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A convenient synthesis and the mesomorphic properties of new chiral ferroelectric thiobenzoates†

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A secondary chiral (*R*)-(−)-2-alcohol underwent the Mitsunobu reaction with triphenylphosphine, diethyl azodicarboxylate and ethyl 4-hydroxybiphenylcarboxylate, resulting in the desired (*S*)-(+)-product with high enantiomeric purity ($>99\%$ ee), with the chiral branched chain attached to the biphenyl. This method is operationally simple and provides the very important chiral precursor in good yields (62% in dry THF and 72% in dry Et_2O). The condensation of the (*S*)-(+)-acid chloride from this material and a suitable 4-*n*-alkylthiophenol in toluene in the presence of pyridine or triethylamine furnishes the chiral (*S*)-(+)-thiobenzoate liquid crystals in good yields (80–83% in pyridine and 65–68% in Et_3N). (*S*)-(+)-4-(1-Methylheptyloxy)biphenyl 4-alkylthiobenzoates are abbreviated **(*S*)-MHOBS*n***, where *n* varies from 4 to 10 and denotes the number of carbon atoms in the alkyl chain. DSC, polarizing microscopy and X-ray diffraction showed that the **(*S*)-MHOBS*n*** series possesses a rich phase polymorphism: two highly ordered tilted phases CrG* and SmI*, as well as the ferroelectric smectic C (SmC*) and chiral nematic (N*) phase. In this series, the seldom observed transition between the chiral phases SmI*–SmC* is seen. All the compounds possess stable enantiotropic SmC* and N* phases. The existence of weak intermolecular hydrogen-bonding in **(*S*)-MHOBS*n*** was confirmed by FTIR spectroscopy.

1. Introduction

Phase polymorphism is very dependent on chemical and optical purity, so the synthesis of chiral liquid crystals with high enantiomeric purity is very important [1, 2]. The (*R*)- or (*S*)- chiral configuration in liquid crystal phases changes or induces, for example, the size of pitch of the cholesteric (N*) and smectic phases (e.g. SmC*), or leads to other chiral structures by short or long range orientational order. The interest in chiral liquid crystals is mainly due to their potential for application in display technology [3, 4]. Until very recently, in the synthesis of chiral liquid crystalline thioesters containing two benzene rings [5–7], three benzene rings [8–11] and a biphenyl group [12–14], the chiral groups of the branched terminal chain have been connected to benzene rings. Only in two cases of chiral thioesters have the chiral branched groups been connected to a biphenyl system: specifically, the 2-methylbutoxy group [15] and 3-fluoro-2-methylbutyric acid [16]. It was of interest to detemine how the addition of the chiral branched chain, 2-methylheptyloxy, directly to the biphenyl group would influence the phase behaviour of the thiobenzoate. Here are reported the convenient synthesis and properties of ferroelectric liquid crystals belonging to a new homologous series of chiral thiobenzoates, the (*S*)-(+)-4-(1-methylheptyloxy)-biphenyl 4-alkylthiobenzoates, $C_6H_{13}C^*H(CH_3)$–O–Ph–Ph–COS–Ph–C_nH_{2n+1}, abbreviated **(*S*)-MHOBS*n*** (*n* varies from 4 to 10 and denotes the number of carbon atoms in the alkyl chain), in which the chiral branched chain (*S*)-(1-methylheptyloxy) is attached to the biphenyl.

2. Experimental

2.1. *Characterization*

The structure of the compounds was confirmed by elemental analysis, and IR and ^1H NMR spectroscopies. The NMR spectra were obtained on a Varian 500 MHz spectrometer ($CDCl_3$, TMS as internal standard); IR spectra were recorded on a FTIR Nicolet Magna 760 spectrometer using a minimum of 64 co-added scans at a resolution of $1\,cm^{-1}$. The temperature was controlled with a Linkam controller with accuracy of $\pm 0.1°C$; heating and cooling rates were $\pm 2K\,min^{-1}$. The mass spectrum was obtained using an MS spectrometer. The optical purity of compounds was

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determined by chiral HPLC. Transition temperatures were determined by means of a polarizing microscope with Linkam programmable heating stage THMSE 600. DSC measurements were performed using a (DSC822^e Mettler Toledo Star System differential scanning calorimeter. X-ray measurements were performed using a Philips X'Pert diffractometer and a Guinier symmetrical focusing transmission camera.

2.2. *Synthesis*

The typical Mitsunobu reaction of primary or secondary alcohols with an acid or acid compounds, such as phenols, in the presence of triphenylphosphine Ph_3P (TPP) and diethyl azodicarboxylate (DEAD) is widely used for the synthesis of alkyl-aryl ethers [17, 18]. The mechanism of the Mitsunobu reaction is a nucleophilic substitution S_N2 with inversion of configuration [19, 20]. Recently, Hulst *et al.* [21], Chanrasekhar and Kulkarni [22], Shi *et al.* [23], and Tang *et al.* [24] reported chiral versions of Mitsunobu reactions. The very important initial stage in our synthesis of these novel chiral liquid crystalline thiobenzoates was the Mitsunobu reaction. The acid compound was ethyl 4-hydroxybiphenylcarboxylate, **1**, and the secondary chiral alcohol was (*R*)-(−)-2-octanol, **(*R*)-2** (Chira Select >99%) with TPP and DEAD (see the scheme). To a solution of phenol **1** and TPP in anhydrous ether, chiral alcohol **(*R*)-2** with DEAD in dry ether was added at room temperature over 0.5 h.

The compound **(*S*)-3** was isolated from the reaction mixture using silica gel column chromatography (2.5 × 40 cm) in $CHCl_3$ and stepwise elution with $CHCl_3$:C_6H_{14} (1:1). The fractions showing a single TLC spot were pooled and the solvent evaporated. For confirmation of the expected S_N2 displacement of the inversion of configuration, chiral HPLC was used. The sample of **(*S*)-3**, showed the formation of the desired **(*S*)-3** with >99% ee with respect to the starting compound **(*R*)-2**. Thus, complete inversion took place, confirming that the course of the Mitsunobu reaction is the typical nucleophilic substitution S_N2. The molar ratio between reactants **1** and **(*R*)-2**, and the Mitsunobu reaction conditions influenced the yield of **(*S*)-3** (see table 1). The yield increased when the molar ratio increased from 1:1 to 1:1.7, and when the reaction was performed in the presence of anhydrous Et_2O rather than THF, from 39 to 72% and from 30 to 62%, respectively.

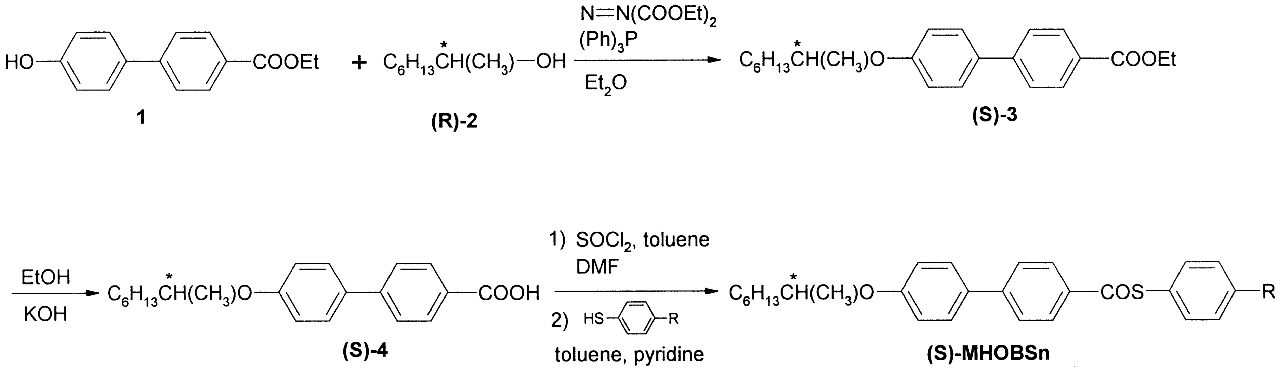
The pure compound **(*S*)-3** was hydrolysed in a solution of KOH in ethanol/water. Acid **(*S*)-4** was isolated by adding hydrochloric acid to the reaction mixture at 0°C and stirring vigorously for 1 h; it was purified by recrystallization from ethanol. The final compounds **(*S*)-MHOBS*n*** were obtained by condensation of the (*S*)-acid chloride and 4-*n*-alkylthiophenol in toluene in the presence of pyridine or triethylamine. It was confirmed that the use of pyridine is more effective than Et_3N in giving high yields (80–83 vs. 65–68%).

2.2.1. *Preparation of compound (S)-4*

To a solution of ethyl 4-hydroxybiphenyl carboxylate **1** (2 g, 8.8 mmol) in diethyl ether (50 ml) was added a solution of (*R*)-(−)-2-octanol **(*R*)-2** (1.82 g, 14 mmol) in anhydrous ether (30 ml) and DEAD (1.53 g, 8.8 mmol).

Table 1. The influence of molar ratio **1:(R)-2** on yields of (*S*)-3.

Molar ratio **1:(R)-2**	Yield/% (dry Et_2O)	Yield/% (dry THF)
1:1	39	30
1:1.2	42	33
1:1.3	48	41
1:1.4	54	52
1:1.5	63	59
1:1.6	69	60
1:1.7	72	62



Scheme. Synthesis of **(*S*)-MHOBS*n***.

The mixture was held at room temperature for 0.5 h; and then stirred for 3 h. The solution was evaporated to dryness and the residue chromatographed on a silica gel column (Kieselgel 100, Merck) and eluted with $CHCl_3$:C_6H_{14} (1:3). Fractions showing a single TLC spot were pooled and evaporated to give **(*S*)-3** as an off-white solid (m.p. 66.5–67.1°C). The configuration of a sample of **(*S*)-3** was confirmed by chiral HPLC assay. Compound **(*S*)-3** was dissolved in ethanol (60%, 60 ml) and KOH (4 g) added; the solution was heated under reflux for 2.5 h. The mixture was then cooled to room temperature and added to water with ice and hydrochloric acid. This suspension was left at 0°C for 1 h, filtered, and the white precipitate washed with water. An analytical sample was recrystallized from ethanol. The final product, 1.4 g (48%) of **(*S*)-4**, was obtained as a white solid: m.p. 171.1–172°C, 1H NMR ($CDCl_3$), ppm) δ 0.9 (m, 6H, $2xCH_3$).

2.2.2. *General procedure for the preparation of (S)-HMOBSn*

Details for **(*S*)-MHOBS5** are given as typical. To a suspension of the acid **(*S*)-4** (1.4 g, 4.3 mmol) in toluene was added thionyl chloride and the mixture heated to 50–60°C. The reaction mixture was stirred and heated under reflux for 5 h, then evaporated to dryness. The acid chloride, residue was dissolved in anhydrous toluene and added to a solution of 4-*n*-pentylthiophenol (0.8 g, 4.4 mmol) in a mixture of anhydrous toluene (50 ml) and pyridine (0.36 g, 4.5 mmol) held at 20°C. This reaction mixture was then stirred at 35–40°C for 4 h, and the progress of the reaction monitored by TLC; R_f 0.6 ($CHCl_3$:C_6H_{14} 1:1) and R_f 0.9 ($CHCl_3$). After evaporation of the toluene the residue was dissolved in hot ethanol; the solution was cooled slowly to room temperature and filtered. The final product was chromatographed on a silica gel column and eluted with $CHCl_3$:C_6H_{14} (1:3). The crude product thus obtained was recrystallized from ethanol; m.p. 63.2–64.2°C. ^1H NMR ($CDCl_3$, ppm) δ 0.9 (s, 6 H, $2\times CH_3$), 1.34 (m, 16 H, –CH_2–), 1.64 (m, 3 H, –C*–CH_3–), 2.78 (t, 2 H, –CH_2–Ar), 4.4 (s, 1 H, –C*H–), 6.97 (d, 2 H, Ar *ortho* to Ar–*R*), 7.27 (d, 2 H, Ar *ortho* to Ar–Ar), 7.43 (d, 2 H, Ar *ortho* to Ar–Ar), 7.56 (d, 2 H, Ar *ortho* to –OCS–Ar), 7.65 (d, 2 H Ar, *ortho* to Ar–COS–), 8.06 (d, 2 H Ar, *ortho* to –OCO–Ar). IR ν/cm^{-1} 2928, 1670, 1600, 1524, 1185. MS *m*/*z* 488 λ_1 (1.5%) (M^+), 309 λ_2 (100%) ($[C_6H_{13}C^*H(CH_3)O–C_6H_4C_6H_4CO]^+$), 197 λ_3 (37%) ($[HOC_6H_4C_6H_4CO]^+$), λ_4 168 (10.5%), 139 (10%), 115 (7.5%), 57 (9.0%), 43 (10.5%).

3. Results and discussion

Differential scanning calorimetry (DSC), thermal polarizing microscopy, X-ray diffraction, FTIR spectroscopy and measurement of spontaneous polarization (SP) were used to study the thermal behavior of **(*S*)-MHOBS4**, **5**, **6**, **7**, **8**, **9** and **10**. The phase behaviour was examined during heating and cooling at 2 K min^{-1}. Transition temperatures and associated enthalpy changes for **(*S*)-MHOBS*n*** are presented in table 2.

The interlayer distances from X-ray measurements, e.g. for **(*S*)-MHOBS5**, are shown in figure 1. The temperature dependence of the layer spacing corresponds with the temperatures and enthalpy changes of the phase transitions N*–SmC*, SmC*–SmI* and SmI*–CrG*. As can be seen from figure 1, the

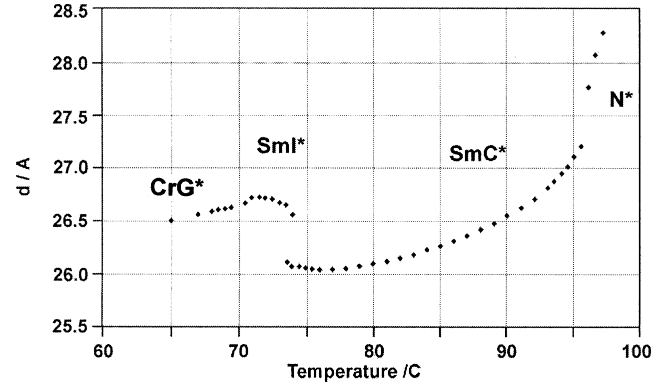


Figure 1. Temperature dependence of layer spacing for **(*S*)-MHOBS5**.

Table 2. Phase behaviour of the **(*S*)-MHOBS*n*** series obtained during heating. Transition temperatures (°C) and enthalpies (in parentheses, kcal mol^{-1}) were determined DSC method at 2 K min^{-1}; Cr denotes crystalline phase; CrG*, SmI* and SmC* are chiral smectic phases; N* is chiral nematic and I isotropic phases.

Compound	Phase transitions
(*S*)-MHOBS4	Cr 71.7 (3.95) CrG* 73.2 (0.12) SmC* 91.0 (0.16) N* 122 (0.12) I
(*S*)-MHOBS5	Cr 64.1 (5.63) CrG* 71.4 (0.07) SmI* 74.2 (0.36) SmC* 95.5 (0.24) N* 128.0 (0.19) I
(*S*)-MHOBS6	Cr 61.6 (3.36) CrG* 70.2 (0.02) SmI* 76.4 (0.31) SmC* 99.0 (0.36) N* 121.5 (0.10) I
(*S*)-MHOBS7	Cr 66.4 (2.77) CrG* 78.4 (0.24) SmC* 102.1 (0.17) N* 124.3 (0.19) I
(*S*)-MHOBS8	Cr 78.0 (6.27) CrG* 80.4 (0.41) SmC* 104.0 (0.30) N* 120.5 (0.31) I
(*S*)-MHOBS9	Cr 92.3 (4.56) SmC* 105.1 (0.11) N* 121.1(0.14) I
(*S*)-MHOBS10	Cr 92.4 (7.77) SmC* 106.1 (0.24) N* 118.6(0.31) I

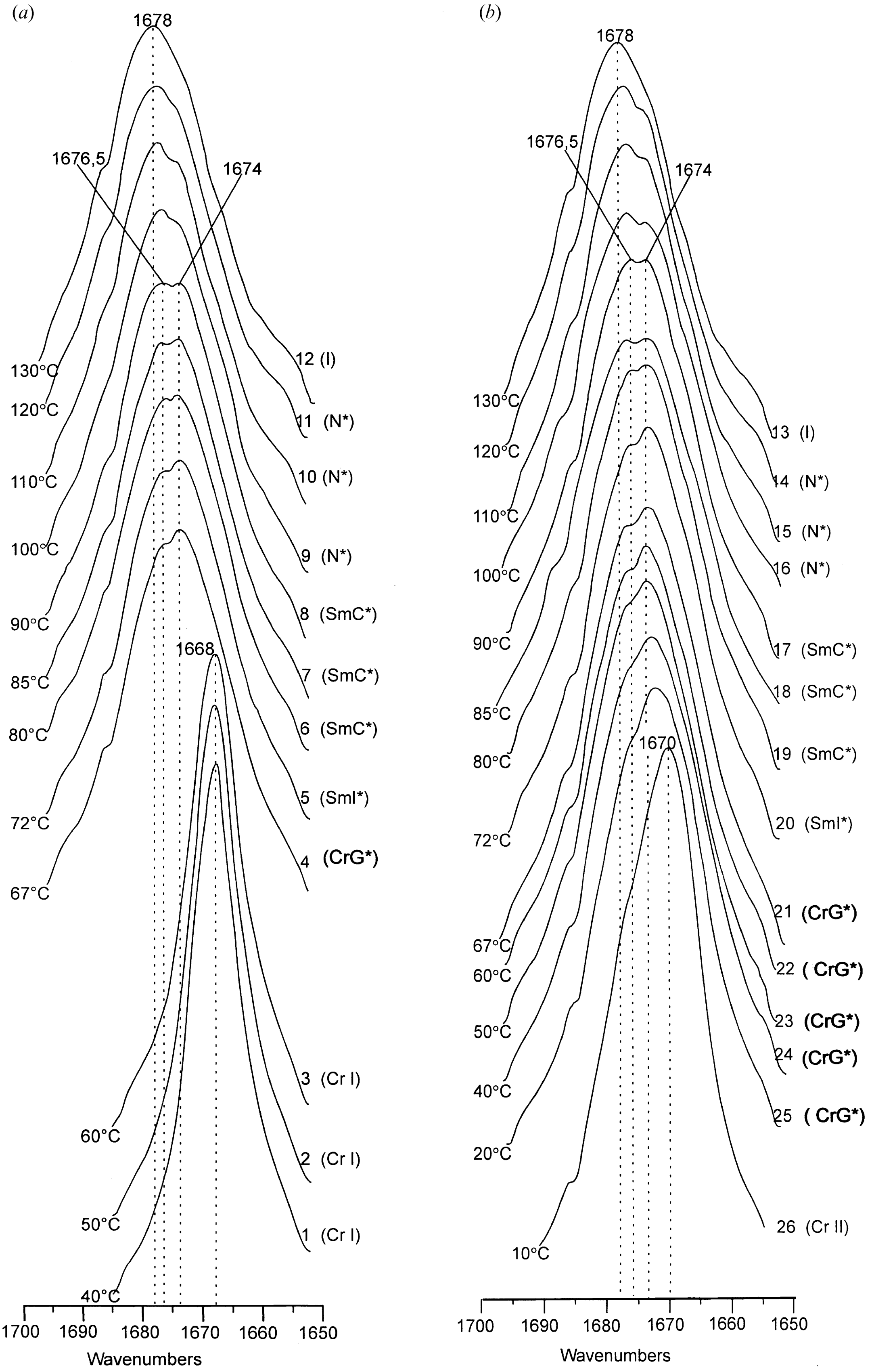

(a)
1678
1676,5
1674
1668
130°C
120°C
110°C
100°C
90°C
85°C
80°C
72°C
67°C
60°C
50°C
40°C
12 (I)
11 (N*)
10 (N*)
9 (N*)
8 (SmC*)
7 (SmC*)
6 (SmC*)
5 (SmI*)
4 (CrG*)
3 (Cr I)
2 (Cr I)
1 (Cr I)
1700
1690
1680
1670
1660
1650
Wavenumbers
(b)
1678
1676,5
1674
1670
130°C
120°C
110°C
100°C
90°C
85°C
80°C
72°C
67°C
60°C
50°C
40°C
20°C
10°C
13 (I)
14 (N*)
15 (N*)
16 (N*)
17 (SmC*)
18 (SmC*)
19 (SmC*)
20 (SmI*)
21 (CrG*)
22 (CrG*)
23 (CrG*)
24 (CrG*)
25 (CrG*)
26 (Cr II)
1700
1690
1680
1670
1660
1650
Wavenumbers

Table 3. Carbonyl stretching region of the FTIR spectrum of **(*S*)-MHOBS5**. Cr denotes crystalline phase; CrG*, SmI* and SmC* are chiral smectic phases; N* is chiral nematic and I isotropic phases.

Phase	Spectral position/cm^{-1}	Characteristics
Cr	1668	sharp single band
CrG*	1674–1676.5	asymmetrical doublet, 1674 more intense
SmI*	1674–1676	asymmetrical doublet, 1674 more intense
SmC*	1674–1676	equal two bands
N*	1676	band at 1676 and a weak shoulder near 1674
I	1678	broad single band

interlayer distances for the smectic phases of **(*S*)-MHOBS5** differ from the length of the molecules. In the SmC* phase the layer spacing *d* is approximately 0.88–0.84 of the actual molecular length *l* (30.67 Å calculated from semiempirical MINDO3) in its fully extended conformation, including the covalent radii of H-atoms.

All the compounds possess a rich phase polymorphism in the range from room temperature to 130°C, including monotropic and enantiotropic phases. The mesomorphic phases were identified using miscibility and XRD [25]. The compounds **(*S*)-MHOBS5** and **6** exhibit four mesophases; **(*S*)-MHOBS4**, **7** and **8** has three; **(*S*)-MHOBS9** and **10** show two enantiotropic liquid crystalline phases. **(*S*)-MHOBS5** and **6** show two highly ordered tilted mesophases, CrG* and SmI*. They show a very interesting and seldom observed phase transition between the highly ordered tilted chiral smectic I phase (SmI*) and the ferroelectric smectic C phase (SmC*). The clearing temperatures show a typical odd–even effect, decreasing on increasing the length of the alkyl chain. All the liquid crystals synthesized possess two enantiotropic phases: chiral nematic (N*) and chiral ferroelectric smectic C (SmC*). Spontaneous polarization studies were carried out using two methods: the so-called 'reversal current method' and the 'Diamant bridge method'. The SP values in the ferroelectric SmC* phase changed in the range 50–70 nC cm^{-2}. These are relatively high values which may reveal possible application potential.

Spectroscopic studies of mesomorphic substances have been performed for many years, including conventional IR measurements and polarized/unpolarized FTIR spectroscopy; see, for example [26, 27]. We have recently reported crystal and molecular structure studies on homologues of the series, the 4-*n*-pentylphenyl-4-*n*-alkoxythiobenzoates (in short ***n*OS5**, where *n* denotes the number of carbon atoms in the alkoxy chain); specifically **4OS5** [28], **5OS5** [29] and **6OS5** [30]. The unit-cell packing in crystals of ***n*OS5** is characterized and stabilized by the occurrence of a net of weak C–H····O intermolecular hydrogen bonds. Infrared spectroscopy is particularly useful in the study of hydrogen bonding and in certain systems also shows a sensitivity to weaker intermolecular interactions and hence modes of packing. This region of the infrared spectrum is surprisingly complex [31]. The carbonyl stretching region is very sensitive to phase transitions; figure 2 and table 3 show its variation with temperature (heating and cooling) for **(*S*)-MHOBS5** in the region 1650–1700 cm^{-1} using KBr pellets.

In the crystalline phase a sharp band was observed at 1668 cm^{-1}; IR spectra 1, 2 and 3 in figure 2 (*a*). As the temperature is increased the carbonyl stretching mode is shifted to slightly higher wavenumbers, indicating a difference in local arrangement. The clearest changes are observed when the crystalline phase transforms to the CrG* phase (at 64°C; IR spectrum 4 in figure 2 (*a*), table 3). The apparently single band characteristic for the solid phase is replaced by a doublet and becomes broader in the liquid crystalline and isotropic phases. The carbonyl stretching mode observed in the CrG* phase is an asymmetrical doublet. The right-hand band at 1674 cm^{-1} is more intense than the shoulder near 1676.5 cm^{-1}. The situation remains the same in the SmI* phase. A change in the character of the doublet is seen at the SmC*–N* phase transition. The intensities of the two bands, one near 1674 cm^{-1} and the other near 1676 cm^{-1}, are equal. The spectra of **(*S*)-MHOBS5** in the liquid crystalline phases have very similar structures, but are not exactly the same; an apparent doublet observed in this region appears to be characteristic for the CrG*, SmI*, SmC* and N* phases. At higher temperatures in the N* phase the

Figure 2. FTIR spectra of a KBr pellet of **(*S*)-MHOBS5** obtained during (*a*) heating and (*b*) cooling: 1, 40°C (CrI), 2, 50°C (CrI); 3, 60°C (CrI), 4, 67°C (CrG*); 5, 72°C (SmI*); 6, 80°C (SmC*); 7, 85°C (SmC*); 8, 90°C (SmC*); 9, 100°C (N*); 10, 110°C (N*); 11, 120°C (N*); 12, 130°C (I), 13, 130°C (I); 14, 120°C (N*); 15, 110°C (N*); 16, 100°C (N*); 17, 90°C (SmC*); 18, 85°C (SmC*); 19, 80°C (SmC*); 20, 72°C (SmI*); 21, 67°C (CrG*); 22, 60°C (CrG*); 23, 50°C (CrG*); 24, 40°C (CrG*); 25, 20°C (CrG*); 26, 67°C (CrII).

carbonyl stretching mode observed at $1676\,\mathrm{cm}^{-1}$ dominates, but a weak shoulder near $1674\,\mathrm{cm}^{-1}$ is still discernable. As might be expected the doublet band is replaced by a broad apparently single band near $1678\,\mathrm{cm}^{-1}$ in the isotropic phase.

During cooling from the isotropic to solid phase the situation is very similar, figure 2 (*b*). During cooling, a distinct supercooling of the CrG* phase takes place leading to a solid phase, see spectrum 26, figure 2 (*b*). The carbonyl stretching is observed as a single broad band at $1670\,\mathrm{cm}^{-1}$ during cooling to 10°C (spectrum 26) and at $1668\,\mathrm{cm}^{-1}$ at 50°C during heating (spectrum 2) in the solid phase. The broad apparently single band in the solid phase obtained during cooling, suggests that there is a different crystal structure, which is confirmed by the texture obtained from polarizing microscopy.

The results obtained suggest that the liquid crystalline structures of **(*S*)-MHOBS5** can be characterized by a splitting in the carbonyl stretching region. As can be seen from figures 2 (*a*) and 2 (*b*) the mode observed at $1668\,\mathrm{cm}^{-1}$ in the solid phase shifts abruptly in frequency to 1674 and $1676.5\,\mathrm{cm}^{-1}$, with a gradual increase in wavenumber with temperature to $1678\,\mathrm{cm}^{-1}$ in the isotropic phase. The shift of this mode from higher frequency (isotropic phase) to lower frequency (solid phase) proves the existence of weak intermolecular hydrogen bonding. It is well known that the wavenumber shift is proportional to the strength of the hydrogen bond. The aromatic C–H groups and the carbonyl groups of adjacent molecules lead to the formation of weak hydrogen bonds between these groups and free electron pairs of the carbonyl oxygen. Such arrangements have been observed by ourselves in a number of thiobenzoate structures [28–30]. The splitting of the carbonyl stretching modes observed in the spectra of liquid crystalline phases of **(*S*)-MHOBS*n*** can be related to disorder between the arrangements of the carbonyl groups in liquid crystalline layers. This interpretation is confirmed by changes in other regions of the spectrum, particularly in the out-of-plane aromatic CH bonding modes and bands connected to CH_2 wagging modes and the aromatic C–O ether stretching mode.

4. Conclusions

A convenient synthesis of a new class of thiobenzoate ferroelectric liquid crystals, the **(*S*)-MHOBS*n*** homologous series, is described. The well known Mitsunobu reaction was applied to obtain ethyl (*S*)-(+)-4-(1-methylheptyloxy)biphenylcarboxylate in relatively high yields. The **(*S*)-MHOBS*n*** series possesses a rich phase polymorphism, including chiral ferroelectric smectic C (SmC*) and cholesteric (N*) phases. The fundamental mesomorphic and physical properties were determined. The carbonyl stretching mode is sensitive to molecular arrangements within the liquid crystalline phases. The FTIR spectra are sensitive to the modes of weak intermolecular hydrogen bonds. These compounds are also very interesting from an application point of view.

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