield, elemental data and IR data of all the title compounds are given in Table 1. While the representative ¹H and ¹³C NMR spectra of S-MB-12B-BC are depicted in



Scheme 1. Synthetic routes towards the formation of intermediates and target compounds S-MB-nB-BC.

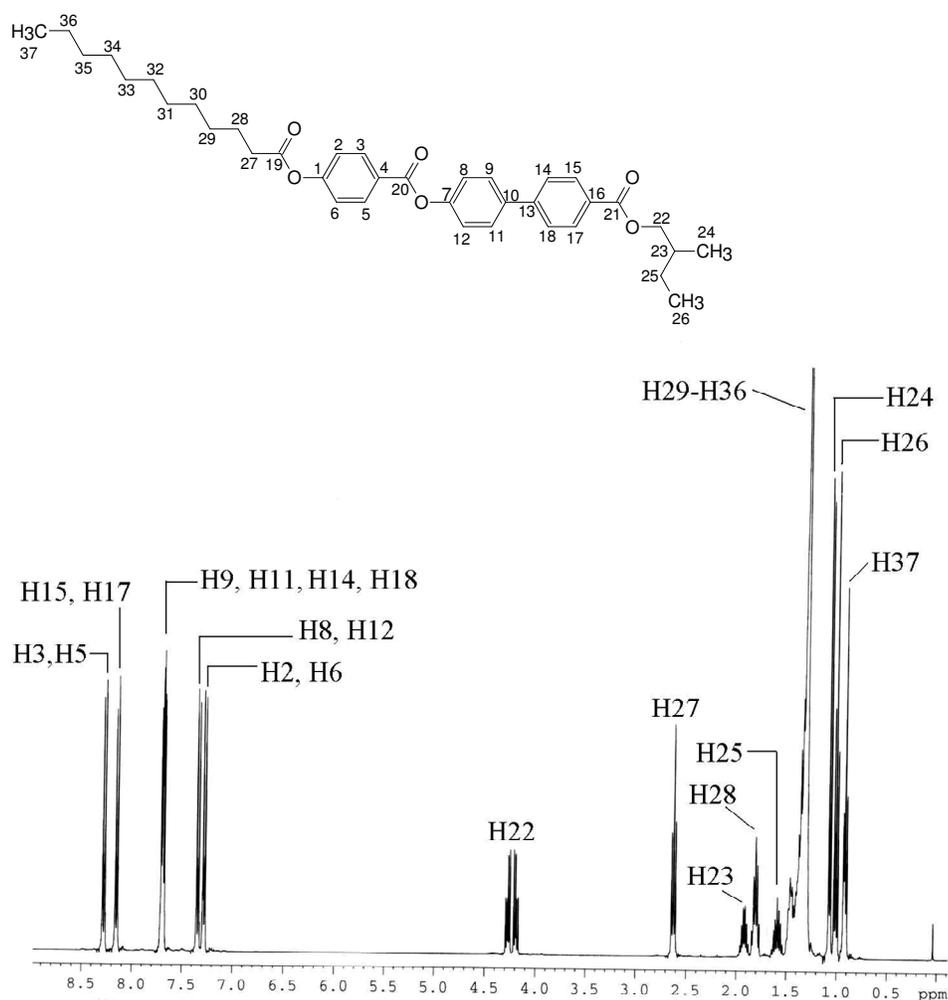


Figure 1. ^1H NMR spectrum and structural assignment of S-MB-12B-BC.

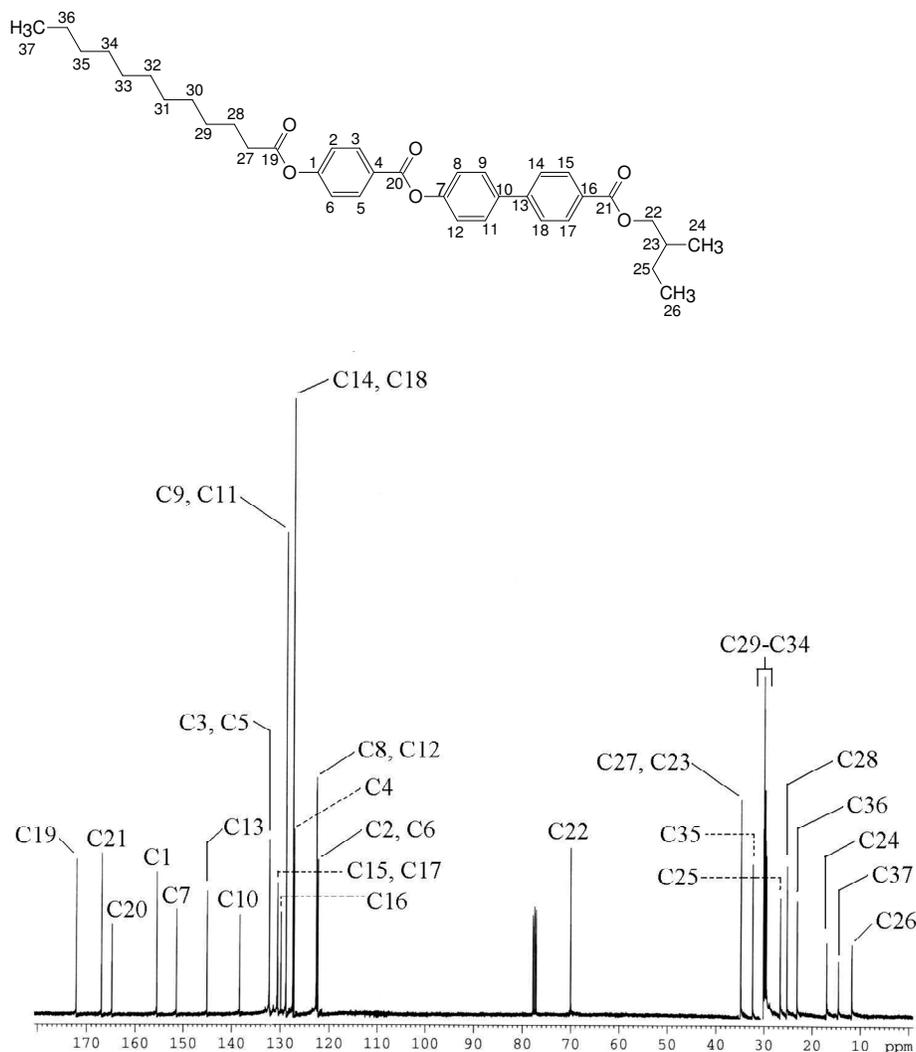


Figure 2. ^{13}C NMR spectrum and structural assignment of S-MB-12B-BC.

The respective Figure 1 and 2, the NMR data of S-MB-12B-BC is summarized as follows:

(C20), 166.88 (C21) and 172.04 (C19).

S-MB-12B-BC

The ^1H and ^{13}C NMR spectral data were assigned based on the numbering scheme as shown in Figure 1 and 2, respectively. Abbreviation: s = singlet, d = doublet, t = triplet, dd = double of doublets, qt = quintet, st = sextet, m = multiplet. ^1H NMR (400 MHz, CDCl_3): δ 0.90-0.93 (t, 3H, H37), 0.99-1.03 (t, 3H, H26), 1.06-1.08 (d, 3H, H24), 1.31-1.48 (m, 16H, H29-H36), 1.54-1.64 (m, 2H, H25), 1.77-1.84 (qt, 2H, H28), 1.88-1.96 (st, 1H, H23), 2.60-2.64 (t, 2H, H27), 4.17-4.29 (m, 2H, H22), 7.27-7.29 (dd, 2H, H2 & H6), 7.33-7.35 (dd, 2H, H8 & H12), 7.68-7.71 (m, 4H, H9, H11, H14 & H18), 8.14-8.16 (dd, 2H, H15 & H17), 8.27-8.29 (dd, 2H, H3 & H5). ^{13}C NMR (100 MHz, CDCl_3): 11.71 (C26), 14.52 (C37), 16.96 (C24), 23.10 (C36), 25.25 (C28), 26.61 (C25), 29.50-30.10 (C29-C34), 32.34 (C35), 34.75 (C23), 34.82 (C27), 69.99 (C22), 122.33 (C2 & C6), 122.60 (C8 & C12), 127.18 (C4), 127.42 (C14 & C18), 128.81 (C9 & C11), 129.85 (C16), 130.53 (C15 & C17), 132.33 (C3 & C5), 138.30 (C10), 145.04 (C13), 151.37 (C7), 155.52 (C1), 164.75

RESULTS AND DISCUSSION

The structural analogy of the title compounds is evident from the elemental analysis, IR, ^1H and ^{13}C NMR. The elemental analyses of all the compounds were found to be satisfactory and have been depicted in Table 1. The IR spectrum of S-MB-12B-BC showed the characteristic bands at 2958, 2918 and 2849 cm^{-1} for the aliphatic CH bond, 1752, 1732 and 1713 cm^{-1} for the ester C=O bond and 1605 cm^{-1} for the aromatic C=C bond (Table 1). The ^1H and ^{13}C NMR assignments of the representative compound S-MB-12B-BC as listed in the experimental section were obtained with the aid of ^1H - ^1H COSY, ^{13}C - ^1H HMQC and ^{13}C - ^1H HMBC correlations. The representative ^1H and ^{13}C NMR spectra of S-MB-12B-BC are shown in Figures 1 and 2, respectively. S-MB-14B-BC, S-MB-16B-

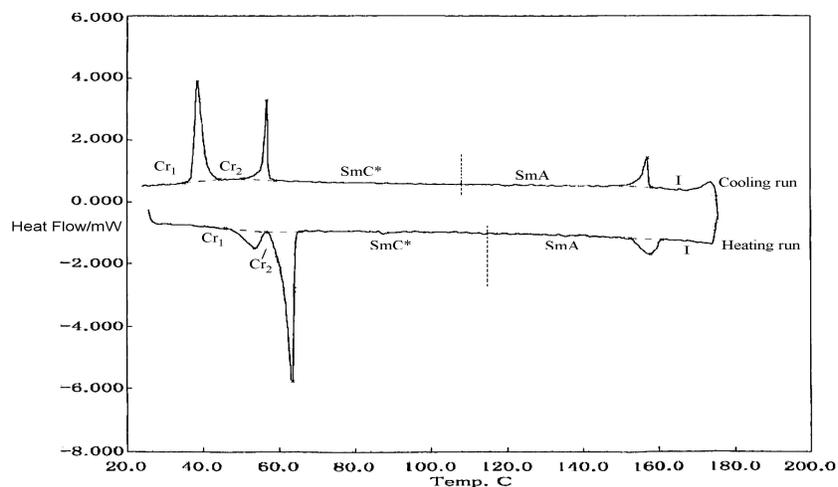
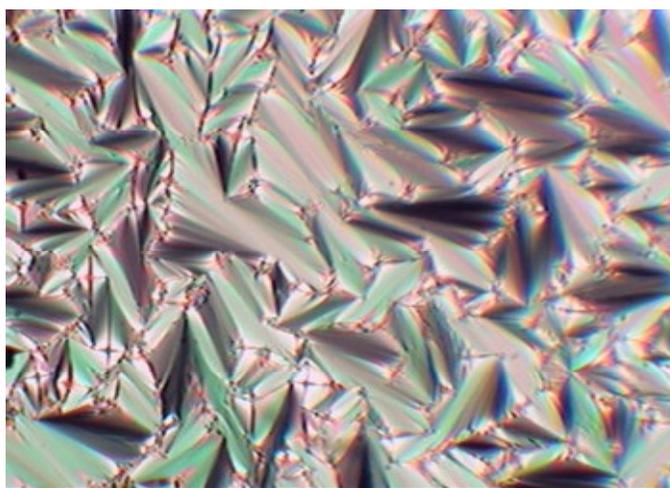
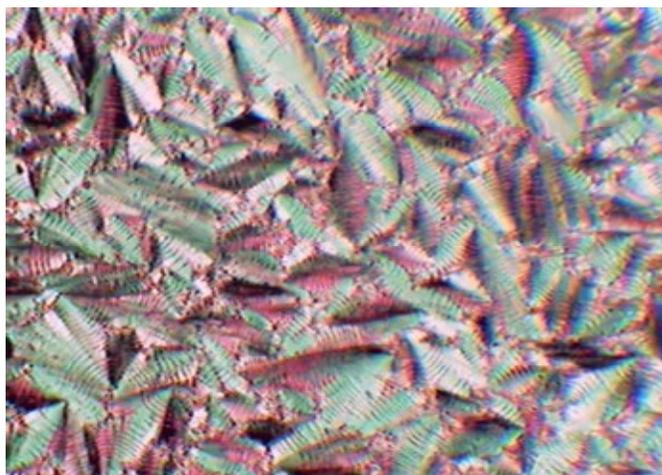


Figure 3. DSC thermogram of S-MB-12B-BC during heating and cooling run.



(a)



(b)

Figure 4. (a) Optical photomicrograph of S-MB-12B-BC exhibiting SmA phase with fan-shaped texture (100x). (b) Optical photomicrograph of S-MB-12B-BC exhibiting SmC*

BC and S-MB-18B-BC showed the similar IR and NMR characteristics as those discussed for S-MB-12B-BC.

Optical and thermal studies

All the compounds synthesized in the present study have been characterized using polarizing optical microscope (POM) and differential scanning calorimetry (DSC). Figure 3 shows the representative DSC thermogram of S-MB-12B-BC during the heating and cooling scans. Table 2 shows the phase transition temperatures, their associated enthalpy (ΔH) and molar entropy (ΔS) values of all the compounds. Observation under crossed polarizer upon heating found that all compounds exhibited endotherms characteristic of the crystal-mesophase and mesophase-isotropic transitions at temperature greater than the melting temperature (T_m).

Upon heating and cooling, optical studies have found that all compounds exhibited enantiotropic non-tilted and tilted smectic phases. The cooling scan upon S-MB-12B-BC showed the presence of mesophase [Figure 4 (a)] with fan-shaped texture. This feature is characteristic of the SmA phase owing to the formation of batonnets that coalesced to form the fan-shaped texture (Yeap et al., 2006b). Upon further cooling on the fan-shaped texture of S-MB-12B-BC, periodical disclination lines parallel to the smectic layer were clearly observed under POM in the temperature range of 108–56°C, indicating the chiral smectic C (SmC*) phase where the molecules are tilted with respect to the layer plane and formed a helix (Yeap et al., 2000a). The photomicrograph of S-MB-12B-BC exhibiting SmC* phase with helical texture is shown in Figure 4 (b). The appearance of SmA and SmC* phases in S-MB-12B-BC is found to conform with its analogue compounds, (S)-2-methylbutyl 4-(4'-(d₁₇)-octyloxyphenyl)benzoate (Yeap et al., 2000a), (S)-2-methylbutyl 4'-(4"-alkanoyloxyphenyl)benzoates (Goodby et al., 1987) and (S)-2-methylbutyl 4'-(4"-n-octyloxybenzoyloxy)-biphenyl-4-carboxylate (Kondo et al., 1988). S-MB-14B-BC, S-MB-16B-BC and S-MB-18B-BC showed the similar liquid crystalline phase characteristics as those discussed for S-MB-12B-BC.

The enthalpy change values (Table 2) as obtained from the DSC measurements can also provide useful information for identifying the crystal-mesophase and mesophase-isotropic transitions in all the compounds. Among all title compounds, S-MB-12B-BC and S-MB-14B-BC showed an endotherm in the DSC thermogram (Table 2) before the crystal-to-smectic C* transition at 53.6 and 51.8°C, respectively. The texture observed under POM is indicative of the presence of subphases within the crystal phase (Cr₁-Cr₂) which resembled the phenomena reported in our recent finding on ortho-hydroxy-para-alkanoyloxybenzylidene-para-substituted anilines (Yeap et al., 2004). The crystal-to-smectic C* and smectic A-to-isotropic transitions for both of the heating and cooling scans have relatively large enthalpies

associated with them, indicating that the transitions were generally first order in nature (Goodby et al., 1987). Typically, the enthalpy for the smectic A-to-smectic C* phase transition was relatively small, indicating second order phase changes (Goodby et al., 1987). However, the enthalpy change for the smectic A-to-smectic C* phase transition was too small to be detected in the present compounds (Figure 3) as that observed for biphenyl-4-carboxylate derivatives (Waugh et al., 1992).

Influence of structural changes on mesomorphic properties

The influence of the terminal alkyl chain length on the clearing temperature (or SmA-I transition temperature) for this series of compounds in general, followed that characteristically seen for calamitic systems. As the number of carbons in the alkanoyloxy chain increased from $n = 12$ to $n = 18$, the clearing temperature (T_c) decreased following the order: S-MB-12B-BC: $T_c = 157.8^\circ\text{C} < \text{S-MB-14B-BC: } T_c = 153.5^\circ\text{C} < \text{S-MB-16B-BC: } T_c = 153.2^\circ\text{C} < \text{S-MB-18B-BC: } T_c = 152.4^\circ\text{C}$. The decrease in the clearing temperature is attributed to the dilution of the core induced by the increasing length of the terminal alkyl chain (Berdague et al., 1993). In Figure 5, the crystal-to-smectic C*, smectic C*-to-smectic A and smectic A-to-isotropic (T_c) transition temperatures upon the heating cycle for the title compounds are plotted as a function of the carbon chain length in the alkanoyloxy substituent. The temperature at which the SmC* phase appeared increased in a typical sequential manner as the chain length of the alkanoyloxy substituent was increased. For the SmC*-SmA transition, the transition temperature remained relatively constant as the series is ascended wherein the transition temperature of SmC*-SmA of S-MB-nB-BC (where $n = 12, 14, 16$ and 18) are 115, 114, 112 and 112°C, respectively. The net cumulative effect of these two trends is shown in Figure 5, where the absolute phases range of the SmC* mesophase is plotted as a function of the carbon chain length in the alkanoyloxy substituent. From this graph, the phase range of SmC* phase was shown to decrease as the length of the alkanoyloxy substituent increased. This might be due to the dilution of the chirality of the molecule as the length of the terminal alkyl chain increased. The average phase range of the SmA phase is 41°C (Figure 5) and did not appear to change substantially with an increase in the chain length of the alkanoyloxy substituent.

Upon cooling the phase behaviors including the transition temperatures and phase (SmA and SmC*) range of all the title compounds are also plotted as a function of the carbon chain length in the alkanoyloxy substituent in Figure 6. From the graph (Figure 6), it is clearly shown that upon the cooling scan all the title compounds exhibited the similar phase characteristics as that observed for the heating scan. As the number of the carbons in the alkanoyloxy chain ascended from $n = 12$ to $n = 18$, the

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

Compound	Cycle	Transition	T /°C	ΔH /kJ mol ⁻¹	ΔS /(10 ⁻³) kJ K ⁻¹ mol ⁻¹
S-MB-12B-BC	Heating	Cr ₁ -Cr ₂	53.6	4.6	14.0
		Cr ₂ -SmC*	63.5	23.4	69.6
		SmC*-SmA	115.0 ^a	-	-
		SmA-Iso	157.8	4.3	9.1
		Iso-SmA	156.9	3.9	9.1
	Cooling	SmA-SmC*	108.7 ^a	-	-
		SmC*-Cr ₂	56.6	5.8	17.6
		Cr ₂ -Cr ₁	38.5	14.6	46.9
S-MB-14B-BC	Heating	Cr ₁ -Cr ₂	51.8	6.1	18.9
		Cr ₂ -SmC*	62.5	27.8	82.7
		SmC*-SmA	114.0 ^a	-	-
		SmA-Iso	153.5	5.5	12.8
		Iso-SmA	154.1	4.7	10.9
	Cooling	SmA-SmC*	102.5 ^a	-	-
		SmC*-Cr ₂	55.5	6.5	19.9
		Cr ₂ -Cr ₁	37.7	15.1	48.7
S-MB-16B-BC	Heating	Cr-SmC*	64.0	38.9	115.4
		SmC*-SmA	112.4 ^a	-	-
		SmA-Iso	153.2	6.2	14.7
		Iso-SmA	152.8	5.5	12.9
	Cooling	SmA-SmC*	102.4 ^a	-	-
		SmC*-Cr ₂	60.7	9.3	27.8
		Cr ₂ -Cr ₁	52.4	17.5	53.8
S-MB-18B-BC	Heating	Cr-SmC*	73.3	48.4	139.8
		SmC*-SmA	112.0 ^a	-	-
		SmA-Iso	152.4	6.6	15.5
		Iso-SmA	151.8	6.4	15.1
	Cooling	SmA-SmC*	104.5 ^a	-	-
		SmC*-Cr ₂	68.5	20.7	60.6
		Cr ₂ -Cr ₁	62.7	20.8	62.1

^a Polarized optical microscopy data, Cr₁ and Cr₂, crystal; SmA, smectic A; SmC*, chiral smectic C; Iso, isotropic.

Table 3. The average smectic thermal stabilities and molecular structure of series S-MB-nB-BC, A, B and C.

Series	Thermal stabilities (°C)		References
	SmC*	SmA	
S-MB-nB-BC (n = 12, 14, 16, 18)	113.4	154.2	-
A (n = 10, 12, 14)	49.6	63.4	(Goodby et al., 1987)
B (n = 10, 12, 14, 16)	95.7	125.2	(Waugh, 1992)

the clearing temperature decreased, the SmA phase range remained relatively constant and the SmC* phase range decreased.

The average thermal stabilities as well as molecular structure of the present compounds S-MB-nB-BC and the

structurally related series A (Figure 7) (Goodby et al., 1987) and B (Figure 9) (Waugh et al., 1992) reported in the literature is tabulated in Table 3. Compounds of series S-MB-nB-BC are found to be different from analogue compounds of series A owing to the presence of

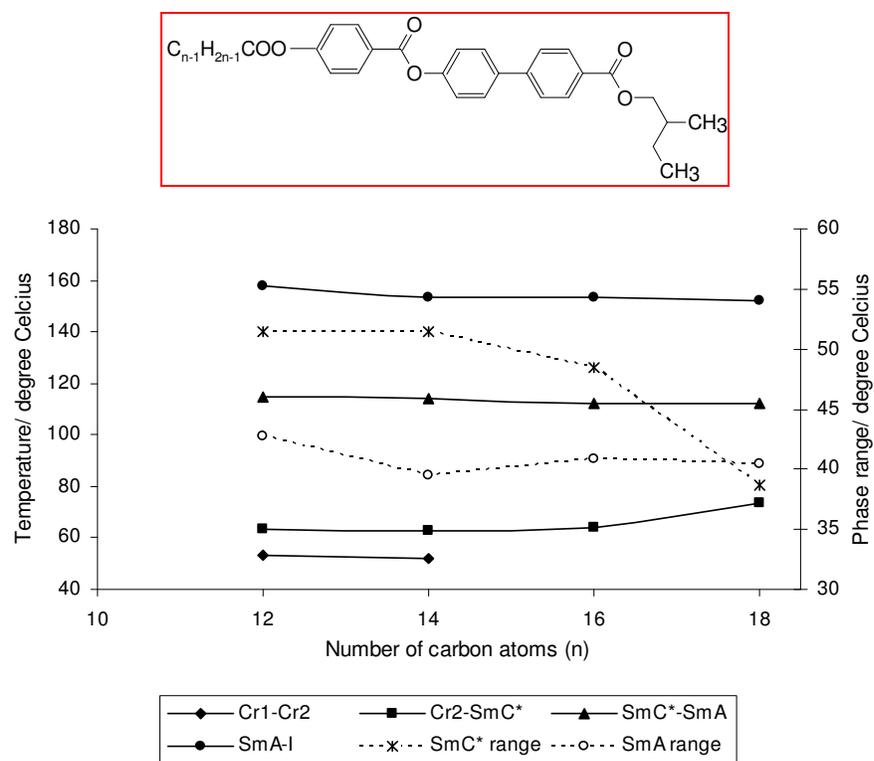


Figure 5. Plot of the transition and phase (SmC* and SmA) range upon heating cycle for S-MB-nB-BC as a function of the number of carbons in the *n*-alkanoyloxy chain.

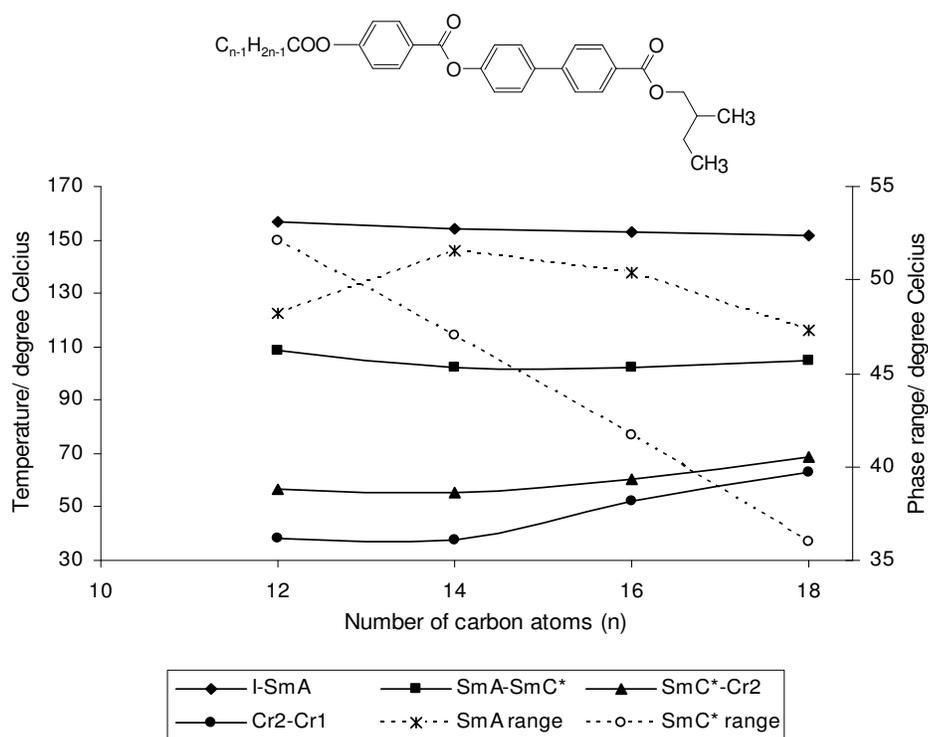


Figure 6. Plot of the transition and phase (SmC* and SmA) range upon cooling cycle S-MB-nB-BC as a function of the number of carbons in the *n*-alkanoyloxy chain.

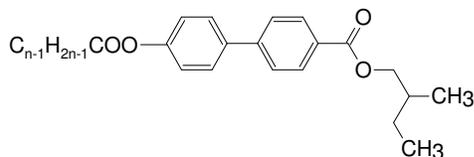


Figure 7. Structure of series A.

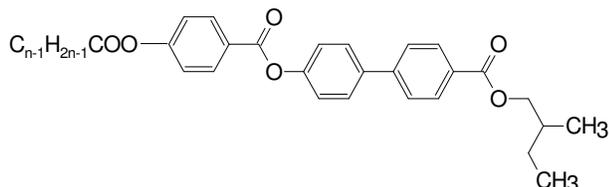


Figure 8. Structure of S-MB-nB-BC.

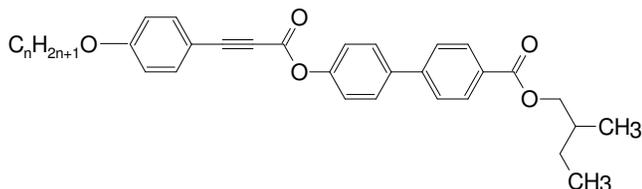


Figure 9. Structure of series B.

an additional aromatic joined to the biphenyl core system via an ester bond. Comparison between thermal stabilities of S-MB-nB-BC and compounds of series A shows that the thermal stability of the SmC* and SmA phases in the series S-MB-nB-BC are greater by 63.8°C and 90.8°C, respectively compared to the series A. Gray (1962) has explained that the increase in the length of the molecules with little or no change in the width, as a result of its polarizability, increases the intermolecular cohesive forces which would be responsible for higher thermal stability as well as the wider mesophase length of S-MB-nB-BC molecules.

The smectic thermal stabilities of the title compounds are higher as compared to those of the structurally related series B. Gray (1962) also defined that a compound which requires more thermal energy to disorganize the molecular arrangement of the smectic phase has greater smectic thermal stability. It can be seen from Table 3 that more thermal energy has to be supplied to disorganize the molecular arrangement of the smectic phase of the title compounds, as can be evidenced by the fact that the average SmC* and SmA phase stabilities are higher by 17.7°C and 29.0°C, respectively than those of compounds of series B. The slightly higher smectic thermal stabilities of the title compounds is due to the structure difference in their connecting group (Z) between the phenyl and biphenyl molecules wherein the connecting group (Z) of series S-MB-nB-BC and series B (Figures 8

and 9) are -COO- and -C≡C-COO-, respectively. The oxygen atom of the alkanoyloxy group in S-MB-nB-BC has the chance to come into conjugative interaction with the C=O of the connecting group (Z) as that observed by Sakurai et al. (1989) when studying the conjugative effect of phenyl 4-(4-tetradecyloxybenzoyloxy)benzoate and 4-tetradecyloxyphenyl 4-benzoyloxybenzoate. As for series B system, the conjugative interaction between the oxygen atom of the alkoxy group and the C=O of the connecting group (Z = -C≡C-COO-) in the molecule was diffused due to the presence of -C≡C- group which appeared before the C=O group of the connecting group (Z = -C≡C-COO-) in the molecule. The better conjugative interaction in the molecular structure of S-MB-nB-BC has caused the polarity of the carbonyl oxygen to increase and this mesogen will have more stable mesophase compared with the analogue compounds in series B. Thus, the smectic thermal stabilities of the title compounds are higher as compared to those of the structurally related series B (Table 3). Similar characteristic was also observed for 1-alkylheptyl 4'-(4-n-nonyloxybenzoyloxy) biphenyl-4-carboxylates and 1-alkylheptyl 4'-(4-n-nonyloxyphenylpropyloxy) biphenyl-4-carboxylates which possessed the connecting group (Z = -COO- and -C≡C-COO-) between the phenyl and biphenyl group, respectively (Nishiyama and Goodby, 1993).

Conclusion

A series of chiral ester (*S*)-(-)-2-methylbutyl 4'-(4"-n-alkanoyloxybenzoyloxy) biphenyl-4-carboxylates were prepared and found to possess mesomorphic properties whereby all members displayed SmA and tilted SmC* phases.

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