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Effect of connectivity and terminal functionality on mesophase behaviour of thermotropic liquid crystals containing biphenyl units

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A series of 4,4'-disubstituted biphenyls, designated as series HBC, in which, one substituent is an ester group linked directly to the ring and the other is the hydroxy-containing group $O(CH_2)_nOH$, have been prepared and analysed by differential scanning Calorimetry, polarizing optical microscopy and X-ray diffraction. The introduction of a trimethylene unit between the ester functional group and the biphenyl moiety of the HBC series gives rise to the HBB series, which did not exhibit liquid crystalline behaviour. Interestingly, mesophase behaviour could be restored by replacing the methylene group (of the trimethylene unit) that was directly attached to the biphenyl ring by a keto group (HBOB series). When the terminal hydroxy group of these three series was substituted by a group such as acetoxy or hydrogen, the transition temperatures were reduced, and the disappearance of mesophase behaviour was observed in some cases. However, this could be recovered by the replacement of the ester group by a carboxylic acid group.

1. Introduction

The biphenyl and terphenyl moieties are found in many liquid crystalline compounds (both low molar mass and polymeric) because the long, linear and rigid aromatic ring system contributes to the thermal stability of mesophases [1–6]. Of the biphenyl-based low molar mass liquid crystals, the *n*-alkyl and *n*-alkoxy cyanobiphenyls (*n*CB and *n*OCB) are well known commercially important mesogens, used in liquid crystal displays (LCDs) [1, 2]. In the case of 4,4'-disubstituted biphenyls, various terminal groups such as alkyl, alkoxy and alkanoyl are used to impart liquid crystalline properties [3–5]. The dipole which acts across the molecular long axis has been shown to increase the stability of a smectic phase to a much greater extent than a nematic phase [7]. Thus, a terminal ester group in low molar mass liquid crystals would promote smectic properties due to its dipole across the molecular long axis. The resultant dipole of the ester carbonyl group, which acts across the molecule, will make a considerable contribution to the lateral cohesions between molecules in a smectic layer packing, in which the molecules lie parallel to one another, with their ends in line. Gray *et al.* [8] investigated the mesomorphic properties of a series of 4'-*n*-alkoxybiphenyl-4-carboxylic acids and

their methyl, ethyl and *n*-propyl esters. The alkoxy-carboxylic acid series exhibited nematic and/or smectic mesophases depending on the alkoxy chain length, and the esters containing longer alkoxy spacers showed smectic phases. It was also observed that as the terminal alkoxy chain length was increased, there was a natural, smooth progression to esters which exhibit tilted smectic B phases (later in 1980 designated as G phases [9]) rather than tilted smectic C phases [10, 11]. Cohen *et al.* [12] reported the synthesis of various *n*-alkylbiphenyl dicarboxylates (*n*=3–15) but none were shown to exhibit liquid crystalline behaviour. However, upon selective hydrolysis of these diesters to the corresponding monoesters, liquid crystallinity was induced and the monoesters exhibited nematic and several smectic phases such as B, F and C. The formation of dimers in the monoesters via hydrogen bonding was shown by X-ray diffraction (XRD) [13].

It is clear from this discussion that the biphenyl-containing liquid crystals are very important commercially and also that their properties are very sensitive to the nature of the terminal group. However, there are no literature reports of systematic studies on the effect of connectivity of these biphenyl units on the mesophase properties. Therefore, it is important to study the effect of connectivity along with that of the terminal functionality in the case of these biphenyl-containing mesogens. In this paper, we report, for the first time, the

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synthesis and mesophase characterization of various series of biphenyl-based liquid crystals, differing in the way that the mesogen is connected with the functional groups and also in the nature of the terminal groups.

2. Results and discussion

A number of biphenyl-based compounds have been synthesized in order to study the effect of connectivity of the mesogen to the functional groups (ester and

carboxylic acid) and the effect of terminal substitution (figure 1). The liquid crystalline properties of these compounds were analysed by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and XRD. The compounds are divided into three classes having as basic units: (i) a hydroxy group, the biphenyl moiety and the carboxylate group (HBC); (ii) a hydroxy group, the biphenyl moiety and the butyrate group (HBB); and (iii) a hydroxy group, the biphenyl moiety and the oxobutyrate group (HBOB). In

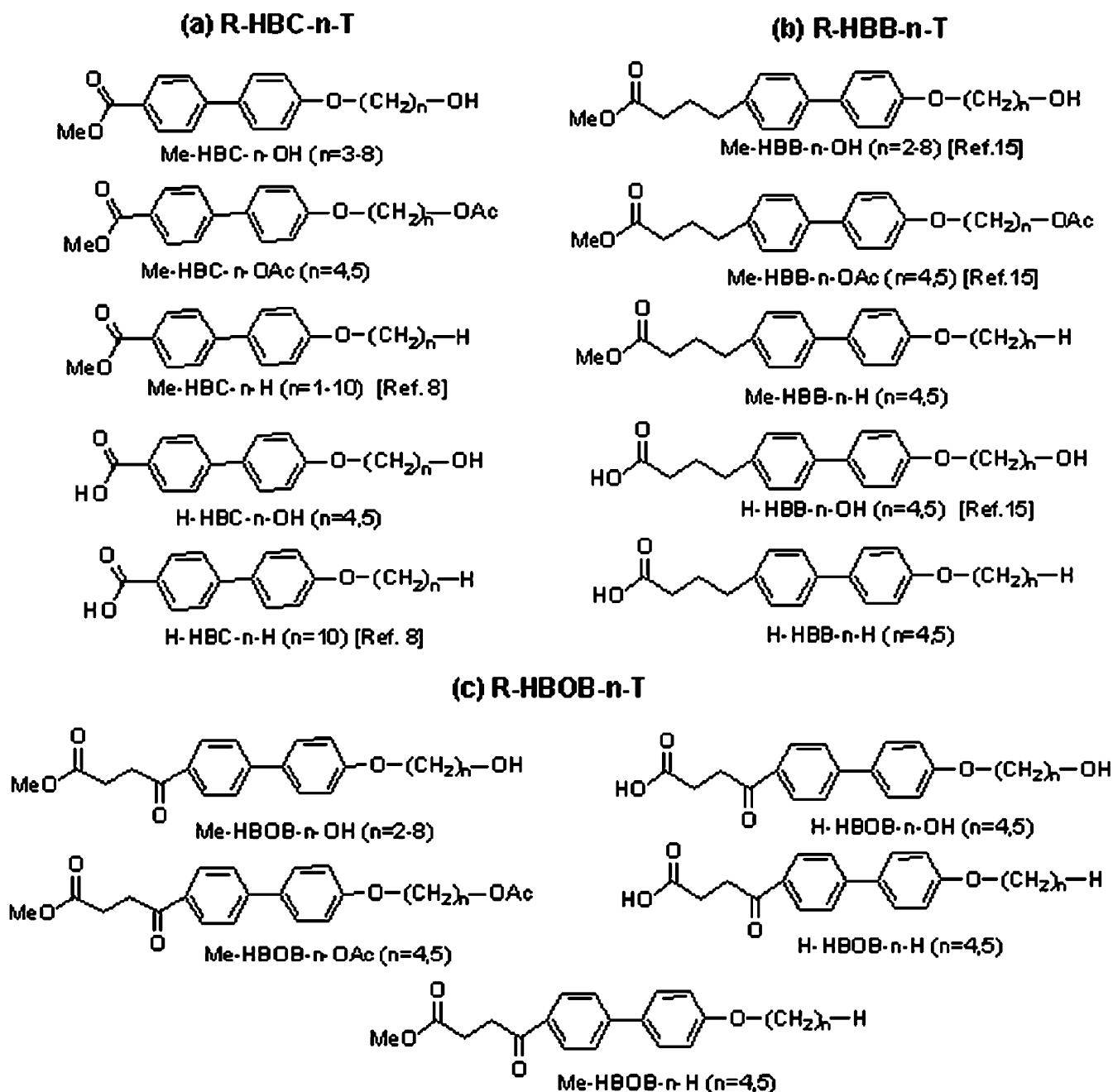


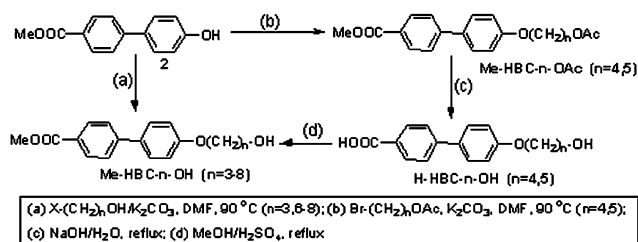
Figure 1. Structures of various biphenyl based liquid crystals.

all cases, different methylene spacers were built onto the hydroxy side of the biphenyl moiety, and the terminal groups were varied between hydroxy, acetoxy and hydrogen. These compounds are denoted as, in general, *R-B-n-T* (*R* is the alkyl group of the carboxylate moiety, *B* is the basic unit, *n* is the number of carbon atoms in the methylene spacer unit and *T* is the terminal group attached to the spacer unit). For example, methyl 4'-hydroxyhexoxybiphenyl-4-carboxylate is represented as Me-HBC-6-OH. First, the synthesis and mesophase characterization of the various series of biphenyl-based compounds are discussed, and then the effects of connectivity and terminal functionality on the mesophase properties are considered.

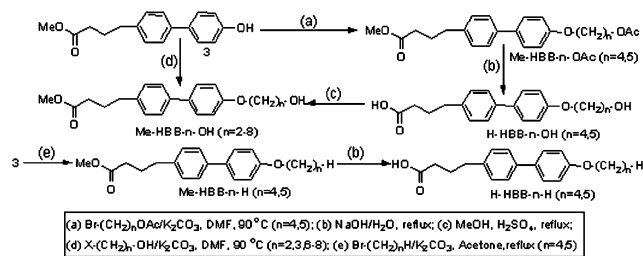
2.1. Synthesis

The reaction sequences for the synthesis of compounds containing the HBC basic unit are depicted in scheme 1. First, 4'-hydroxybiphenyl-4-carboxylic acid (**1**) was converted into its methyl ester, methyl 4'-hydroxybiphenyl-4-carboxylate (**2**) by esterification with methanol using conc. sulphuric acid as catalyst. The flexible methylene spacers were then incorporated into **2** either by reacting with α,ω -haloalkanols differing in the number of methylene spacers ($n=3,6-8$) or α,ω -haloalkyl acetate ($n=4,5$) [14] to obtain, respectively, methyl 4'-hydroxyalkoxybiphenyl-4-carboxylates, Me-HBC-*n*-OH ($n=3,6-8$) or methyl 4'-acetylalkoxybiphenyl-4-carboxylates, Me-HBC-*n*-OAc ($n=4,5$). The hydrolysis of the acetylalkoxy esters (Me-HBC-*n*-OAc, $n=4,5$) was carried out under basic conditions to obtain the corresponding hydroxyalkoxy acids (H-HBC-*n*-OH, $n=4,5$), which were then converted into their methyl esters Me-HBC-*n*-OH ($n=4,5$) by esterification with methanol in the presence of acid catalyst.

The synthesis and structural characterization of compounds having the basic unit HBB with different terminal functionalities (hydroxyalkoxy esters, Me-HBB-*n*-OH ($n=2-8$), acetylalkoxy ester (Me-HBB-*n*-OAc, $n=4,5$) and hydroxyalkoxy acids (H-HBB-*n*-OH, $n=4,5$) have already been described in a previous



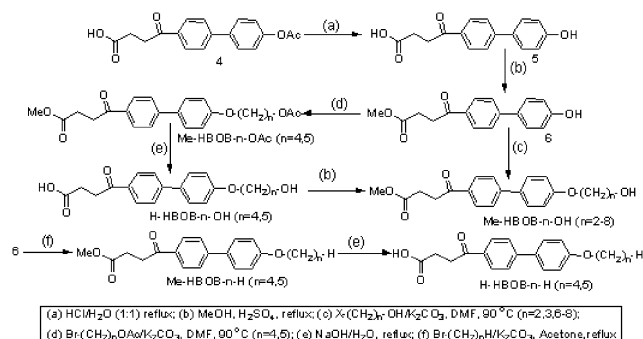
Scheme 1. Synthesis of HBC derivatives.



Scheme 2. Synthesis of HBB derivatives.

publication [15]. The hydroxyalkoxy esters (Me-HBB-*n*-OH) were studied by DSC and POM and found to be non-mesomorphic. The liquid crystalline properties of the acetylalkoxy esters and hydroxyalkoxy acids are analysed in this paper. The synthesis and thermal characterization of alkoxy esters (Me-HBB-*n*-H, $n=4,5$) and alkoxy acids (H-HBB-*n*-H, $n=4,5$) are also described (scheme 2).

The compounds containing the HBOB basic unit with different terminal groups were prepared from the starting material 4-(4'-acetoxybiphenyl-4-yl)-4-oxobutyric acid (**4**) [15] as described in scheme 3. The acid hydrolysis of **4** gave 4-(4'-hydroxybiphenyl-4-yl)-4-oxobutyric acid (**5**) which was converted into its methyl ester by esterification to give methyl 4-(4'-hydroxybiphenyl-4-yl)-4-oxobutyrate (**6**). Methylene spacers were then incorporated into **6** either by reacting with α,ω -haloalkanols ($n=2,3,6-8$) or α,ω -haloalkyl acetates ($n=4,5$), to obtain respectively, methyl 4-[4'-(ω -hydroxyalkoxy)biphenyl-4-yl]-4-oxobutyrate, Me-HBOB-*n*-OH ($n=2,3,6-8$) or methyl 4-[4'-(ω -acetoxyalkoxy)biphenyl-4-yl]-4-oxobutyrate, Me-HBOB-*n*-OAc ($n=4,5$). The basic hydrolysis of the acetylalkoxy esters (Me-HBOB-*n*-OAc, $n=4,5$) yielded the corresponding hydroxyalkoxy acids, H-HBOB-*n*-OH ($n=4,5$), which were then converted into their methyl esters by esterification with methanol to give Me-HBOB-4-OH and Me-HBOB-5-OH. The reaction of **6** with *n*-butyl bromide or *n*-pentyl bromide resulted in alkoxy



Scheme 3. Synthesis of HBOB derivatives.

esters Me-HBOB-4-H or Me-HBOB-5-H, respectively. These esters were hydrolysed to give the corresponding acids, H-HBOB-*n*-H (*n*=4,5).

2.2. Mesophase characterization

The mesophase characterisation of the hydroxyalkoxy esters [Me-HBC-*n*-OH (*n*=3–8) and Me-HBOB-*n*-OH (*n*=2–8)], acetylalkoxy esters [Me-HBC-*n*-OAc, Me-HBB-*n*-OAc and Me-HBOB-*n*-OAc (*n*=4,5)], alkoxy esters [Me-HBB-*n*-H and Me-HBOB-*n*-H (*n*=4,5)], hydroxyalkoxy acids [H-HBC-*n*-OH, H-HBB-*n*-OH and H-HBOB-*n*-OH (*n*=4,5)] and alkoxy acids [H-HBB-*n*-H, H-HBOB-H (*n*=4,5)] was carried out by DSC, POM and XRD.

2.2.1. Hydroxyalkoxy esters. The DSC and POM results for the two series of hydroxyalkoxy esters, Me-HBC-*n*-OH (*n*=3–8) and Me-HBOB-*n*-OH (*n*=2–8) are shown in table 1. All the esters exhibited multiple transitions in heating scans; the peaks are labelled as T_1 , T_2 and T_3 (in °C) in the order of increasing temperature. The peak temperatures obtained in cooling scans are given in parentheses. The enthalpy changes associated with each transition in the heating scan are designated as ΔH_1 , ΔH_2 and ΔH_3 (in kJ mol^{-1}) respectively. Hot stage POM was employed to identify the types of mesophases and their respective transition temperatures. On heating, the onset of the crystal to

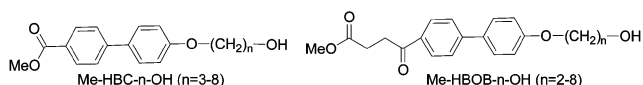
liquid crystal transition is denoted as T_a ; the temperature at which clearing of the mesophase to isotropic liquid occurs is designated as T_c ; and the transition from one mesophase to another, if any, is designated as T_b (table 1). The corresponding temperatures obtained on cooling cycle are given in parentheses. Some optical micrographs are shown in figure 2.

The lower members of the hydroxybiphenylcarboxylate-based esters, Me-HBC-3-OH and Me-HBC-4-OH, exhibited only one mesophase with a mosaic texture. Although Me-HBC-4 showed three peaks in the DSC heating scan, the optical microscope could detect only one mesophase with mosaic structure on both heating and cooling. The intermediate members, Me-HBC-5-OH and Me-HBC-6-OH, exhibited two mesophases. On cooling the melt, a smectic A (SmA) phase was observed to be separating from the isotropic liquid in the form of bâtonnets. On further cooling, the bâtonnets coalesced to form a typical focal-conic fan texture compatible with that of a SmA phase. Further cooling produced a transition to another mesophase that was characterized by a mosaic texture. The presence of two mesophases in these esters was in agreement with the DSC results, which indicated three peaks. The higher members of the series, Me-HBC-7-OH and Me-HBC-8-OH, showed only one mesophase with focal-conic textures characteristic of the SmA phase. The DSC thermogram of these esters showed

Table 1. DSC and POM results for various hydroxyalkoxy esters: transition temperatures in °C, enthalpy changes in kJ mol^{-1} .

Compound	DSC ^a						POM ^b		
	T_1	T_2	T_3	ΔH_1	ΔH_2	ΔH_3	T_a	T_b	T_c
Me-HBC-3-OH	118(110)	—	187(184)	1.6	—	17.8	115(112)	—	190(189)
Me-HBC-4-OH	119(99)	143	185(182)	2.0	3.1	22.2	110(114)	—	189(188)
Me-HBC-5-OH	124(96)	159(155)	170(167)	11.0	7.9	11.2	121(120)	156(161)	170(172)
Me-HBC-6-OH	141(110)	146(143)	162(158)	20.1	5.0	11.3	129(106)	155(148)	167(165)
Me-HBC-7-OH	115(86)	(125)	138(131)	7.0	—	17.5	122(127)	—	141(135)
Me-HBC-8-OH	101(94)	113	136(128)	9.2	5.2	27.8	128(126)	—	141(133)
Me-HBOB-2-OH	128(67)	142(139)	160(156)	12.4	8.5	9.0	113(60)	141(140)	168(162)
Me-HBOB-3-OH	99	129(125)	156(154)	0.7	6.6	8.3	97(90)	131(128)	165(159)
Me-HBOB-4-OH	—	121(117)	151(149)	—	7.0	7.8	—	124(123)	160(155)
Me-HBOB-5-OH	95(71)	115(111)	146(143)	12.6	7.2	9.3	98(75)	117(114)	150(147)
Me-HBOB-6-OH	67(35)	112(108)	143(140)	4.5	6.9	9.0	85(40)	117(115)	150(146)
Me-HBOB-7-OH	107(102)	112(109)	149(147)	1.8	2.1	9.6	105(100)	117(110)	159(156)
Me-HBOB-8-OH	(87)	111(97)	134(131)	—	23.2	9.5	95(90)	114(105)	140(135)

^aCalorimetric data on heating; transition temperatures observed in the cooling scan are given in parentheses. ^bTransition temperatures observed under POM during the heating cycle; cooling cycle data are given in parentheses.



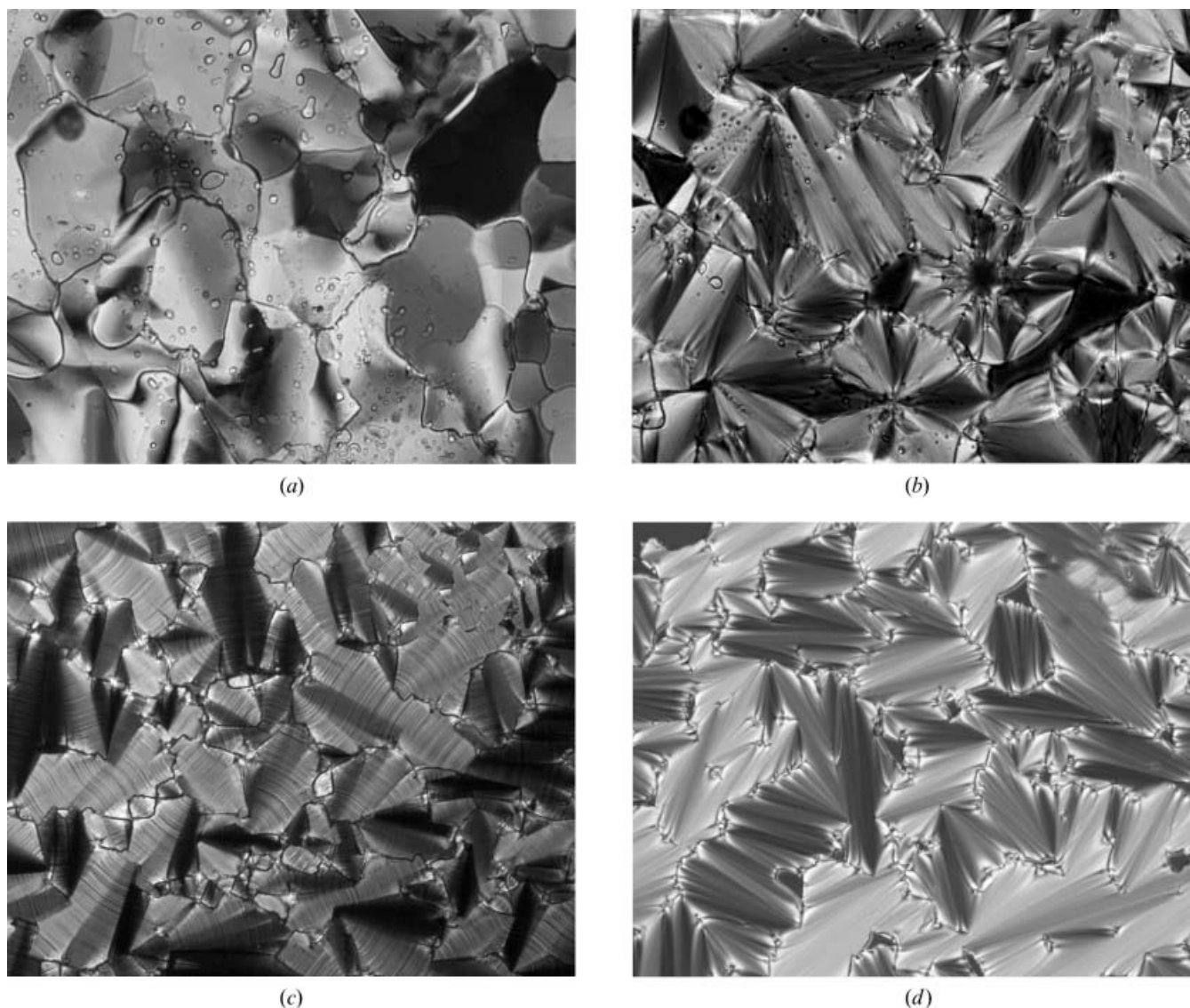


Figure 2. Optical micrographs of (a) Me-HBC-4-OH at 159°C; (b) Me-HBC-5-OH at 161°C; (c) Me-HBOB-2-OH at 133°C; (d) Me-HBOB-5 at 141°C.

three peaks in both cooling and heating scans. However, the POM results indicate that the first peak may correspond to the transition between two crystalline states.

To characterize the mesophase which exhibited mosaic texture in the POM studies of the Me-HBC- n -OH esters ($n=3-6$), the mutual miscibility method was employed using the standard low molar mass mesogen terephthal-bis(4-butylaniline), TBBA [16, 17]. The mesophases present in TBBA were named in the order of increasing temperature as smectic H, smectic G, smectic C, smectic A and nematic (H, G, SmC, SmA, N) according to the recommendations by Demus *et al.* [9]. For miscibility experiments, accurately weighed

mixtures of Me-HBC- n -OH and TBBA were crimped into a DSC sample pan, heated to the isotropic state and held for 5–10 min to ensure thorough mixing. After cooling to room temperature, the DSC heating and cooling scans were recorded and the cooling scan data used for constructing the binary phase diagram. A representative miscibility diagram of state for binary mixtures of Me-HBC-5-OH and TBBA is shown in figure 3. The binary phase diagram indicates that the mesophases present in this system are G and SmA phases since these phases were found to be miscible over the entire composition range.

All the members of the HBOB series (Me-HBOB- n -OH) showed two mesophases. On cooling the isotropic

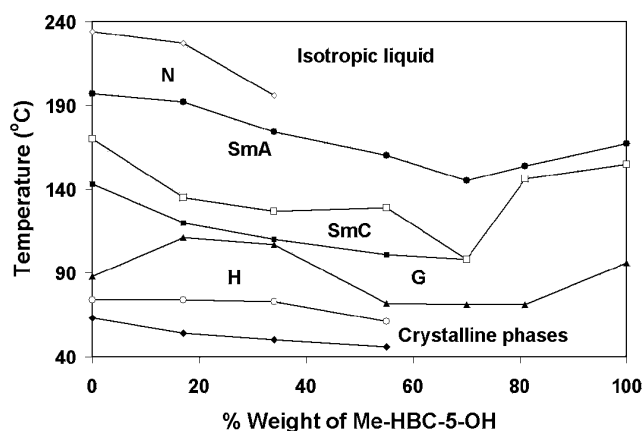


Figure 3. Phase diagram for TBBA and Me-HBC-5-OH binary mixture.

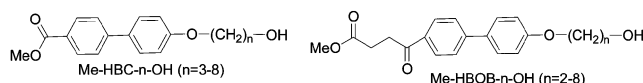
liquid, bâtonnets and fan-shaped textures characteristic of a SmA mesophase were observed under POM in the crossed polarizer mode. Further cooling produced another mesophase with fan-shaped structure with concentric arcs (E phase).

Variable temperature wide-angle X-ray diffraction studies were carried out for further analysis of the mesophases present in the hydroxy esters (Me-HBC-*n*-OH and Me-HBOB-*n*-OH). XRD experiments in the cooling scan could not be done due to sublimation of the samples at high temperatures under high vacuum. The heating scan data were therefore used for analysis.

The Bragg spacing values observed for the two series of hydroxyalkoxy esters are given in table 2. The phase-I in table 2 denotes the G phase (Me-HBC-*n*-OH, *n*=3–6), crystalline phase (Me-HBC-OH, *n*=7,8) or E phase (Me-HBOB-*n*-OH, *n*=2–8); the phase-II represents the SmA mesophases in all cases. The sharp inner peak observed in the SmA phase of the HBC series is comparable to that of the respective molecular lengths of these esters. The presence of several sharp outer peaks in the G and crystalline phases of these esters shows that there is ordering within the layers. The tilted nature of the G phase was indicated by the observation that the *d*-spacing of the inner peak is less than the molecular length.

A representative XRD pattern of Me-HBC-4-OH is now discussed, and the diffractogram is given in figure 4. For this ester, only one mesophase (G phase) was observed in POM studies even though DSC indicated three peaks (two mesophases) on heating. The XRD pattern of Me-HBC-4-OH shows the presence of two mesophases, in accordance with the DSC results. The high temperature mesophase showed an inner peak with *d*-spacing of 19.4 Å, which is comparable to the molecular length of 19.1 Å. Hence the mesophase must be a normal one and is assigned as SmA from the focal-conic textures observed by POM. In the low temperature mesophase, the *d*-spacing value of the inner peak decreased to 16.7 Å and several sharp outer peaks appeared. The peaks at 16.7, 8.4 and 4.8 Å correspond

Table 2. XRD results for the hydroxyalkoxy esters.



Compound	<i>d</i> -spacings/Å ^a		Molecular length/ Å ^d
	Phase-I ^b	Phase-II ^c	
Me-HBC-3-OH	32.1,16.1,8.0,6.4,4.5,4.3,3.7,3.1	—	17.7
Me-HBC-4-OH	33.3,16.7,8.4, 4.8,3.7,3.1	19.4,4.8	19.1
Me-HBC-5-OH	38.4,18.9,12.6,7.5,4.1,3.7,3.4	20.8,4.1	20.6
Me-HBC-6-OH	39.3,19.6,13.3,7.9,6.6,4.4,3.7	21.9,4.4	21.6
Me-HBC-7-OH	45.3,22.1,13.7,6.9,4.5,4.3,3.7	21.8,4.3	22.0
Me-HBC-8-OH	49.1,24.5,7.4,4.3,3.7,3.1	24.1,4.6	24.1
Me-HBOB-2-OH	39.4,19.6,9.9,6.7,5.0,4.4,3.8,3.3	19.4,4.1	19.3
Me-HBOB-3-OH	40.2,20.1,10.2,4.5,3.9,3.2	20.4,4.1	20.7
Me-HBOB-4-OH	43.1,22.1,11.3,4.5,3.8,3.3	21.3,4.7	21.8
Me-HBOB-5-OH	45.9,23.0,11.6,4.5,3.7,3.1	23.1,4.5	23.2
Me-HBOB-6-OH	47.1,24.2,12.0,4.5,4.3,3.7	23.9,4.5	24.3
Me-HBOB-7-OH	49.1,25.4,12.4,7.7,4.3,3.7	25.1,4.8	25.7
Me-HBOB-8-OH	51.4,26.6,17.3,10.6,8.9,6.6,3.8	26.6,4.6	26.9

^aThe Bragg spacing values obtained from XRD experiments. ^bPhase-I represents G, E or crystalline phases. ^cPhase-II denotes SmA phase. ^dMolecular length calculated using bond length and bond angles (HyperChem software).

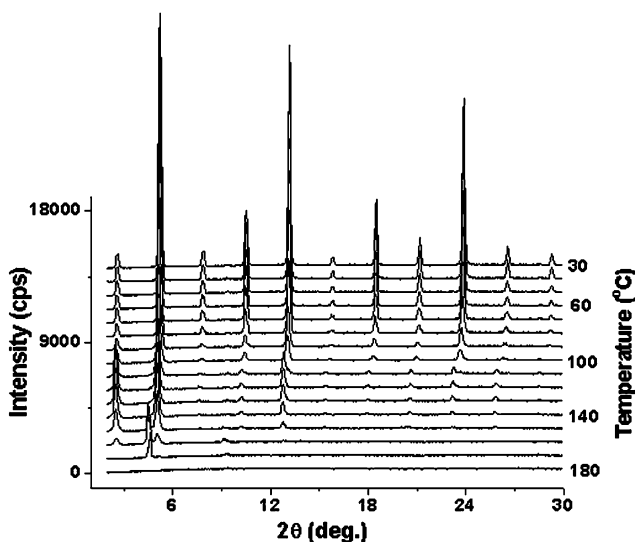


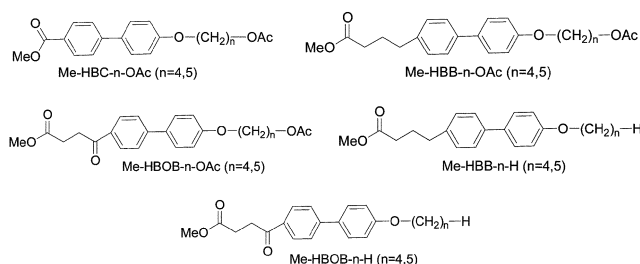
Figure 4. XRD pattern for Me-HBC-4-OH at various temperatures.

to the 1st, 2nd and 3rd order reflections, respectively. The observation of these peaks and more outer reflections (4.5, 4.3, 3.7 and 3.1 Å) confirms ordering within the layer. The presence of an inner peak (with

d -spacing value less than the molecular length) and several outer peaks (ordering within layers) is a characteristic pattern for the G phase. Another interesting feature of the room temperature XRD patterns of the hydroxy esters is that all of them showed an innermost peak with d -spacing values about twice the molecular length. For example, Me-HBC-4-OH exhibited an innermost peak with d -spacing of 33.3 Å, which is almost double the length of the molecule observed in the tilted phase.

The variable temperature XRD patterns of the hydroxyalkoxy esters Me-HBOB- n -OH ($n=2-8$) confirmed the SmA and E mesophases observed by POM (table 2). The diffractogram of the higher temperature mesophase consists of a sharp inner peak (whose d -spacing values correlate with the molecular length) and a broad outer peak (4.1–4.8 Å), which is characteristic of the SmA mesophase. The XRD pattern of the lower temperature mesophase showed an inner peak with d -spacing corresponding to the molecular length (normal phase) and several outer peaks (layer structure) indicating the presence of E phases in these compounds. The observation of peaks with d -spacing values double the molecular length shows that these esters also exist as dimers.

Table 3. DSC and POM results for various acetylalkoxy esters and alkoxy esters: transition temperatures in °C, enthalpy changes in kJ mol⁻¹.



Compound	DSC ^a						POM ^b		
	T_1	T_2	T_3	ΔH_1	ΔH_2	ΔH_3	T_a	T_b	T_c
Me-HBC-4-OAc	108(49)	–	139(137)	20.9	–	18.6	–	–	142(140)
Me-HBC-5-OAc	90	–	127(124)	29.6	–	17.2	–	–	129(128)
Me-HBB-4-OAc	(17)	–	75(53)	–	–	39.2	–	–	75(58)
Me-HBB-5-OAc	(29)	–	56(38)	–	–	35.7	–	–	67(64)
Me-HBOB-4-OAc	90(51)	106(103)	113(110)	8.9	6.1	4.9	97(62)	108(106)	116(114)
Me-HBOB-5-OAc	55	77(73)	103(97)	3.4	6.1	6.2	62(60)	87(80)	107(103)
Me-HBB-4-H	(47)	–	60(56)	–	–	17.7	–	–	63(60)
Me-HBB-5-H	30(20)	47(34)	55(49)	4.4	0.4	15.8	–	–	57(53)
Me-HBOB-4-H	58(45)	120(118)	136(134)	4.3	7.9	8.2	60(49)	122(121)	140(138)
Me-HBOB-5-H	94(81)	106(104)	132(130)	15.6	7.0	7.7	94(81)	109(107)	135(133)

^aCalorimetric data on heating; transition temperatures observed in the cooling scan are given in parentheses. ^bTransition temperatures observed under POM during the heating cycle; cooling cycle data are given in parentheses.

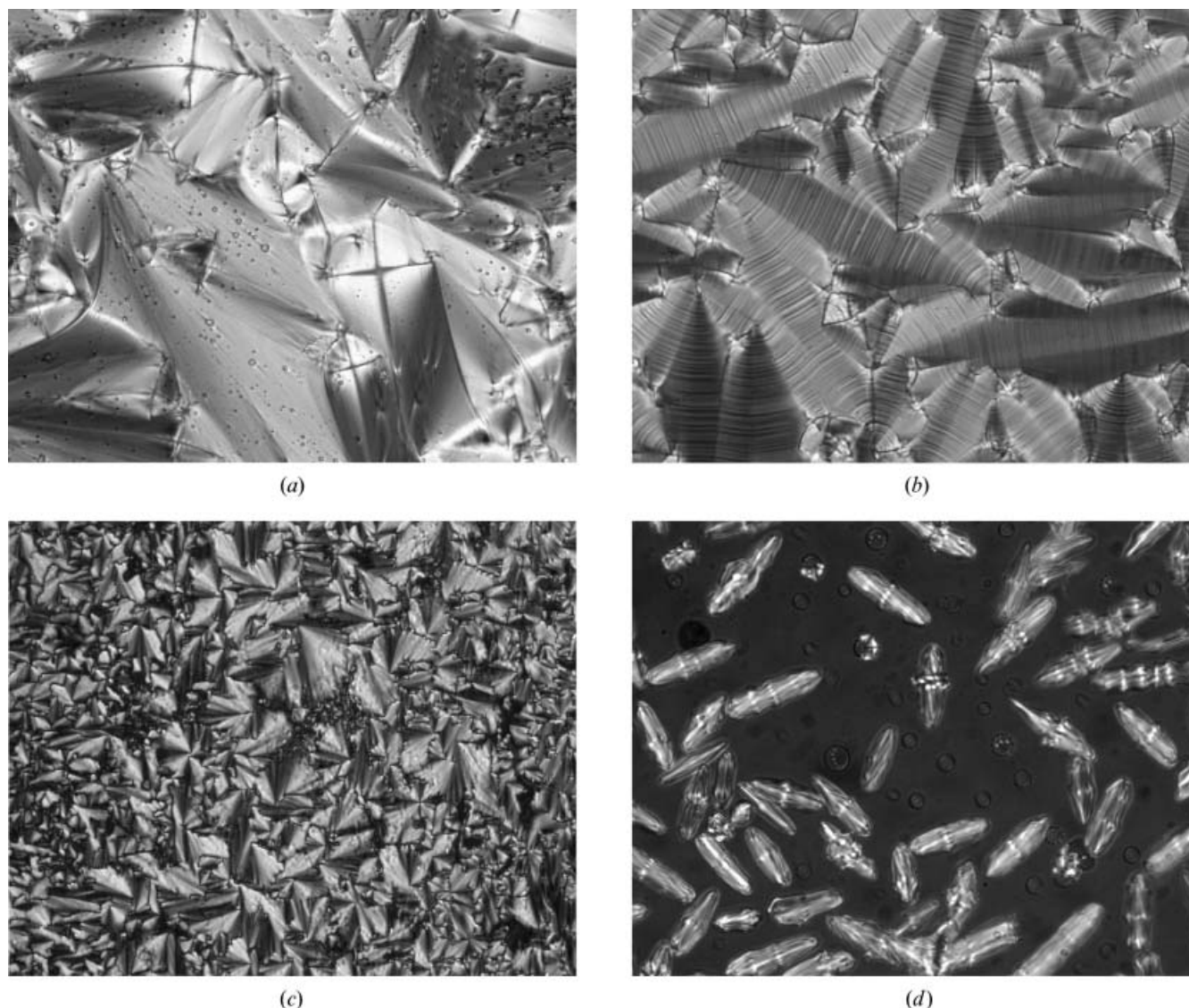
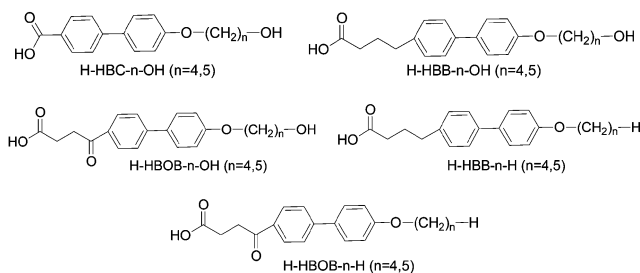


Figure 5. Optical micrographs of (a) Me-HBOB-5-OAc at 85°C; (b) Me-HBOB-5-H at 103°C; (c) H-HBC-4-OH at 219°C; (d) H-HBB-4-OH at 178°C.

2.2.2. Acetylalkoxy esters. The DSC and POM results for the three series of acetylalkoxy esters Me-HBC- n -OAc, Me-HBB- n -OAc and Me-HBOB- n -OAc ($n=4,5$) are given in table 3. The acetylalkoxy esters Me-HBC- n -OAc and Me-HBB- n -OAc were concluded not to exhibit liquid crystallinity since POM indicated birefringence but not fluidity. The multiple transitions exhibited in DSC studies of these esters may be due to the transition between different crystalline states. However, both members of the Me-HBOB- n -OAc ($n=4,5$) series were shown to exhibit SmA and E phases characterized, respectively, by focal-conic and fan-like textures with concentric arcs. The SmA mesophase texture of Me-HBOB-5-OAc is given as representative in figure 5(a).

2.2.3. Alkoxy esters. The lower members (methoxy to pentoxy) of the alkoxy esters based on the HBC unit, reported by Gray *et al.* [8] did not exhibit liquid crystalline behaviour, whereas the higher members (hexoxy ester onwards) exhibited a smectic mesophase. The HBB-based alkoxy esters (Me-HBB- n -H, $n=4,5$) were found to be non-mesomorphic by DSC and POM (table 3). However, the corresponding esters of HBOB derivatives (Me-HBOB- n -H, $n=4,5$) exhibited E, figure 5(b), and SmA mesophases with a typical fan-like texture with concentric arcs and focal-conic texture, respectively.

2.2.4. Hydroxyalkoxy acids. All three series of hydroxyalkoxy acids (H-HBC- n -OH, H-HBB- n -OH

Table 4. DSC, POM and XRD data for hydroxyalkoxy acids and alkoxy acids: transition temperatures in °C, enthalpy changes in kJ mol⁻¹.

Carboxylic acids	DSC ^a				POM ^b		<i>d</i> -spacings at SmA/Å ^c	Molecular length/Å ^d
	<i>T</i> ₁	<i>T</i> ₂	Δ <i>H</i> ₁	Δ <i>H</i> ₂	<i>T</i> _a	<i>T</i> _b		
H-HBC-4-OH	183(179)	238(229)	1.3	5.2	182(213)	238(227)	33.2,16.8,4.4	16.7
H-HBC-5-OH	188(180)	254(249)	10.5	7.4	171(200)	250(243)	34.3,17.3,4.5	17.6
H-HBB-4-OH	168(159)	173(168)	8.7	11.0	152(170)	182(180)	34.7,19.0,4.0	19.3
H-HBB-5-OH	137(129)	151(150)	1.1	11.5	141(151)	163(159)	38.4,20.2,4.5	20.6
H-HBOB-4-OH	255(211)	283(272)	8.7	8.7	220(208)	285(276)	40.3,19.8,3.8	19.5
H-HBOB-5-OH	232(182)	245(232)	5.1	3.2	175(170)	230(222)	39.6,20.5,3.7	20.9
H-HBB-4-H	—	150(144)	—	36.0	—	154(144)	—	—
H-HBB-5-H	52(47)	145(140)	16.7	47.2	—	149(143)	—	—
H-HBOB-4-H	—	205(192)	—	41.2	—	209(194)	—	—
H-HBOB-5-H	—	202(190)	—	41.5	—	205(191)	—	—

^aCalorimetric data on heating transition temperatures observed in the cooling scan are given in parentheses. ^bTransition temperatures observed under POM during the heating cycle; corresponding cooling cycle data are given in parentheses. ^cThe *d*-spacings value of the inner peak observed in XRD studies. ^dMolecular length calculated from bond lengths and bond angles (using HyperChem software).

and H-HBOB-*n*-OH, *n*=4,5) exhibited multiple peaks in DSC heating and cooling scans. The transition temperatures and the corresponding enthalpy changes are given in table 4. All the hydroxyalkoxy acids exhibited SmA mesophases with bâtonnets, focal-conic or broken fan textures when viewed under POM. Two representative optical micrographs are given in figure 5 (*c*, *d*).

The high temperature wide angle XRD studies of these hydroxyalkoxy acids confirmed the SmA phase (table 4). The diffraction pattern showed a sharp inner peak (corresponding to the molecular length) and a broad outer peak, which are typical of the SmA phase. These acids were found to exist in dimerized forms via hydrogen bonding as shown by the presence of peaks with *d*-spacing values equal to twice the molecular length.

2.2.5. Alkoxy acids. The alkoxy acids containing HBB and HBOB units (H-HBB-*n*-H and H-HBOB-*n*-H, *n*=4,5) did not exhibit liquid crystallinity when analysed by DSC and POM (table 4). The absence of a mesophase in the H-HBOB-*n*-H series of carboxylic acids is surprising on consideration that the corresponding esters (Me-HBOB-*n*-H) were mesomorphic.

However, the alkoxy acids of the hydroxybiphenyl-carboxylate derivatives (H-HBC-*n*-H) were reported to exhibit mesomorphism by Gray *et al.* [8]. The lower members (methoxy to butoxy acids) exhibited nematic mesophases and the higher members (pentoxy to decoxy acids) showed nematic and smectic mesophases.

2.3. Effect of connectivity and terminal functionality

Consider the two isomeric hydroxyalkoxy ester series Me-HBB-*n*-OH [15] and Me-HBC-*n*-OH, which differ in the way the biphenyl mesogen is connected with the ester group. In the former series the ester group is separated from the biphenyl mesogen by a trimethylene unit. Interestingly, this change led to the lowering of transition temperatures and disappearance of the mesophase due to increased flexibility imparted by the trimethylene unit. However, the introduction of a keto group in place of one of the methylene units of the Me-HBB-*n*-OH series gives rise to the Me-HBOB-*n*-OH series, which did exhibit liquid crystallinity. The keto group directly attached to the biphenyl mesogen increased the rigidity and polarity of the system and reinstated liquid crystallinity.

The mesophase observed in the case of hydroxyalkoxy esters Me-HBC-*n*-OH (*n*=4,5), was lost upon substitution of the hydroxy group by an acetyl group. The replacement of the hydroxy group by the acetyl group essentially increased the length of the spacer unit, which was reflected in the reduction of transition temperatures and disappearance of the mesophase. The acetyl derivatives of the HBB-based hydroxyalkoxy esters (Me-HBB-*n*-OAc) showed lower melting points and did not exhibit the liquid crystalline properties of the parent hydroxy esters. However, substitution of the hydroxy group by acetyl in the case of HBOB-based esters resulted in Me-HBOB-*n*-OAc, which was shown to be liquid crystalline, of course with reduced transition temperatures. This is because the rigidity and polarity imparted by the keto group could withstand the opposite effect of the acetyl group in these systems.

Replacement of the hydroxy group by hydrogen in case of Me-HBC-*n*-OH gives rise to Me-HBC-*n*-H [8, 9] and led to reduction in the transition temperatures and the mesophase range of the system. For example, the hydroxyalkoxy ester Me-HBC-6-OH showed transitions at 141, 146 and 162°C (G and SmA) whereas the equivalent alkoxy ester (Me-HBC-*n*-H) showed transitions at 124, 132 and 139°C (E and B). Another difference in these two systems is that the lower members of the alkoxy esters (methoxy to pentoxy esters) were not liquid crystalline, whereas the corresponding hydroxyalkoxy esters (Me-HBC-*n*-OH) are mesomorphic. The reason for the hydroxyalkoxy esters showing higher transition temperatures than the alkoxy esters is the ability of the former esters to form dimers through hydrogen bonding (confirmed by XRD studies). This leads to an increase in the rigidity of the system, thereby increasing the transition temperatures. A similar effect was observed for HBB and HBOB esters on replacing the hydroxy group by hydrogen. The SmA and E mesophases observed in Me-HBOB-*n*-OH are retained in the corresponding Me-HBOB-*n*-H. No mesophase was observed in Me-HBB-*n*-H, as in case of the hydroxy derivative Me-HBB-*n*-OH.

A comparison of the mesophase characteristics of the hydroxyalkoxy esters (Me-HBC-*n*-OH, Me-HBOB-*n*-OH and Me-HBB-*n*-OH, *n*=4,5) and the respective acids (H-HBC-*n*-OH, H-HBOB-*n*-OH and H-HBB-*n*-OH, *n*=4,5) reveals that the presence of the carboxylic acid group facilitates stronger hydrogen bonding in the hydroxyalkoxy acids, resulting in higher transition temperatures than for the hydroxyalkoxy esters. However, the mesophase type remains unaltered in the acid derivatives of the Me-HBC-*n*-OH and Me-HBOB-*n*-OH series. Interestingly, in the Me-HBB-*n*-OH series, liquid crystallinity was induced upon substitution of

the ester by an acid group. This could be due to the increased feasibility of hydrogen bonding facilitated by the presence of two polar groups, namely, hydroxy and carboxylic acid. Similarly, the clearing temperatures were found to be higher for the alkoxy acids (H-HBC-*n*-H, H-HBB-*n*-H and H-HBOB-*n*-H) than for the respective alkoxy esters (Me-HBC-*n*-H, Me-HBB-*n*-H and Me-HBOB-*n*-H).

3. Conclusions

Two series of biphenyl-based hydroxyalkoxy esters, methyl 4'-(hydroxyalkoxy)biphenyl-4-carboxylate (Me-HBC-*n*-OH, *n*=3–8) and methyl 4-[4'-(ω -hydroxyalkoxy)biphenyl-4-yl]-4-oxobutyrates (Me-HBOB-*n*-OH, *n*=2–8), containing different numbers of flexible methylene spacers, were synthesized. The Me-HBC-*n*-OH series exhibited SmA and G phases depending on the methylene spacer length, whereas all the members of the Me-HBOB-*n*-OH series showed SmA and E phases. The effect of connectivity was analysed by comparing the transition temperatures of these two ester series with those of another ester series (Me-HBB-*n*-OH) having a trimethylene unit separating the biphenyl mesogen from the ester functionality. Moving the carboxylate group away from the biphenyl moiety resulted in a reduction in rigidity of the system and caused loss of liquid crystallinity. However, substitution of one of the methylenes attached to the biphenyl by a keto group (Me-HBOB-*n*-OH) increased the polarity and rigidity of the system and reinstated the mesomorphic behaviour. The substitution of hydroxy group by acetyl or hydrogen in these three series of esters decreased the transition temperatures and led to the disappearance of the mesophase in the case of HBC-based esters. However, the substitution of the carbomethoxy group by carboxylic acid in the hydroxyalkoxy ester series resulted in an increase in the transition temperatures, and the appearance of liquid crystallinity in the case of systems containing the HBB basic unit.

4. Experimental

4.1. Characterization

¹H NMR spectra were recorded on a VXR 300 NMR spectrometer (300 MHz) using the TMS/solvent signal as an internal reference. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The samples were recorded as thin KBr pellets. Melting points were recorded on a Veego melting point apparatus by the capillary method and were uncorrected. Microanalysis experiments were carried out on a FLASH EA 1112 model of Thermo Finnigan (Italy) with a thermal conductivity detector. DSC measurements

were conducted with a Perkin-Elmer Pyris 6 DSC. The calorimeter was calibrated using indium metal as standard. About 2–5 mg samples were used with a heating rate of $10^{\circ}\text{C min}^{-1}$ under a flow of nitrogen (20 ml min^{-1}). A polarizing optical microscope (Olympus B-12) equipped with a Linkam TP94 hot stage was used for visual observations. The samples were heated between a slide and cover slip, and photomicrographs taken in the crossed-polarizer mode with an Olympus DP-11 digital camera. XRD experiments were performed with a Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator and wide angle powder goniometer with a high temperature attachment. The generator was operated at 40 kV and 125 mA. The sample holder was a copper block and a thin layer of sample was spread on the copper plate at a heating rate of $10^{\circ}\text{C min}^{-1}$. The molecular length was calculated by using HyperChem software.

4.2. Synthesis

4'-Hydroxybiphenyl-4-carboxylic acid, α,ω -haloalkanols, *N,N*-dimethyl formamide (DMF), tetrahydropyran (THP) and terephthal-bis(4-butylaniline) (TBBA) were purchased from Aldrich and used as received. The hydroxyalkoxy esters, Me-HBB-*n*-OH ($n=2-8$), acetyloxy ester (Me-HBB-*n*-OAc, $n=4,5$) and hydroxyalkoxy acids (H-HBB-*n*-OH, $n=4,5$) were synthesized using literature procedures [15].

4.2.1. Methyl 4'-hydroxybiphenyl-4-carboxylate (2). 4'-Hydroxybiphenyl-4-carboxylic acid, **1** (6 g, 28 mmol), was dissolved in 50 ml of anhydrous methanol; to this was added 1.5 ml of conc. sulphuric acid and the solution was heated at reflux for 8 h. The excess methanol was then removed *in vacuo* and the pasty mass obtained poured into an excess of water. The grey solid formed was filtered, washed first with sodium bicarbonate solution, then with water and dried to obtain the crude product. Column purification (10% ethyl acetate in petroleum ether as eluant) yielded a white solid; 6.1 g (94%), mp $219-220^{\circ}\text{C}$. $^1\text{H NMR}$ (DMSO- d_6 , ppm): δ 3.86 (s, 3H), 6.88 (d, 2H, $J=8.79\text{ Hz}$), 7.58 (d, 2H, $J=8.79\text{ Hz}$), 7.73 (d, 2H, $J=8.42\text{ Hz}$), 7.98 (d, 2H, $J=8.42\text{ Hz}$), 9.72 (s, 1H). IR (KBr, cm^{-1}): 3406, 3026, 2960, 1753, 1703, 1604, 1310, 1205, 861, 774. Anal: calcd for $\text{C}_{14}\text{H}_{12}\text{O}_3$, C 73.67, H 5.30; found, C 73.81, H 5.49%.

4.2.2. Methyl 4'-(ω -hydroxyalkoxy)biphenyl-4-carboxylate (Me-HBC-*n*-OH, $n=3,6-8$) and methyl 4'-(ω -acetyloxy)biphenyl-4-carboxylate (Me-HBC-*n*-OAc, $n=4,5$). Compound **2** (1 equiv), ω -bromoalkyl acetate

($n=4,5$) or ω -bromoalkanol ($n=3,6-8$) (1 equiv) and anhydrous potassium carbonate (3 equiv) were taken into a minimum amount of DMF and the mixture was heated at 90°C for 24 h. The solution was then cooled to room temperature, poured into an excess of water and extracted with chloroform. The organic layers were combined and washed with water. The organic layer was then dried over anhydrous sodium sulphate and concentrated to obtain a pale yellow solid. This was purified by column chromatography (10–20% ethyl acetate in petroleum ether as eluant) to give the product as a white crystalline solid. Me-HBC-3-OH: yield 63%, m.p. $178-179^{\circ}\text{C}$. $^1\text{H NMR}$ (CDCl_3 , ppm): δ 2.1 (m, 2H), 3.90 (t, 2H, $J=4.03\text{ Hz}$), 3.92 (s, 3H), 4.2 (t, 2H, $J=5.86\text{ Hz}$), 7.00 (d, 2H, $J=8.79\text{ Hz}$), 7.57 (d, 2H, $J=8.79\text{ Hz}$), 7.69 (d, 2H, $J=8.42\text{ Hz}$), 8.07 (d, 2H, $J=8.42\text{ Hz}$). IR (KBr, cm^{-1}): 3416 (b), 3020, 1719, 1604, 1525, 1434, 1282, 1215, 1113, 1047, 923, 759, 670. Anal: calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4$, C 71.31, H 6.34; found, C 71.21, H 6.27%. Me-HBC-4-OAc: yield 65%, m.p. $135-136^{\circ}\text{C}$. $^1\text{H NMR}$ (CDCl_3 , ppm): δ 1.83 (m, 4H), 2.06 (s, 3H), 3.93 (s, 3H), 4.04 (t, 2H, $J=5.68\text{ Hz}$), 4.16 (t, 2H, $J=6.04\text{ Hz}$), 6.98 (d, 2H, $J=8.79\text{ Hz}$), 7.56 (d, 2H, $J=8.60\text{ Hz}$), 7.62 (d, 2H, $J=8.24\text{ Hz}$), 8.08 (d, 2H, $J=8.42\text{ Hz}$). IR (KBr, cm^{-1}): 2948, 2875, 1724, 1601, 1520, 1495, 1437, 1287, 1216, 1114, 1038, 957, 824, 767. Anal: calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5$, C 70.16, H 6.48; found, C 70.21, H 6.32%.

4.2.3. 4'-(ω -Hydroxyalkoxy)biphenyl-4-carboxylic acid (H-HBC-*n*-OH, $n=4,5$). Me-HBC-*n*-OAc ($n=4,5$) was heated under reflux in 10% aqueous NaOH for 8 h. As the reaction progressed the solid dissolved in the alkaline solution and a clear solution was obtained. The reaction mixture was then cooled to room temperature, poured into an excess of water and acidified with concd HCl. The precipitated white solid was then extracted with ethyl acetate; the organic layers were combined and washed with water. The ethyl acetate layer was dried over anhydrous sodium sulphate and concentrated to obtain the product as white solid. H-HBC-4-OH: yield 98%, m.p. $219-220^{\circ}\text{C}$. $^1\text{H NMR}$ (DMSO- d_6 , ppm): δ 1.5 (m, 2H), 1.76 (m, 2H), 3.46 (t, 2H, $J=5.86\text{ Hz}$), 4.03 (t, 2H, $J=6.59\text{ Hz}$), 4.47 (t, 2H, $J=5.13\text{ Hz}$), 7.04 (d, 2H, $J=8.42\text{ Hz}$), 7.67 (d, 2H, $J=8.63\text{ Hz}$), 7.75 (d, 2H, $J=8.42\text{ Hz}$), 7.98 (d, 2H, $J=8.42\text{ Hz}$). IR (KBr, cm^{-1}): 3289, 2951, 2872, 1681, 1601, 1412, 1275, 1200, 1129, 1051, 956, 831, 774. Anal: calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4$, C 71.31, H 6.34; found, C 70.89, H 6.00%.

4.2.4. Methyl 4'-(ω -hydroxyalkoxy)biphenyl-4-carboxylate (Me-HBC-*n*-OH, $n=4,5$). H-HBC-*n*-OH ($n=4,5$)

was dissolved in a minimum amount of anhydrous methanol and heated at reflux for 6 h in the presence of a catalytic amount of concd sulphuric acid. Excess methanol was removed and the pasty mass obtained was poured into an excess of water. The precipitated yellow solid was filtered, washed with water and dried. Column purification (20% ethyl acetate in petroleum ether as eluant) of the product yielded a white solid. Me-HBC-4-OH: yield 90%, m.p. 176–177°C. ¹H NMR (CDCl₃, ppm): δ 1.76 (m, 2H), 1.88 (m, 2H), 3.75 (t, 2H, *J*=6.23 Hz), 3.93 (s, 3H), 4.06 (t, 2H, *J*=6.23 Hz), 6.97 (d, 2H, *J*=8.79 Hz), 7.60 (dd, 4H), 8.06 (d, 2H, *J*=8.42 Hz). IR (KBr, cm⁻¹): 3485 (b), 3020, 2946, 1712, 1604, 1527, 1432, 1363, 1216, 1113, 1029, 957, 767, 670. Anal: calcd for C₁₈H₂₀O₄, C 71.98, H 6.71; found, C 72.10, H 6.35%.

4.2.5. Methyl 4-(4'-alkoxybiphenyl)-4-yl-butyrate (Me-HBB-*n*-H, *n*=4,5). Methyl 4-(4'-hydroxybiphenyl-4-yl)-butyrate, **3** (1 equiv), 1-bromobutane or 1-bromopentane (1 equiv) and anhydrous potassium carbonate (3 equiv) were taken into acetone and heated under reflux for 42 h. The reaction mixture was filtered, and the filtrate concentrated and loaded onto a column. The product was eluted with 2% ethyl acetate in petroleum ether to yield a white crystalline solid. Me-HBB-4-H: yield 33%, m.p. 68–69°C. ¹H NMR (CDCl₃, ppm): δ 0.98 (t, 3H, *J*=7.32 Hz), 1.55 (m, 2H), 1.78 (p, 2H), 1.98 (p, 2H), 2.36 (t, 2H, *J*=7.32 Hz), 2.68 (t, 2H, *J*=7.32 Hz), 3.67 (s, 3H), 3.99 (t, 2H, *J*=6.59 Hz), 6.95 (d, 2H, *J*=8.78 Hz), 7.22 (d, 2H, *J*=8.05 Hz), 7.48 (m, 4H). IR (KBr, cm⁻¹): 3454, 2955, 2920, 2870, 1739, 1607, 1500, 1465, 1250, 1174, 803. Anal: calcd for C₂₁H₂₆O₃, C 77.27, H 8.03; found, C 77.47, H 7.88%.

4.2.6. 4-(4'-Alkoxybiphenyl)-4-yl-butyric acid (H-HBB-*n*-H, *n*=4,5). Methyl 4-(4'-alkoxybiphenyl)-4-yl-butyrate (Me-HBB-*n*-H, *n*=4,5) was heated at reflux with 10% aqueous NaOH for 12 h. The clear solution obtained was poured into cold water and acidified with concd HCl. The precipitated white solid was extracted with ethyl acetate; the organic layers were combined and washed with water. The ethyl acetate solution was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain the product as white solid. H-HBB-4-H: yield 85%, m.p. 148–149°C. ¹H NMR (CDCl₃, ppm): δ 0.98 (t, 3H, 7.68 Hz), 1.52 (m, 2H), 1.78 (p, 2H), 1.99 (p, 2H), 2.40 (t, 2H, *J*=8.7 Hz), 2.70 (t, 2H, *J*=7.68 Hz), 4.00 (t, 2H, *J*=6.22 Hz), 6.95 (d, 2H, *J*=8.78 Hz), 7.24 (d, 2H, *J*=8.78 Hz), 7.47 (m, 4H). IR (KBr, cm⁻¹): 3432, 2957, 2928, 2872, 1693, 1605, 1498, 1441, 1281, 1250, 1174,

1032, 803. Anal: calcd for C₂₀H₂₄O₃, C 76.89, H 7.74; found, C 76.58, H 7.50%.

4.2.7. 4-(4'-Hydroxybiphenyl-4-yl)-4-oxobutyric acid (5). 4-(4'-Acetylbiphenyl-4-yl)-4-oxobutyric acid, **4** (5 g, 16.03 mmol) was heated at reflux with concd HCl/H₂O (1/1) for 6 h. The reaction mixture was then cooled to room temperature and poured into an excess of cold water. The precipitate was filtered, washed with water and dried under reduced pressure to obtain a pale yellow spongy solid; yield 4.2 g (97%), m.p. >210°C (dec). ¹H NMR (DMSO-*d*₆, ppm): δ 2.59 (t, 2H, *J*=6.1 Hz), 3.26 (t, 2H, *J*=6.7 Hz), 6.88 (d, 2H, *J*=8.55 Hz), 7.60 (d, 2H, *J*=8.55 Hz), 7.74 (d, 2H, *J*=8.55 Hz), 8.00 (d, 2H, *J*=7.33 Hz), 9.74 (s, 1H), 12.14 (s, 1H). IR (KBr, cm⁻¹): 3313, 2914, 1719, 1680, 1600, 1592, 1446, 1360, 1265, 1169, 970, 814, 704, 567. Anal: calcd for C₁₆H₁₄O₄, C 71.10, H 5.22; found, C 71.59, H 4.72%.

4.2.8. Methyl 4-(4'-hydroxybiphenyl-4-yl)-4-oxobutyrate (6). Compound **5** (1.5 g, 5.55 mmol) was dissolved in 30 ml of anhydrous methanol and heated under reflux for 8 h in the presence of 0.5 ml of concd sulphuric acid. Excess methanol was removed under reduced pressure and the resulting pasty mass was poured into water. The solid obtained was filtered, washed with NaHCO₃ solution, then with water and dried to obtain a yellow solid. Further purification by column chromatography using 20% ethyl acetate in petroleum ether as the eluant resulted in a white crystalline solid; yield 1.3 g (82%), m.p. 175–176°C. ¹H NMR (DMSO-*d*₆, ppm): δ 2.66 (t, 2H, *J*=6.22 Hz), 3.30 (t, 2H, *J*=6.22 Hz), 3.60 (s, 3H), 6.88 (d, 2H, *J*=8.6 Hz), 7.59 (d, 2H, *J*=8.78 Hz), 7.73 (d, 2H, *J*=8.42 Hz), 7.99 (d, 4H, *J*=8.6 Hz), 9.8 (s, 1H). IR (KBr, cm⁻¹): 3381, 2997, 2948, 2910, 1715, 1681, 1699, 1531, 1446, 1285, 1236, 1192, 980, 825, 652. Anal: calcd for C₁₇H₁₆O₄, C 71.82, H 5.67; found, C 72.03, H 5.72%.

4.2.9. Methyl 4-[4'-(ω-hydroxyalkoxy)biphenyl-4-yl]-4-oxobutyrate (Me-HBOB-*n*-OH, *n*=2, 3, 6–8) and methyl 4-[4'-(ω-acetylalkoxy)biphenyl-4-yl]-4-oxobutyrate (Me-HBOB-*n*-OAc *n*=4,5). Compound **5** (1 equiv), ω-haloalkyl acetate (*n*=4,5) or ω-haloalkanol (*n*=2,3,6–8) (1 equiv) and anhydrous potassium carbonate (3 equiv) were taken into a minimum amount of DMF and heated at 90°C for 21–24 h. The reaction mixture was then cooled to room temperature, poured into an excess of water and extracted with chloroform. The organic layers were combined and washed with water. The chloroform layer was dried over anhydrous sodium sulphate and concentrated to obtain a pale yellow solid.

The acetyl esters, Me-HBOB-*n*-OAc (*n*=4,5) (5% ethyl acetate in petroleum ether as eluant) and the hydroxy esters, Me-HBOB-*n*-OH (*n*=2,3,6–8) (10% petroleum ether in chloroform as eluant) were purified by column chromatography to obtain products as white crystalline solids. Me-HBOB-2-OH: yield 53%, m.p. 160–161°C. ¹H NMR (CDCl₃, ppm): δ 2.79 (t, 2H, *J*=6.59 Hz), 3.35 (t, 2H, *J*=6.59 Hz), 3.72 (s, 3H), 4.0 (t, 2H, *J*=4.39 Hz), 4.14 (t, 2H, *J*=4.39 Hz), 7.03 (d, 2H, *J*=8.78 Hz), 7.56 (d, 2H, *J*=8.78 Hz), 7.63 (d, 2H, *J*=8.05 Hz), 8.03 (d, 2H, *J*=8.78 Hz). IR (KBr, cm⁻¹): 3435, 2943, 2865, 1731, 1681, 1600, 1531, 1496, 1441, 1375, 1232, 1158, 1074, 818. Anal: calcd for C₁₉H₂₀O₅, C 69.50, H 6.14; found, C 69.63, H 6.02%. Me-HBOB-4-OAc: yield 81%, m.p. 112–113°C. ¹H NMR (CDCl₃, ppm): δ 1.87 (m, 4H), 2.06 (s, 3H), 2.79 (t, 2H, *J*=6.78 Hz), 3.35 (t, 2H, *J*=6.72 Hz), 3.72 (s, 3H), 4.04 (t, 2H, *J*=5.8 Hz), 4.16 (t, 2H, *J*=6.42 Hz), 6.98 (d, 2H, *J*=8.56 Hz), 7.56 (d, 2H, *J*=8.56 Hz), 7.64 (d, 2H, *J*=8.23 Hz), 8.04 (d, 2H, *J*=8.25 Hz). IR (KBr, cm⁻¹): 3447, 2952, 2911, 2877, 1735, 1677, 1601, 1529, 1473, 1323, 1257, 1178, 1048, 967, 825, 699. Anal: calcd for C₂₃H₂₆O₆, C 69.33, H 6.58; found, C 69.02, H 6.90%.

4.2.10. 4-[4'-(ω -Hydroxyalkoxy)biphenyl-4-yl]-4-oxobutyric acid (H-HBOB-*n*-OH, *n*=4,5). Me-HBOB-*n*-OAc (*n*=4,5) was taken into 10% aqueous NaOH and heated at reflux for 24 h. The reaction mixture was cooled to room temperature, poured into excess of water and the mixture acidified with concd HCl. The white solid obtained was filtered, washed with water and dried to obtain the product. H-HBOB-4-OH: yield 93%, m.p. 173–174°C. ¹H NMR (DMSO-*d*₆, ppm): δ 1.55 (m, 2H), 1.79 (m, 2H), 2.59 (t, 2H, *J*=6.04 Hz), 3.27 (t, 2H, *J*=5.86 Hz), 3.45 (t, 2H, *J*=5.31 Hz), 4.04 (t, 2H, *J*=6.4 Hz), 4.5 (t, 1H), 7.04 (d, 2H, *J*=8.78 Hz), 7.69 (d, 2H, *J*=8.78 Hz), 7.77 (d, 2H, *J*=8.42 Hz), 8.02 (d, 2H, *J*=8.42 Hz), 12.2 (bs, 1H). IR (KBr, cm⁻¹): 3420 (b), 2950, 2911, 2872, 1714, 1675, 1598, 1399, 1247, 1192, 1041, 944, 810, 625. Anal: calcd for C₂₀H₂₂O₅, C 70.16, H 6.48; found, C 70.29, H 6.71%.

4.2.11. Methyl 4-[4'-(ω -hydroxyalkoxy)biphenyl-4-yl]-4-oxobutyrate (Me-HBOB-*n*-OH, *n*=4,5). H-HBOB-*n*-OH (*n*=4,5) was dissolved in anhydrous methanol and heated under reflux for 15 h in the presence of a catalytic amount of concd sulphuric acid. The reaction mixture was cooled to room temperature, poured in water, and the precipitated pale yellow solid filtered, washed with water and dried. The product was purified by column chromatography using 10% petroleum ether in chloroform as eluant. Me-HBOB-4-OH: yield 76%, m.p. 181–182°C. ¹H NMR (CDCl₃, ppm): δ 1.6–1.8 (m,

4H), 2.79 (t, 2H, *J*=4.03 Hz), 3.38 (t, 2H, *J*=2.8 Hz), 3.72 (s, 3H), 3.78 (t, 2H, *J*=6.22 Hz), 4.06 (t, 2H, *J*=6.04 Hz), 6.97 (d, 2H, *J*=8.96 Hz), 7.56 (d, 2H, *J*=8.96 Hz), 7.64 (d, 2H, *J*=8.42 Hz), 8.03 (d, 2H, *J*=8.42 Hz). IR (KBr, cm⁻¹): 3434, 2948, 2866, 1737, 1688, 1601, 1528, 1497, 1255, 1196, 1048, 818, 794. Anal: calcd for C₂₁H₂₄O₅, C 70.77, H 6.79; found, C 70.46, H 6.25%.

4.2.12. Methyl 4-(4'-alkoxybiphenyl)-4-yl-oxobutyrate (Me-HBOB-*n*-H, *n*=4,5). Compound **6** (1 equiv), 1-bromobutane or 1-bromopentane (1 equiv) and anhydrous potassium carbonate (3 equiv) were taken into acetone and heated under reflux for 24 h. The reaction mixture was then filtered; the filtrate was concentrated and loaded onto a column. The product was obtained as a white crystalline solid using 30% petroleum ether in chloroform as eluant. Me-HBOB-4-H: yield 53%, m.p. 138–139°C. ¹H NMR (CDCl₃, ppm): δ 0.99 (t, 3H, *J*=7.32 Hz), 1.52 (m, 2H), 1.80 (m, 2H), 2.79 (t, 2H, *J*=6.83 Hz), 3.35 (t, 2H, *J*=6.83 Hz), 3.72 (s, 3H), 4.02 (t, 2H, *J*=6.83 Hz), 6.99 (d, 2H, *J*=8.78 Hz), 7.67 (d, 2H, *J*=8.78 Hz), 7.65 (d, 2H, *J*=8.29 Hz), 8.03 (d, 2H, *J*=8.78 Hz). IR (KBr, cm⁻¹): 3452, 2956, 2871, 1739, 1677, 1601, 1527, 1497, 1326, 1254, 1175, 1070, 974, 822, 793. Anal: calcd. for C₂₁H₂₄O₄, C 74.09, H 7.11; found, C 73.67, H 7.33%.

4.2.13. 4-(4'-Alkoxybiphenyl)-4-yl-oxobutyric acid (H-HBOB-*n*-H, *n*=4,5). Me-HBOB-*n*-H (*n*=4,5) was heated at reflux with 10% aqueous NaOH for 12 h. The clear solution obtained was poured into cold water and acidified with concd HCl. The precipitated white solid was extracted with ethyl acetate, and the organic layers combined and washed with water. The ethyl acetate solution was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain the product as a yellow solid. Further purification by column chromatography with chloroform as eluant gave a white solid. H-HBOB-4-H: yield 85%, m.p. 205–206°C. ¹H NMR (CDCl₃, ppm): δ 0.94 (t, 3H, *J*=7.32 Hz), 1.45 (m, 2H), 1.72 (p, 2H), 2.59 (t, 2H, *J*=6.34 Hz), 3.27 (t, 2H, *J*=6.34 Hz), 4.03 (t, 2H, *J*=6.34 Hz), 7.05 (d, 2H, *J*=8.78 Hz), 7.70 (d, 2H, *J*=8.78 Hz), 7.85 (d, 2H, *J*=8.78 Hz), 8.03 (d, 2H, *J*=8.29 Hz), 12.15 (s, 1H). IR (KBr, cm⁻¹): 3437, 2956, 2873, 1703, 1675, 1602, 1527, 1410, 1335, 1257, 1197, 1040, 997, 910, 828. Anal: calcd for C₂₀H₂₂O₄, C 73.60, H 6.79; found, C 73.47, H 7.09%.

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References

- [1] G.W. Gray. *Molecular Structure and the Properties of Liquid Crystals*. Academic Press, London and New York (1962); G.W. Gray, K.J. Harrison and J.A. Nash. *Electron. Lett.*, **9**, 130 (1973); G.W. Gray, K.J. Harrison and J.A. Nash. In *Proceedings of Liquid Crystal International Conference*, edited by S. Chandrasekhar (Indian Academy of Sciences, Bangalore, India), p381 (1975).
- [2] G.W. Gray. *J. Physique*, **36**, C1–337 (1975).
- [3] D. Demus, L. Ritcher, C.-E. Rurup, H. Sackmann, H. Schubert. *J. Physique*, **36**, C1–349 (1975).
- [4] A.J. Eagle, T.M. Herrington, N.S. Isaacs. *Liq. Cryst.*, **24**, 735 (1998).
- [5] K. Czuprynski, J. Przedmojski, R. Dabrowski, M. Brodzik. *Mol. Cryst. liq. Cryst.*, **299**, 503 (1997).
- [6] A.J. Leadbetter, P.A. Tucker, G.W. Gray, A.R. Tajbakhsh. *Liq. Cryst.*, **8**, 1 (1990).
- [7] G.W. Gray, B. Jones. *J. chem. Soc. Abstr.*, 236 (1955).
- [8] G.W. Gray, J.B. Hartley, B. Jones. *J. chem. Soc. Abstr.*, 1412 (1955).
- [9] D. Demus, J.W. Goodby, G.W. Gray, H. Sackmann. *Mol. Cryst. liq. Cryst.*, **56**, 311 (1980).
- [10] J.W. Goodby, G.W. Gray. *J. Physique*, **37**, C3–17 (1976).
- [11] J.W. Goodby, G.W. Gray. *Mol. Cryst. liq. Cryst.*, **48**, 127 (1978); D. Demus, J.W. Goodby, G.W. Gray and H. Sackmann. *Mol. Cryst. liq. Cryst. Lett.*, **56**, 311 (1980); G.W. Gray and J.W. Goodby. *Smectic Liquid Crystals*, (Leonard Hill), p106 (1984).
- [12] S.D. Cohen, C.A.R. Diuguid, J.C. Poirier, J.K. Swadesh. *Mol. Cryst. liq. Cryst.*, **78**, 135 (1981).
- [13] J. Swadesh, H. Fischer. *Mol. Cryst. liq. Cryst.*, **275**, 175 (1996).
- [14] A. Oku, T. Harada, K. Kita. *Tetrahedron Lett.*, **23**, 681 (1982).
- [15] T. Ranganathan, C. Ramesh, A. Kumar. *J. polym. Sci. polym. Chem. Ed.*, **42**, 2734 (2004).
- [16] M.E. Neubert, L.J. Maurer. *Mol. Cryst. liq. Cryst.*, **43**, 313 (1977).
- [17] L. Richter, D. Demus, H. Sackmann. *Mol. Cryst. liq. Cryst.*, **71**, 269 (1981).