Accepted Manuscript

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PII: S0022-2860(16)30007-2

DOI: 10.1016/j.molstruc.2016.01.007

Reference: MOLSTR 22123

To appear in: Journal of Molecular Structure

Received Date: 16 November 2015

Accepted Date: 4 January 2016

Please cite this article as: G.-Y. Yeap, F. Osman, C.T. Imrie, Non-symmetric chiral liquid crystal dimers. Preparation and characterisation of the *(S)*-(benzylidene-4'-substitutedaniline)-2"-methylbutyl-4"'-(4""-phenyloxy)-benzoateoxy)hexanoates, *Journal of Molecular Structure* (2016), doi: 10.1016/j.molstruc.2016.01.007.

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Non-symmetric chiral liquid crystal dimers. Preparation and characterisation of the (S)-(benzylidene-4'substitutedaniline)-2"-methylbutyl-4""-(4"""-phenyloxy)benzoateoxy)hexanoates

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Abstract

The properties of six chiral non-symmetric dimers belonging to the family of (*S*)-(benzylidene-4'-substitutedaniline)-2''-methylbutyl-4'''-(4''''-phenyloxy)benzoateoxy)hexanoates are described. The terminal substituents on the 4-benzylidene-4'substituted fragment are H, Cl, Br, I, CH₃ and C_2H_5 . All six dimers exhibit an enantiotropic chiral nematic phase. The relationship between the chiral nematicisotropic transition temperature and the terminal substituent is discussed in terms of the size of the substituent and its effect of the molecular shape, and its ability to interact with mesogenic group to which it is attached. The C_2H_5 -substituted dimer also shows an enantiotropic monolayer chiral smectic C phase, the formation of which is attributed to the enhanced molecular inhomogeneity arising from the longer alkyl chain. The weak smectic tendencies seen for the halogen-substituted dimers are attributed to potentially repulsive interactions between the ester links that would occur in an intercalated smectic arrangement which would be expected for dimers of this type.

Keywords: liquid crystal dimers; non-symmetric dimers; chirality

1. Introduction

Liquid crystal dimers consist of molecules containing two mesogenic units connected via a flexible spacer, and continue to be the focus of significant research interest [1-3]. If the two mesogenic units in the molecule are identical, then the dimers are referred to as being symmetric, whereas if they differ, they are termed nonsymmetric. Initial interest in liquid crystals dimers arose from their role as model compounds for both main chain [4] and side chain liquid crystal polymers [5]. However, it soon became clear that their transitional properties differed significantly from those of conventional low molar mass materials consisting of molecules having just a single mesogenic core, and thus, quickly became of fundamental interest in their own right [6]. In particular, the study of non-symmetric dimers led to the discovery of the intercalated smectic phases.[7-10] This created interest in higher oligomers such as trimers and tetramers consisting of molecules containing either three or four mesogenic units, respectively. [11-15] More recently, research involving dimers has included, for example, new non-symmetric dimers [16-18], discotic dimers [19, 20], H-shaped dimers [21-23], bent-core dimers [24, 25], disulfide-linked spacers [26, 27], carbohydrate-based non-symmetric dimers [28], their elastic and viscoelastic behaviour [19, 29, 30], hydrogen bonded dimers [31, 32] as well as continued interest in higher oligomers. [33-37] However, the most exciting research area involving dimers is the recently discovered twist bend nematic phase (see, for example, [38-48]).

The structural requirement for a liquid crystal dimer to exhibit the twist bend nematic phase is a bent molecular shape, and this is largely controlled by the number of atoms connecting the two mesogenic units, and the chemical nature of the groups linking the spacers to the mesogenic units. In the majority of dimers reported in the literature, ether links are used to connect the spacer to the liquid crystal groups. [1-3] The considerable interest focussed on the twist bend nematic phase has led to significant interest in replacing the ether links by methylene groups as these give rise to a more bent structure in odd-membered dimers (see, for example, [38, 39, 42, 49]).

We have recently considered the effects of using ester links to connect the spacer to the mesogenic units. [10, 50, 51] Here we extend these studies to chiral materials and report the liquid crystalline behaviour of the (S)-(benzylidene-4'-substitutedaniline)-2''-methylbutyl-4'''-(4''''-phenyloxy)benzoateoxy)hexanoates,



We refer to these dimers using the acronym (S)MB-6E-X in which (S)MB denotes the (S)-2-methylbutyl group, 6 is the number of carbon atoms linking the two mesogenic units, E indicates the ester linkage in the spacer, and X the terminal substituent on the Schiff's base moiety.

2. Experimental

2.1 Synthesis

The syntheses of the (*S*)-(benzylidene-4'-substituted-aniline)-2''-methylbutyl-4'''-(4''''-phenyloxy)benzoateoxy)hexanoate dimers, (*S*)MB-6E-X, were carried out according to the method summarized in Scheme 1. The preparation of the intermediates **1-X** and **2-X** have been described in detail elsewhere [51]. 4-(4hydroxyphenyl)benzoic acid reacted with (*S*)-methyl-1-butanol in acetone in the presence of a catalytic amount of hydrochloric acid to give **3**. A Williamson ether reaction between **2-X** and **3** in the presence of anhydrous potassium carbonate and potassium iodide in acetone gave (*S*)MB-6E-X. The method used for each member of the series was identical, and so a representative synthesis and characterisation data are described in detail for just one final compound, namely (*S*)MB-6E-Br.

2.1.1 Synthesis of (S)-4-(4-hydroxyphenyl)benzoate-2-methyl-1-butyl (3)

3 was prepared according to the method described in our earlier study [50]. Thus, 4-(4-hydroxyphenyl)benzoic acid (2.0g, 9.34 mmol) was added to (*S*)-2-methyl-1-butanol (25ml) which served both as a reactant and the solvent medium. As the temperature was increased to 90 $^{\circ}$ C, a catalytic amount of concentrated HCl was added drop wise, and the reaction mixture was refluxed for 24h. The mixture was evaporated under reduced pressure. The white precipitate obtained was recrystallized from chloroform.

Yield 80%. Elemental analysis (%): Found, C 75.98, H 7.11; calculated $C_{18}H_{20}O_3$, C 76.03, H 7.09. IR (KBr) v/cm⁻¹, 3410 (OH), 2968-2875 (C-H alkyl), 1690 (C=O ester). ¹H-NMR (CDCl₃) δ /ppm, 0.93 (t, 3H, CH₃), 0.99 (d, 3H, CH₃), 1.34 (m, 1H,

CH₂), 1.57 (m, 1H, CH₂), 1.91 (m, 1H, CH), 4.12-4.18 (2dd, 2H, COOCH₂), 6.89 (d, 2H, Ar), 7.59 (d, 2H, Ar), 7.75 (d, 2H, Ar), 7.99 (d, 2H, Ar), 9.72 (s, 1H, OH).

2.1.2 Synthesis of (S)-(benzylidene-4'-bromoaniline)-2''-methylbutyl-4'''-(4''''phenyloxy)benzoateoxy)hexanoate ((S)MB-6E-Br)

(*S*)MB-6E-Br was prepared as described in detail elsewhere [51]. Yield 45%. Elemental analysis (%): Found, C 67.34, H 5.87, N 2.15; calculated C₃₇H₃₈BrNO₅, C 67.68, H 5.83, N 2.13. IR (KBr) *v*/cm⁻¹, 2875-2960 (C-H alkyl), 1760 (C=O ester), 1713 (C=O ester), 1621 (C=N), 1253 (O-CH₂). ¹H-NMR (CDCl₃) δ/ppm, 0.97 (t, 3H, CH₃), 1.03 (t, 3H, CH₃), 1.34 (m, 1H, CH), 1.56-1.95 (m, 8H, CH₂), 2.65 (t, 2H, COCH₂), 4.08 (t, 2H, OCH₂), 4.14-4.28 (2dd, 2H, COOCH₂), 6.98 (d, 2H, Ar), 7.08 (d, 2H, Ar), 7.18 (d, 2H, Ar), 7.48 (d, 2H, Ar), 7.62 (dd, 4H, Ar), 7.83 (d, 2H, Ar), 8.10 (d, 2H, Ar), 8.34 (s, 1H, CH=N).

2.2 Characterization

The Fourier transform infrared (FTIR) spectra of the intermediate and target compounds were obtained using a Perkin-Elmer 2000 FTIR spectrophotometer. The samples were mixed with KBr and the spectra recorded in the frequency range 4000-400 cm⁻¹. ¹H-NMR spectra were obtained using a Bruker 300 MHz UltrashieldTM spectrometer. The samples were dissolved in CDCl₃ with tetramethylsilane (TMS) as the internal standard. Carbon, hydrogen and nitrogen (CHN) microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyser. The liquid crystalline textures were observed using a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Linkam LTS350 hot stage and TMS94 temperature controller. The phase transition temperatures and associated enthalpy changes of the dimers were determined with a Mettler Toledo DSC822^e differential scanning calorimeter equipped with a TSO 801RO sample robot and calibrated using indium and zinc standards. The heating and cooling rates used were ±5 °C min⁻¹.

3. Result and discussion

3.1 Transitional behaviour of the (S)MB-6E-X dimers

The transitional properties of the (*S*)MB-6E-X dimers are listed in Table 1, and all six dimers show an enantiotropic chiral nematic phase. Throughout chiral nematic phases have been identified on the basis of the observation of characteristic

fan and oily streak textures when viewed through the polarised microscope; representative examples are shown as Figures 1 and 2, respectively. The initial DSC heating trace for (*S*)MB-6E-H contains an endothermic peak corresponding to the crystal-chiral nematic transition which overlaps a peak associated with a crystalcrystal transition, and at higher temperatures an endotherm associated with the chiral nematic-isotropic transition, see Figure 3(a). On cooling, the sample does not crystallise and a new exotherm is observed at 28°C (Δ H = 1.89 kJ mol⁻¹), see Figure 3(b). On subsequent reheating, a glass transition is seen with a mid-point value of -25°C (see Figure 4) followed by cold crystallisation, which appears to be triggered by the onset of the phase transition observed on cooling at 28°C, crystal-crystal and melting endotherms and finally the endotherm associated with the chiral nematicisotropic transition, see Figure 3(c). The exotherm at 28°C seen in the cooling trace (Figure 3(b)) may be associated with a smectic-chiral nematic transition, but crystallisation precluded its detailed study using polarised light microscopy.

The DSC traces for (*S*)MB-6E-Cl and (*S*)MB-6E-Br are similar to those discussed for (*S*)MB-6E-H. On cooling, again extensive crystallisation does not occur but instead a number of weak exotherms are seen beginning at about 40°C for (*S*)MB-6E-Cl and at 49°C for (*S*)MB-6E-Br. Difficulties associated with slow crystallisation prevented the study of these thermal events using polarised light microscopy. On reheating, both dimers also exhibit a glass transition, followed by a cold crystallisation exotherm, and melting and clearing endotherms. The first heating DSC trace for *S*-MB-6E-I shows overlapping endotherms associated with a crystal-crystal and crystal-chiral nematic transition and at higher temperature an endotherm corresponding to the chiral nematic-isotropic transition. On cooling the sample undergoes crystallisation, and the subsequent reheating trace is similar to that observed on initial heating.

Figure 5 shows the DSC traces for *S*-MB-6E-CH₃, and on initial heating a crystal-crystal transition overlaps the melting endotherm and at higher temperature the chiral nematic-isotropic endotherm is seen. The focal conic fan and oily streak optical textures seen through the polarised light microscope for the chiral nematic phase are shown as Figures 1 and 2, respectively. On cooling, the sample does not crystallise, revealing a transition at 60°C, see Figure 5(b). The DSC peak shape suggests that this is in fact two overlapping phase transitions although this was not evident optically. At

this transition, a mosaic optical texture, see Figure 6, develops from the focal conic fan texture shown in Figure 1, and an essentially identical texture was formed from regions of the oily streak texture. This texture is similar to the natural optical texture of the G/J phase, and the associated entropy change is consistent with this view [52]. The monotropic nature of this phase precluded the possibility of its further study. On reheating the sample (Figure 5(c)), a glass transition was observed with a mid-point value of -22°C and an associated small enthalpy overshoot, a weak endotherm was observed at *ca* 5°C, followed by a cold crystallisation exotherm, and endotherms associated with the melting and clearing transitions.

The initial heating DSC trace for (*S*)MB-6E-C₂H₅ shown as Figure 7(a) consists of two endothermic peaks corresponding to the melting and chiral nematicisotropic transitions. On cooling, see Figure 7(b), crystallisation does not occur but instead a new peak is seen at 74°C, and the reheating DSC trace contains endotherms associated with this new event and the clearing transition, see Figure 7(c). On closer examination, both traces contain two additional and very weak endotherms (Figure 8) and a glass transition is seen in the reheat trace with an associated enthalpy overshoot. When viewed under the polarised light microscope, on cooling, the fan texture of the chiral nematic phase becomes crossed suggesting the formation of a smectic C phase, and on further cooling a filamentary texture coexisting with homeotropic regions forms which subsequently transforms into a mosaic texture. This sequence is shown in Figures 9-12.

The phase behaviour of (*S*)MB-6E-C₂H₅ was further studied using X-ray diffraction, and Figure 13 shows patterns collected at 154, 103 and 76 °C. The pattern corresponding to 154 °C shows a very weak reflection in the low angle region corresponding to 39.1 Å, while in the wide angle region, broad diffuse scattering is seen, centred at 4.5 Å, characteristic of a liquid-like arrangement of the molecules. This is a typical pattern for a chiral nematic phase. At 103 °C, a sharper first order and also a weak second order reflection are seen in the low angle region while in the wide angle a broad reflection is still observed. The sharp first order reflection in the low angle scattering indicates a liquid-like arrangement of the molecules with the layer. This is consistent with the assignment of a smectic C phase. The periodicity of the phase is 38.9 Å which is similar to the estimated all-*trans* molecular length of the dimer, 39.1 Å, and

strongly suggests that the smectic C phase has a monolayer arrangement with a small tilt angle. On further cooling to 76°C, the reflections in the low angle become stronger, and the band in the wide angle narrows considerably implying the presence of much longer range ordering within the layers. The layer spacing is 35.0 Å suggesting that the molecules are tilted within the layers. This pattern is consistent with the assignment of a G phase based on the optical texture.

3.2 Comparison of the liquid crystal behaviour of the (S)MB-6E-X dimers

The chiral nematic-isotropic transition temperatures of the (S)MB-6E-X dimers increase in the order of

$$H < C_2H_5 < I < Cl < CH_3 < Br$$

although the differences in T_{N*I} between four of the dimers (I, Cl, CH₃, Br) are very small. As would be expected, this is essentially the same trend as seen for the corresponding racemic materials, and may be accounted for in terms of the size and shape of the substituent, and its ability to interact with the mesogenic unit [53]. Figure 14 shows the dependence of T_{N*I} on the van der Waals volume of each substituent when bound to a phenyl ring, [54] and reveals a linear dependence of T_{N*I} on the size of the substituent with the exception of (*S*)MB-6E-H. This relationship is illustrated in Figure 14 by the line of best fit for the data points but excluding that for (*S*)MB-6E-H.

It is interesting to note that in our previous studies of similar materials, we also observed such behaviour but the line of best fit had a positive gradient [10, 51]. The physical significance of this differing behaviour is unclear, although we note that the differences between the transition temperatures are small. It is clear that T_{N*I} for *(S)*MB-6E-H is considerably lower than would be predicted on the basis of the relationship revealed by Figure 14. Indeed, the percentage increase in T_{N*I} on exchanging H for a Cl substituent is 9.6% which far exceeds the associated increase in the van der Waals molecular volume. Such behaviour has been seen for other liquid crystal dimers and attributed to a change of shape on substituting the mesogenic unit rather than from any significant enhancement of the shape anisotropy [8].

The entropy changes associated with the chiral nematic-isotropic transition are also listed in Table 1 and expressed as the dimensionless quantity $\Delta S_{N*I}/R$. These show a weak dependence on the nature of the substituent with the values ranging from

0.96 to 1.31. These values are rather small for even-membered liquid crystal dimers containing small terminal substituents [49, 55]. The low values of $\Delta S_{N*I}/R$ may be accounted for in terms of the enhanced molecular biaxiality arising from the branched terminal chain, and similarly low clearing entropies have been observed for dimers containing branched terminal chains [56] or mesogenic units having enhanced biaxiality including, for example, cholesteryl-based and pyrene-based units [57, 58].

Smectic behaviour is unambiguously observed for just two of the (S)MB-6E-X dimers, namely (S)MB-6E-CH₃ and (S)MB-6E-C₂H₅. The halogen-substituted dimers may show strongly monotropic smectic behaviour but it was not possible to confirm this by structural studies because of crystallisation. The corresponding halogensubstituted members of a closely related series of dimers in which the ester link between the spacer and the mesogenic unit in the (S)MB-6E-X dimers has been replaced by an ether link were shown to exhibit smectic A behaviour in which the molecules pack in an intercalated arrangement [10]. The driving force for the formation of intercalated smectic phases by non-symmetric dimers is most often attributed to a specific favourable interaction between the unlike mesogenic groups [9] which has been suggested to be an electrostatic quadrupolar interaction between groups having quadrupole moments of opposite signs [59]. The lower smectic phase stabilities seen for the ester-linked materials may be attributed to a repulsive dipolar interaction between the ester group linking the spacer to the mesogenic unit and that connecting the terminal chain that would destabilise an intercalated smectic arrangement. By comparison, (S)MB-6E-C₂H₅ shows an enantiotropic chiral smectic C phase. As we have seen, this is a conventional monolayer chiral smectic C phase and is presumably stabilised by the anisotropic interactions between the mesogenic groups, while the driving force for its formation is the enhanced molecular inhomogeneity arising from the longer terminal chain. (S)MB-6E-CH₃ shows a much lower smectic-chiral nematic transition temperature because there is now a mismatch in the lengths of the chains which creates packing difficulties within the smectic layers.

4. Conculsions

The dependence of the chiral nematic-isotropic transition temperatures on the chemical nature of the terminal substituent of the six new chiral non-symmetric dimers reported here, reinforces the view that it is predominantly the size of the

substituent and how this affects the shape of the molecule that influences the clearing temperature. However, the ability of the substituent to interact with the mesogenic group to which it is attached should also be taken into account. By contrast the smectic forming tendencies of these dimers appear to be controlled by repulsive dipolar interactions between the ester linking groups for the halogen-substituted materials that destabilise the expected intercalated packing arrangement. The driving force for the monolayer enantiotropic chiral smectic C phase observed for (*S*)MB-6E-C₂H₅ appears to be the molecular inhomogeneity arising from the longer terminal group and the phase stabilised by the interactions between the mesogenic units.

Acknowledgements

The author (G.Y.Yeap) would like to thank Universiti Sains Malaysia for providing the research facilities and financial support under RU Research Grant (Account No. 203/PKIMIA/6711192) and PRGS Postgraduate Research Grant (Account No. 1001/KIMIA/835010). Authors also thank Ms Anna Zep and her supervisor Prof E. Gorecka for the powder X-ray diffraction measurement.

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Table 1. Phase transition temperatures, associated enthalpy changes and entropychanges of the (S)MB-6E-X dimers. Cr crystal, Sm smectic, N* chiral nematic phase,I isotropic phase. () denote monotropic transitions.

Dimer	Tg	T _{Cr} -	T _{SmN}	$T_{N^{\ast}I}$	ΔH_{Cr}	ΔH_{SmN}	$\Delta H_{N^{\ast}I}$	ΔS_{SmN}	$\Delta S_{N^{\ast}I}$
	/°C	/°C	/°C	/°C	/kJ mol ⁻¹	/kJ mol ⁻¹	/kJ mol ⁻¹	/R	/R
(S)MB-6E-H	-25	88		124	31.4		3.18		0.96
(S)MB-6E-Cl	-20	86		162	33.9		4.14		1.14
(S)MB-6E-Br	-23	90		164	32.6		4.27		1.18
(S)MB-6E-I		112		160	31.9	5	4.64		1.29
(S)MB-6E- CH ₃	-22	99	(63)	163	35.2	(4.05)	4.74	(1.45)	1.31
$(S)MB-6E-C_2H_5^a$	-30	89	106	156	28.6	0.32	4.25	0.10	1.19

^a G-Sm 78°C, 5.31 kJ mol⁻¹, ΔS/R = 1.82; Sm-Sm 89°C (see text).



Figure 1 The fan texture of the chiral nematic phase shown by S-MB-6E-CH₃ at 140°C.



Figure 2 The oily streak texture of the chiral nematic phase shown by *S*-MB-6E- CH_3 at 120°C.



Figure 3 DSC traces for *S*-MB-6E-H on (a) first heating, (b) cooling and (c) second heating cycles. The traces have been arbitrarily shifted on the *y*-axis in order to separate them for the sake of clarity.



Figure 4 Magnified section of the DSC reheating trace for (*S*)MB-6E-H shown as Figure 1(c) showing the glass transition.



Figure 5 DSC traces for S-MB-6E-CH₃ on (a) first heating, (b) cooling and (c) second heating cycles. The traces have been arbitrarily shifted on the *y*-axis in order to separate them for the sake of clarity.



Figure 6The mosaic texture of the lower temperature phase shown by S-MB- $6E-CH_3$ at 56°C obtained on cooling the fan texture sown in Figure 1.



Figure 7 DSC traces for (*S*)MB-6E- C_2H_5 on (a) first heating, (b) cooling and (c) second heating cycles. The traces have been arbitrarily shifted on the *y*-axis in order to separate them for the sake of clarity.



Figure 8 Magnified sections of the DSC cooling and reheating traces for (*S*)MB- $6E-C_2H_5$ showed as Figure 17(b) and (c) showing the weak phase transitions.



Figure 9 The fan texture of the chiral nematic phase shown by (S)MB-6E-C₂H₅ at 113°C.



Figure 10 The fan texture of the chiral smectic C phase shown by (*S*)MB-6E- C_2H_5 at 98°C obtained on cooling the preparation shown in Figure 9.



Figure 11 The filament texture shown by (S)MB-6E-C₂H₅ at 88°C obtained on cooling the preparation shown in Figure 10.



Figure 12 The mosaic texture of the G phase shown by (S)MB-6E-C₂H₅ at 68°C obtained on cooling the preparation shown in Figure 11.



Figure 13 X-ray diffraction patterns obtained for (*S*)MB-6E-C₂H₅ at (a) 154 $^{\circ}$ C, (b) 103 $^{\circ}$ C and (c) 76 $^{\circ}$ C.



Figure 14 The dependence of the chiral nematic-isotropic transition temperature, T_{N*I} , on the calculated van der Waals volume of the terminal substituent when bound to a phenyl ring [54] for the *(S)*MB-6E-X dimers. The line shows the best fit through the data points excluding *(S)*MB-6E-H.



Scheme 1. Synthetic route used to prepare the (S)MB-6E-X dimers.