

CHAPTER IV

SYNTHESIS AND MESOMORPHIC PROPERTIES OF

- i) [S]-4"-n-Alkoxybiphenyl 4-(2-chloro-3-methyl-butanoyloxy)-2-hydroxybenzoates
- ii) [S]-4"-n-Alkoxybiphenyl 4-(2-chloro-4-methyl-pentanoyloxy)-2-hydroxybenzoates
- iii) [2S,3S]-4"-n-Alkoxyphenyl 4-(2-chloro-3-methyl-pentanoyloxy)-2-hydroxybenzoates

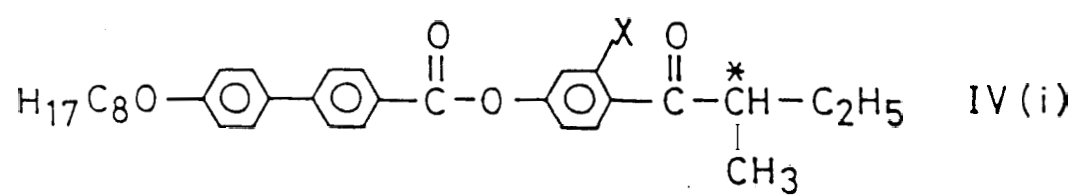
IV-1 SURVEY OF MESOMORPHIC PROPERTIES OF AROMATIC COMPOUNDS CONTAINING HYDROXYL GROUP

The hydroxy substituted aromatic mesogens, reported in the literature, are few in number compared to the halogen substituted analogues.^{1,2} The hydroxyl group is capable of giving a polymeric hydrogen bonding which raises the melting point. This group can also promote the adoption of a non-linear arrangement of molecules. Hence compounds containing a hydroxyl group were not considered to be very favourable for liquid crystal formation.^{3,4}

Schroeder and Schroeder⁵ have synthesised terminally substituted hydroxyphenyl bis-benzoates. These compounds have high melting points ($>200^{\circ}\text{C}$) and exhibit mostly nematic phases. Other examples of compounds with terminally substituted hydroxyl group, found in the literature^{1,6-8} are also characterised by nematic phases observed at relatively high temperatures. Lateral hydroxyl group has been introduced in a variety of substituted Schiff's bases.⁹⁻¹⁶ Teucher et al.¹⁷ introduced an hydroxyl group ortho to the benzylideneamino linkage in 4'-methoxybenzylidene-4-n-butylaniline. Hydroxyl group at such a position was expected to enhance the stability of $-\text{CH}=\text{N}-$ bond by its participation in an intramolecular hydrogen bonding.¹⁸ van der Veen and Hegge¹⁹ synthesised hydroxy substituted azo and azoxy compounds. The azo compounds exhibited a nematic phase at room temperature, however, the azoxy compounds had higher melting points. Lateral hydroxyl substituents have also been introduced in benzalazines.²⁰ Melendez and Serrano²¹ have reported that the intramolecular

hydrogen bonding is exceptionally strong in accordance with the calculations made using the method applied by Schaefer²² to ¹H-NMR data. The higher melting points observed have been attributed to packing, involving larger cohesive forces due to strong hydrogen bonding.

As mentioned in chapter I, the discovery of ferroelectricity in smectic phases²³ led to a search for compounds exhibiting S_{C*} phase at low temperatures with a high value for the spontaneous polarisation. Hallsby et al.²⁴ reported lateral hydroxy substituted Schiff's bases which had tendency to exhibit SC_* phases at relatively low temperatures. Otterholm et al.²⁵ have carried out a detailed study about the association of mesomorphic behaviour with molecular structure in such compounds. Sakurai et al.²⁶ have also observed an increase in the spontaneous polarisation values on introduction of a lateral hydroxyl group in the Schiff's bases. Nakauchi et al.²⁷ have reported compounds with optically active groups derived from [R]-3-hydroxynonanoic acid. In these compounds hydroxyl group is directly attached to the chiral carbon atom. Yoshino et al.²⁸ and Taniguchi et al.²⁹ observed that substitution of hydroxyl group in a position favourable for intramolecular hydrogen bonding in some biphenyl esters enhances the spontaneous polarisation values. They explain this increase in terms of relative orientation of bond moments around the chiral carbon atom. Kobayashi and Ishibashi³⁰ have investigated alkanoyl phenyl esters with substituted core IV(i). They observed that the value for spontaneous polarisation decreases when a halogen is introduced as compared to the unsubstituted compound.



$\text{X} = \text{H}, \text{F}, \text{Cl} \text{ or } \text{OH}$

However this value is found to increase when a hydroxyl group is introduced at the same position. This has been explained on the basis of group moments of substituent and the conformation of the compound. When $X=OH$, hydrogen bond stabilises the conformation in which the carbonyl and the hydroxyl are on the same side of molecular long axis. In case of halogen atoms, on the other hand, the carbonyl and the substituent will be oriented in opposite directions by their mutual electrostatic repulsion. They have also reported³, similar compounds with chiral groups derived from lactic acid placed on either side of the core. One compound with hydroxyl group present at the ortho position to the alkanoyl group shows a value for spontaneous polarisation as high as 11.3 mC/m^2 . This compound exhibits a monotropic S_{C^*} phase.

IV-2. RESULTS AND DISCUSSION

A carbonyl group adjacent to the chiral carbon atom carrying the chloro group can restrict the internal rotations and increase the dipolar ordering in the medium. A lateral hydroxyl group can provide rigidity to the structure by participating in hydrogen bond and also increase the lateral dipole moment of the molecule. To study the mesomorphic properties of compounds having a combination of a lateral hydroxyl group in the core and a 2-chloroalkanoyloxy group as the chiral moiety three homologous series of compounds shown in figure 1 were synthesised. These are diesters containing a biphenyl and a phenyl ring in the core with a lateral hydroxyl group present on the phenyl ring. The compounds differ with respect to the terminal optically active groups. These consist of [S]-2-chloro-3-methylbutanoyloxy, [S]-2-

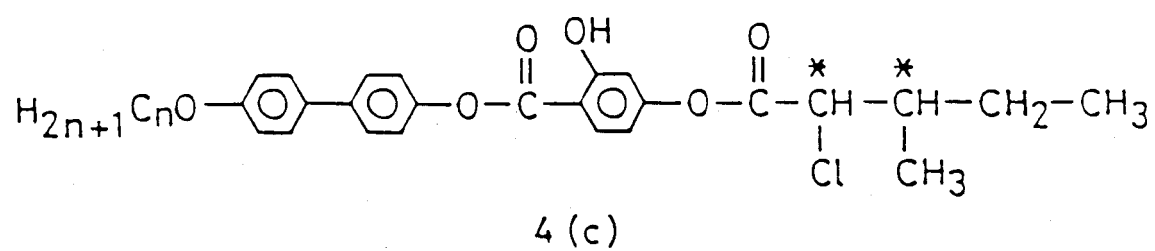
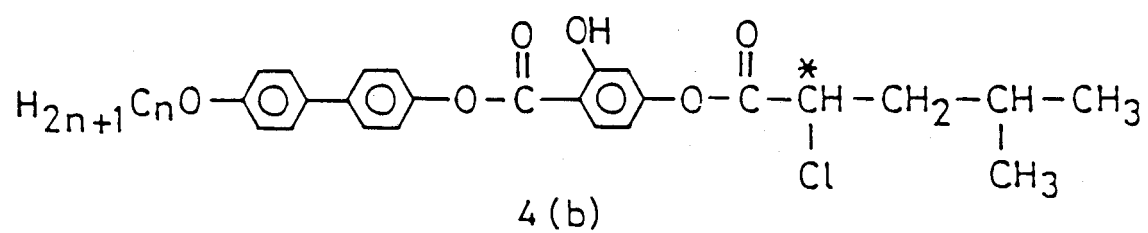
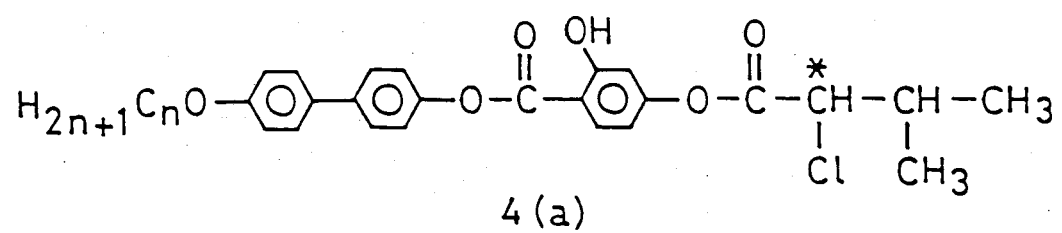


FIGURE 1

chloro-4-methylpentanoyloxy and [2S,3S]-2-chloro-3-methylpentanoyloxy groups.

All the compounds were synthesised according to the scheme shown in figures 2 and 3. 2,4-Dihydroxybenzoic acid was esterified with ethanol using sulphuric acid as the catalyst. The hydroxyl group in 4 position of the ester was protected with a benzyl group. Potassium carbonate was used as the base for benzylation reaction. This ester was then hydrolysed back to the acid using ethanolic potassium hydroxide. 4-Benzyloxy-2-hydroxybenzoic acid so obtained was esterified with 4-n-alkoxy-4'-hydroxybiphenyl using N,N-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine.³² The product was debenzylated by hydrogenolysis carried out in 1,4-dioxane using 5%-palladium on charcoal as a catalyst. 4"-Alkoxybiphenyl 2,4-dihydroxybenzoate so obtained was esterified with [S]-2-chloro-3-methylbutanoic acid, [S]-2-chloro-4-methylpentanoic acid and [2S,3S]-2-chloro-3-methylpentanoic acid to yield the final products 4(a), 4(b) and 4(c) respectively. The esterification reactions were carried in chloroform at room temperature using N,N-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine. 4"-n-Alkoxybiphenyl 4-benzyloxy-2-hydroxybenzoate and 4"-n-alkoxybiphenyl 2,4-dihydroxybenzoates exhibit liquid crystalline behaviour. The former exhibits a smectic and a nematic phase in the higher homologues ($n = 8$ to 12) and a nematic phase in the lower ones ($n = 6$ & 7). The transition temperatures of these compounds are given in table 4 (experimental section). A nematic phase is observed in 4"-n-alkoxybiphenyl 2,4-dihydroxybenzoates. This phase is enantiotropic in the dodecyloxy homo-

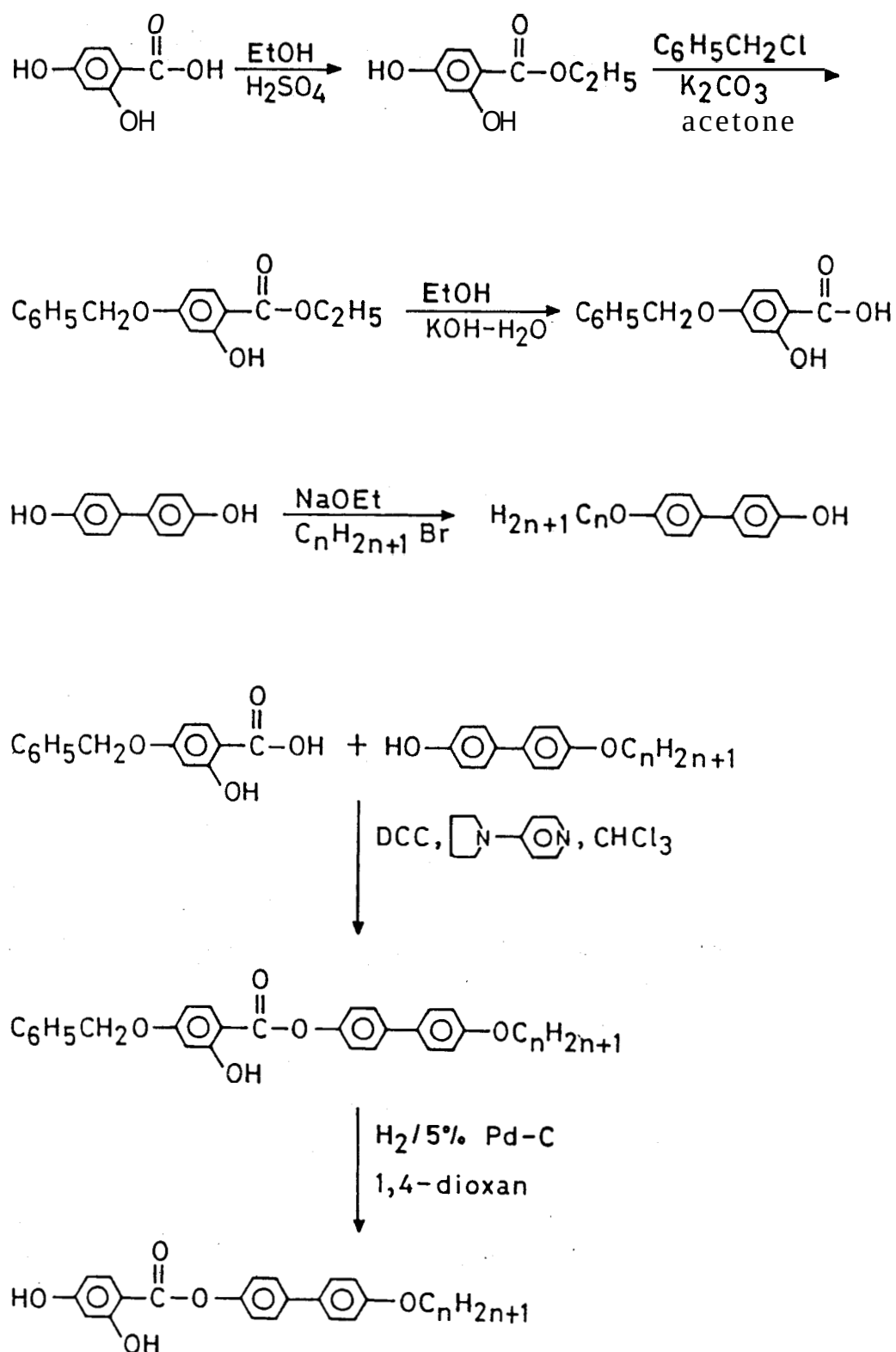


FIGURE 2

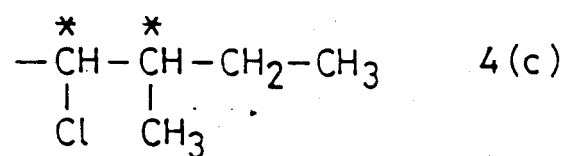
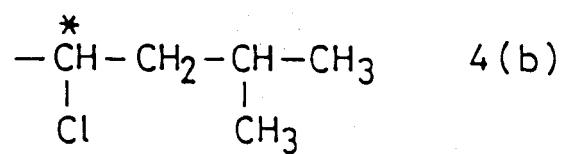
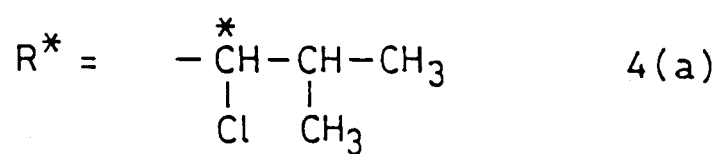
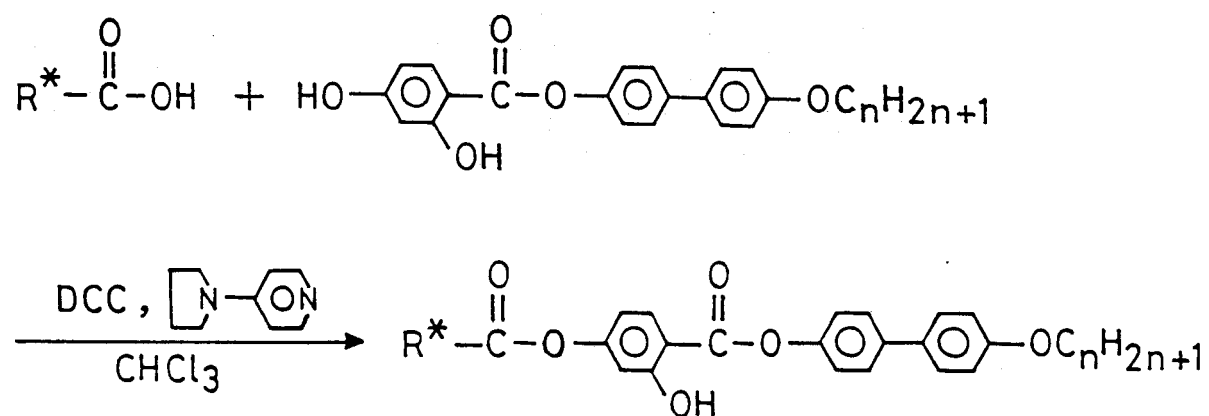


FIGURE 3

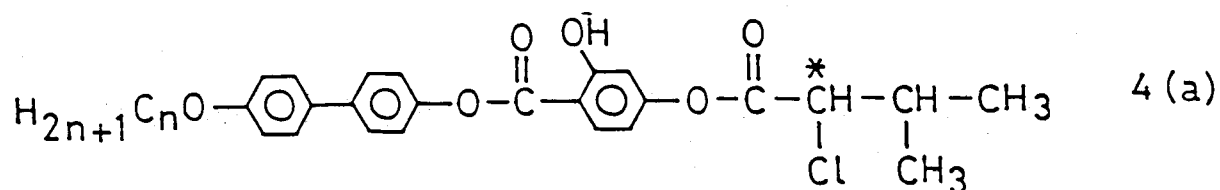
logue and monotropic in others ($n = 6$ to 11). The transition temperatures of these compounds are given in table 5 (experimental section).

The transition temperatures of [S]-4"-n-alkoxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-2-hydroxybenzoates [4(a)] are shown in table 1. The N^* phase present in compounds 4.a.1 to 4.a.4 is absent in the three higher homologues 4.a.5 to 4.a.7. The S_A phase is present in all the homologues. The S_{C^*} phase is injected into the series from compound 4.a.2 ($n=7$) as a monotropic phase. In all the higher homologues 4.a.3 to 4.a.7 ($n = 8 \dots 12$) this phase is enantiotropic. Compounds 4.a.5 and 4.a.2 have the least (79.5°C) and the highest (103.5°C) melting points respectively. The thermal range of the N^* phase decreases from 9°C in compound 4.a.1 to 0.5°C in compound 4.a.4. The thermal range of S_A phase also shows a general decrease upon ascending the homologous series. It is maximum for compound 4.a.1 (-72.5°C). The S_{C^*} phase is absent in the hexyloxy homologue (4.a.1) and is observed as a monotropic phase 5.5°C below the melting point in the heptyloxy homologue (4.a.2). The thermal range of the S_{C^*} phase is about $30\text{--}35^\circ\text{C}$ in compounds 4.a.4 to 4.a.7.

A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain for this series [4(a)] is shown in figure 4. The S_A - N^*/I and the N^* -I transition temperatures exhibit an alternation while the S_{C^*} - S_A transition temperatures form a smooth curve.

The transition temperatures of [S]-4"-n-alkoxybiphenyl 4-(2-

Table 1

Transition temperatures ($^{\circ}\text{C}$) and heats of transition (Kcals/mole) of

Compound number	n	C	S_{C^*}	S_A	N^*	I
4.a.1	6	. 82.0 (1.3)	-	. 154.5 (0.38)	. 163.5 (0.14)	.
4.a.2	7	. 103.5 (7.0)	(. 98.0)	. 151.0 (0.35)	. 156.0 (0.07)	.
4.a.3	8	. 103.5 (6.6)	. 110.0	. 154.5 (0.36)	. 157.5 (0.17)	.
4.a.4	9	. 80.5 (5.8)	. 113.0	. 152.0	. 152.5	.
4.a.5	10	. 79.5 (3.7)	. 113.5	. 151.0 (0.88)	-	.
4.a.6	11	. 80.0 (5.5)	. 112.5	. 148.5 (1.04)	-	.
4.a.7	12	. 80.5 (7.7)	. 112.0	. 147.5 (1.14)	-	.

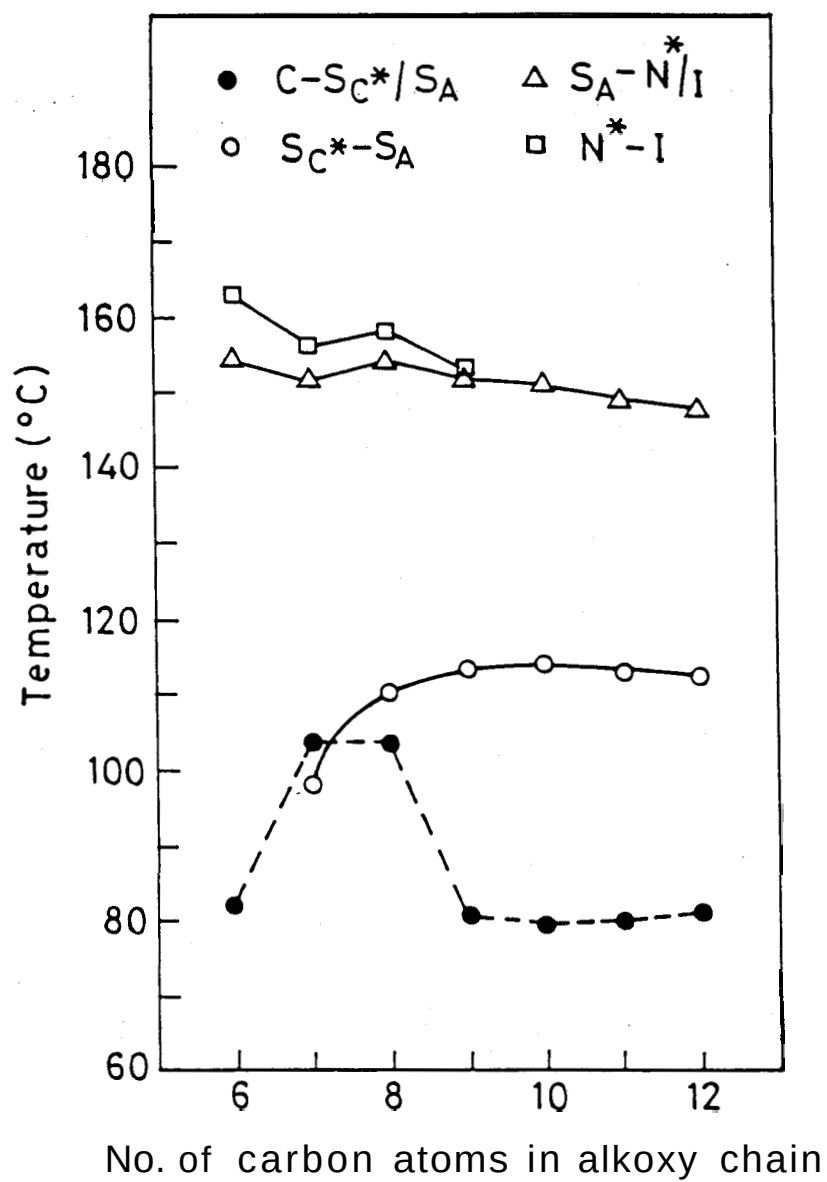


Figure 4: A plot of the transition temperatures versus number of carbon atoms in the alkoxy chain for the homologous series 4(a).

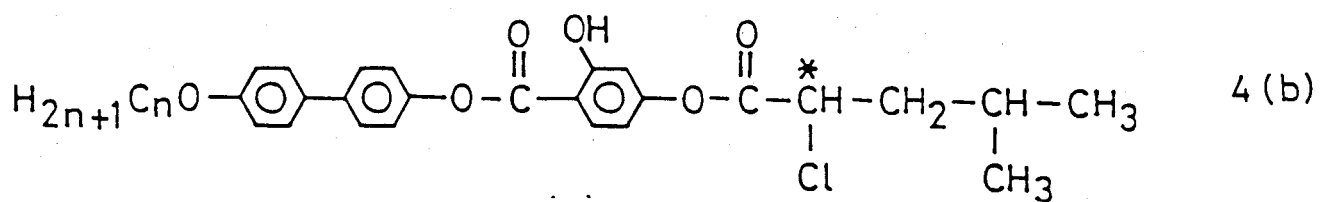
chloro-4-methylpentanoyloxy)-2-hydroxybenzoates [4(b)] are shown in table 2. It is seen that only S_A and S_{C^*} phases are present in these compounds. The S_A phase is present in all the compounds 4.b.1 to 4.b.7. A monotropic S_{C^*} phase is present in compound 4.b.3 ($n=8$) and it is enantiotropic in all the higher homologues 4.b.4 to 4.b.7 ($n = 9 \dots 12$). The melting points of all the compounds lie between 75°C and 100°C . The thermal range of the S_A phase decreases on ascending the homologous series from compound 4.b.2 onwards. The thermal range of the S_{C^*} phase for compound 4.b.6 ($n=11$) is 25.5°C .

A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain is shown in figure 5. An alternation is seen for the S_A -I transition temperatures. The S_{C^*} - S_A transition temperatures fall on a smooth curve.

The transition temperatures of [2S,3S]-4"-n-alkoxybiphenyl 4-(2-chloro-3-methylpentanoyloxy) 2-hydroxybenzoates are shown in table 3. Compounds 4.c.1, 4.c.2 and 4.c.3 ($n=6,7$ and 8) exhibit N^* phase. A blue phase over a range of 0.2°C is also observed for these compounds. All the compounds exhibit enantiotropic S_A and S_{C^*} phases except the compound 4.c.2 in which the S_{C^*} phase is monotropic. The widest range of the N^* phase observed is 4.5°C for compound 4.c.1 ($n=6$). The thermal range of the S_A phase shows a continuous decrease from 81.0°C in compound 4.c.1 ($n=6$) to 23.5°C in compound 4.c.7 ($n=12$). Compound 4.c.5 ($n = 10$) melting at 63.5°C has a S_{C^*} phase range of 51°C . This is the widest range observed for all the compounds of the three series. Compound

Table 2

Transition temperatures ($^{\circ}\text{C}$) and heats of transition (Kcals/mole) of



Compound number	n	C	S_{C^*}	S_A	I
4.b.1	6	.	99.0 (2.6)	-	. 147.0 (0.8)
4.b.2	7	.	85.5 (4.5)	.	144.0 (1.1)
4.b.3	8	.	88.5 (7.4)	(. 78.0)	. 144.0 (1.5)
4.b.4	9	.	79.0 (6.7)	. 95.5	. 140.0 (1.7)
4.b.5	10	.	88.5 (4.7)	. 112.0	. 142.0 (1.2)
4.b.6	11	.	87.5 (7.1)	. 113.0	. 139.0 (1.2)
4.b.7	12	.	93.5 (11.3)	. 114.0	. 138.0 (1.14)

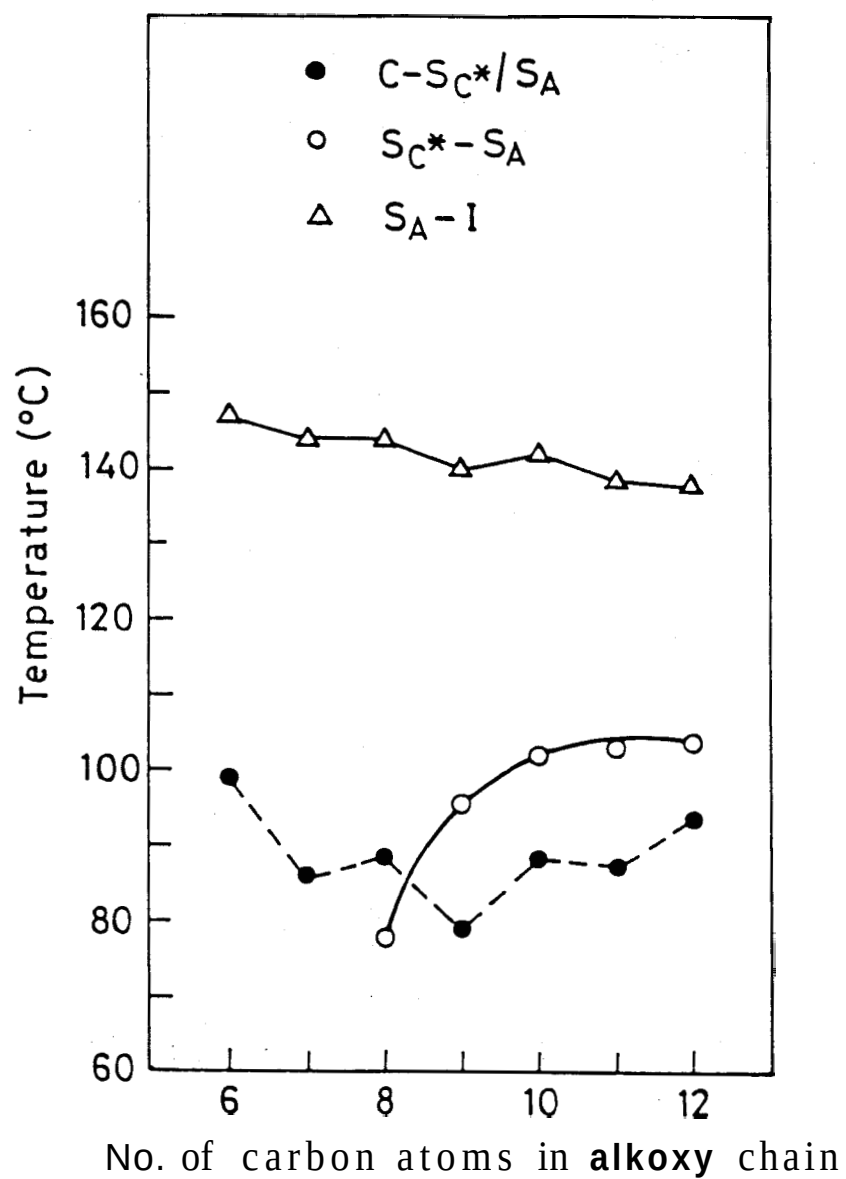
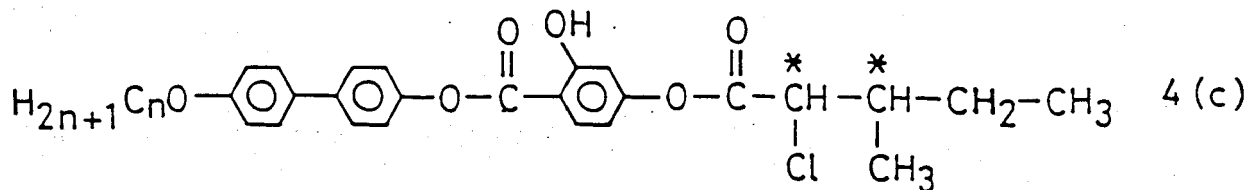


Figure 5: A plot of the transition temperatures versus number of carbon atoms in the alkoxy chain for the homologous series 4(b).

Table 3

Transition temperatures ($^{\circ}\text{C}$) and heats of transition (Kcals/mole) of



Compound number	n	C	S_{C^*}	S_A	N^*	I
4.c.1	6	.	64.0 (1.1)	.	64.5 (0.41)	145.5 (0.14)
4.c.2	7	.	95.0 (6.5)	.	82.5 (0.44)	140.5 (0.15)
4.c.3	8	.	58.0 (3.8)	.	98.0 (0.33)	142.5 (0.33)
4.c.4	9	.	59.0 (2.7)	.	107.0 (1.0)	138.5 (1.0)
4.c.5	10	.	63.5 (3.1)	.	114.5 (0.85)	141.5 (0.85)
4.c.6	11	.	65.5 (4.6)	.	113.0 (0.85)	139.0 (0.85)
4.c.7	12	.	67.5 (4.2)	.	114.0 (0.97)	137.5 (0.97)

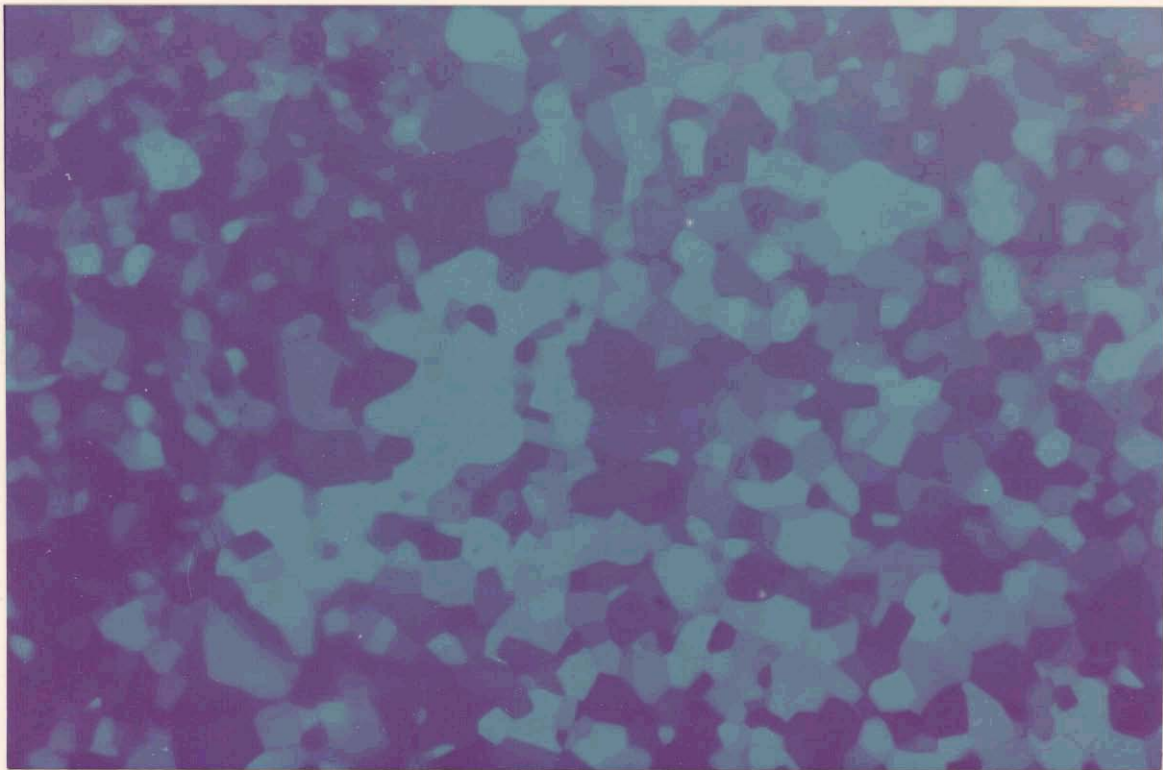


Plate IV.1: The texture of blue phase of the compound 4.c.3
at 143.8°C. (x 300)

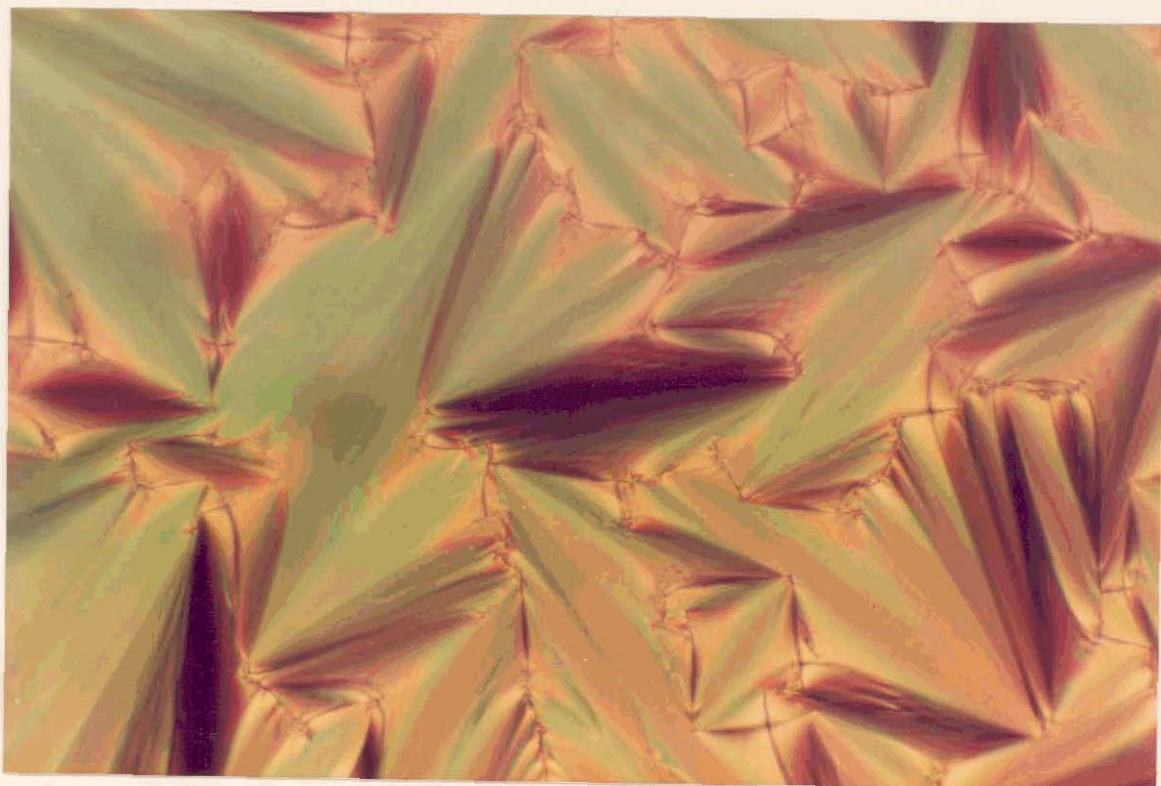


Plate IV.2: The focal-conic texture of S_A phase of the compound 4.c.5 at 120°C. ($\times 300$)

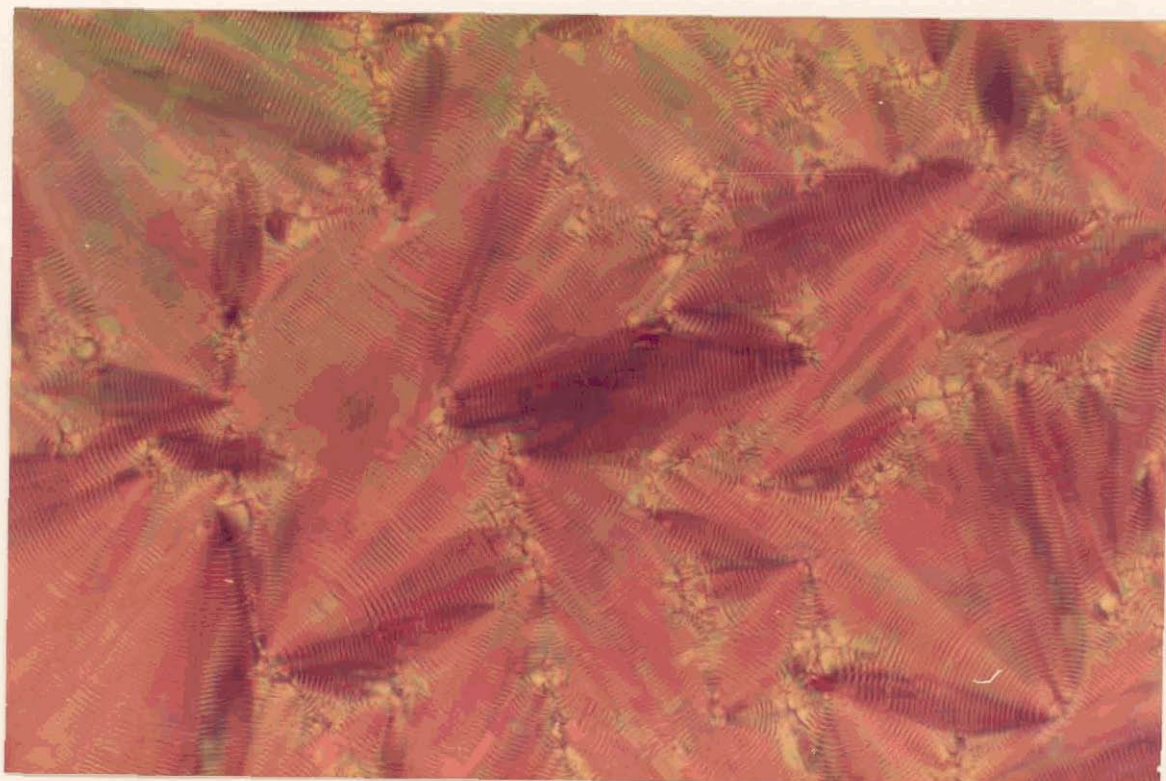


Plate IV.3: The banded focal-conic texture of S_{C^*} phase of the compound 4.c.5 at 100°C ($\times 300$) (Same section as in Plate IV.2).

4.c.3 ($n = 8$) has a melting point of 58.0°C , which is the lowest melting point observed in the three series of compounds.

Figure 6 shows a plot of the transition temperatures versus the number of carbon atoms in the alkoxy chain for the series 4(c). The S_A-N^*/I and the N^*-I transition temperatures show an alternation. The $S_{C^*}-S_A$ transition temperatures lie on a rising curve.

The differences in the structures of compounds of the three series are as follows. Series 4(a) has [S]-2-chloro-3-methyl butanoyl group as the optically active chain. In the compounds of series 4(b) a methylene group is present in between the chiral carbon atom and the terminal isopropyl group. The compounds of series 4(b) and 4(c) are isomeric. The compounds of series 4(c) have two chiral carbon atoms. These structural differences are reflected in the mesomorphic properties as follows. The N^* phase present in the four homologues of the series 4(a) and three homologues of series 4(c) is absent in series 4(b). The N^* phase in series 4(c) is also accompanied by a blue phase with a very narrow range. The clearing temperatures of compounds of series 4(a) are higher than those of the compounds of the other series. The thermal ranges of the S_{C^*} phase of the higher homologues ($n=8$ to 12) belonging to the series 4(a), 4(b) and 4(c) lie between 30 and 35°C , 15 and 30°C and 40 and 50°C respectively. The compounds belonging to the series 4(c) have generally lower melting points.

Sakurai et al.³³ have synthesised the diester IV(ii). The effect of a lateral hydroxyl group on mesomorphism can be seen by

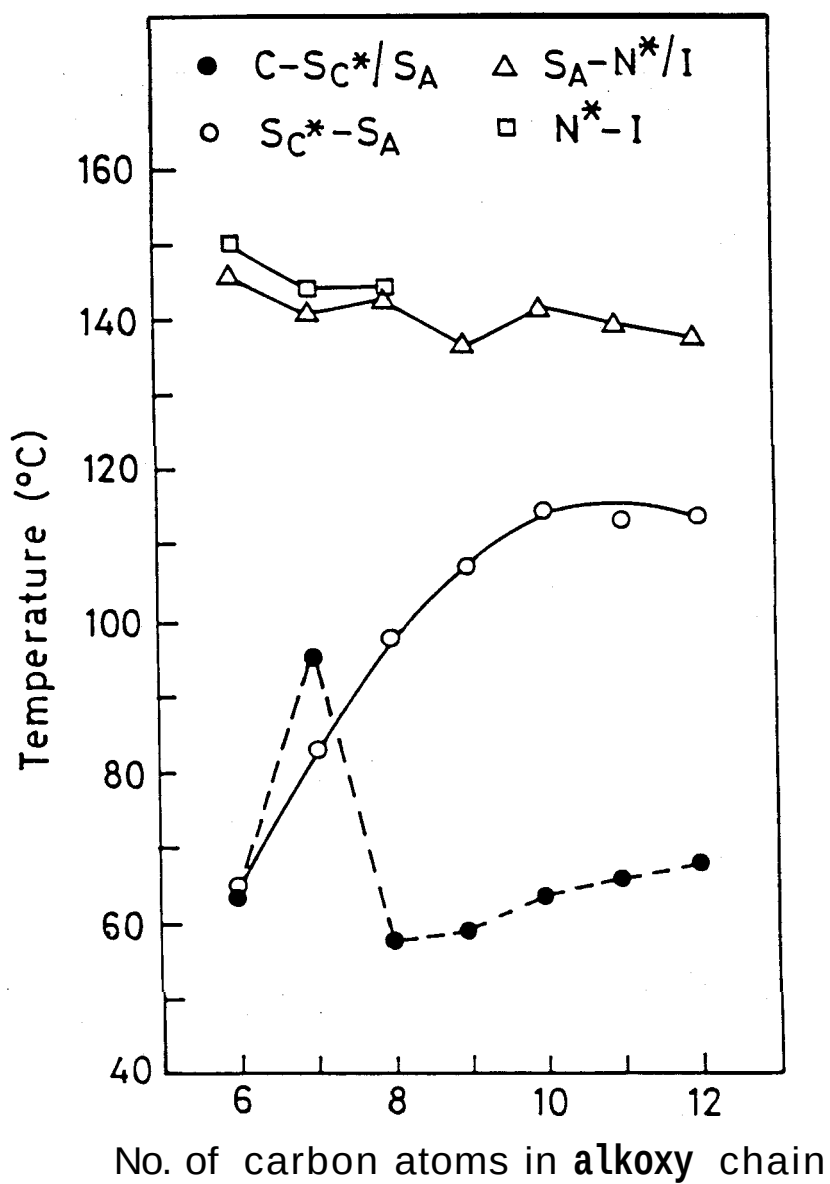
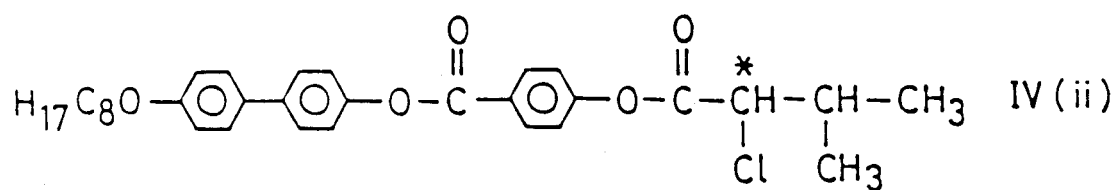
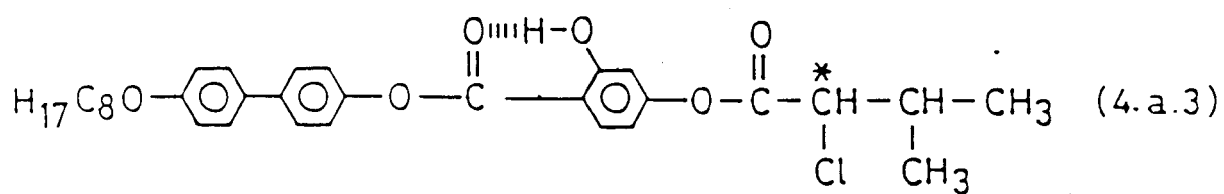


Figure 6: A plot of the transition temperatures versus number of carbon atoms in the alkoxy chain for the homologous series 4(c).



C 104.0 S* 110.0 S_C* 158.0 N* 183.0 I



C 103.5 S_C* 110.0 S_A 154.5 N* 157.5 I

comparing this compound with the compound 4.a.3. The structures and the transition temperatures of these compounds are shown in figure 7. The lateral hydroxyl group is likely to participate in intramolecular hydrogen bonding. It is seen that the introduction of hydroxyl group affects the smectic polymorphism, thermal range of the N^* phase as well as the transition temperatures. The higher order smectic phase observed in compound IV(ii) is absent in compound 4.a.3. However the S_A phase observed in compound 4.a.3 is absent in compound IV(ii). The clearing temperature of compound 4.a.3 is less by 25.5°C whereas the melting points are almost the same. The thermal range of the N^* phase in compound IV(ii) (25°C) is much larger than the 3°C range observed in the compound 4.a.3. The thermal ranges of S_{C^*} phase in compounds IV(ii) and 4.a.3 are 48°C and 6.5°C respectively.

IV-3. EXPERIMENTAL

Ethyl 2,4-dihydroxybenzoate

A mixture of 2,4-dihydroxybenzoic acid (30.8 g, 0.2 mol), absolute ethanol (300 ml) and concentrated sulphuric acid (10 ml) was refluxed while stirring for seventy two hours. Alcohol was removed and the residue was poured into ice water. The precipitate formed was filtered, dried and crystallised from benzene (25.5 g, 70%), m.p. 117.0°C (Reported³⁴ m.p. 118.9°C).

Ethyl 4-benzyloxy-2-hydroxybenzoate

A mixture of ethyl 2,4-dihydroxybenzoate (18.2 g, 0.1 mol), benzyl chloride (13.9 g, 0.11 mol) and potassium carbonate (27.9 g, 0.2 mol) was refluxed in acetone (200 ml) for forty hours with stirring. Then acetone was removed and the mixture poured into ice-water. It was extracted with chloroform (3x100 ml) and the combined chloroform solution was washed with water (3x70 ml) and dried (Na_2SO_4). The residue obtained after removal of the solvent was chromatographed on silica gel and eluted with 50% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol (19.0 g, 70%). m.p. 74.0°C; $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1660, 1510, 1580, 1505, 1460, 1380, 1260 and 1140 cm^{-1} . δ : 1.40 (t, 3H, CH_2CH_3), 4.39 (q, 2H, OCH_2), 5.07 (s, 2H, OCH_2Ph), 6.36-7.90 (m, 8H, ArH), 11.03 (s, 1H, OH).

[Found: C, 70.61; H, 5.87% $\text{C}_{16}\text{H}_{15}\text{O}_4$ requires
C, 70.59; H, 5.88%].

4-Benzyloxy-2-hydroxybenzoic acid

A mixture of ethyl 4-benzyloxy-2-hydroxybenzoate (32.6 g, 0.12 mol), potassium hydroxide (8.6 g, 0.15 mol), water (10 ml) and ethanol (50 ml) was refluxed for six hours. Ethanol was removed by distillation under reduced pressure and the residue was poured into cold water. This **was** then acidified by adding cold concentrated hydrochloric acid. The white precipitate obtained was filtered, dried and crystallised from ethanol-water (27.8 g, 95%). m.p. 185.0 °C; $\nu_{\max}^{\text{nujol}}$: 2900, 2850, 1560, 1620, 1460, 1380, 1270, 1170, 1020 and 780 cm^{-1} .

[Found: C, 68.79; H, 4.91% $\text{C}_{14}\text{H}_{12}\text{O}_4$ requires
C, 68.85; H, 4.92%].

4-n-Dodecyloxy-4'-hydroxybiphenyl

A solution of sodium ethoxide was prepared by dissolving sodium (0.46 g, 0.02 g atom) in absolute ethanol (50 ml). 4,4'-Dihydroxybiphenyl (3.72 g, 0.02 mol) was added to it and the resulting mixture was stirred and refluxed for thirty minutes. n-1-Bromododecane was then added and the refluxing continued for a further thirty hours. Ethanol was distilled off under reduced pressure, the residue poured into cold water, acidified with cold concentrated hydrochloric acid and extracted with 25% ethyl acetate-ether mixture (3x50 ml). The combined organic solution was washed with water (3x100 ml) and dried (Na_2SO_4). The residue obtained after removal of the solvent was chromatographed on silica gel and eluted with chloroform. Removal of solvent from

the eluate afforded a white solid which was crystallised from ethanol (3.2 g, 45%). m.p. 147.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3370, 2925, 2850, 1610, 1500, 1460, 1380, 1275, 1130, 1040 and 810 cm^{-1} ; δ : (acetone d_6): 0.83–1.82 (m, 23H, CH_3 and $10 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.77–7.67 (m, 8H, ArH), 8.2 (s, 1H, OH).

[Found: C, 81.64; H, 9.29% $\text{C}_{24}\text{H}_{34}\text{O}_2$ requires
C, 81.35; H, 9.60%].

The physical data of the cognate preparations of other 4-n-alkoxy-4'-hydroxybiphenyls are given below.

4-n-Hexyloxy-4'-hydroxybiphenyl

Yield, 488; m.p. 155.5°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3275, 2920, 2850, 1610, 1505, 1460, 1380, 1250, 1130 and 820 cm^{-1} ; δ : (acetone d_6): 0.75–1.56 (m, 11H, CH_3 , $4 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.77–7.67 (m, 8H, ArH), 8.4 (s, 1H, OH).

[Found: C, 80.46; H, 8.54% $\text{C}_{18}\text{H}_{22}\text{O}_2$ requires
C, 80.00; H, 8.15%].

4-n-Heptyloxy-4'-hydroxybiphenyl

Yield, 46%; m.p. 153.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3370, 2920, 2850, 1600, 1505, 1460, 1380, 1250, 1135, 1040 and 810 cm^{-1} ; δ : (acetone d_5): 0.75–1.6 (m, 13H, CH_3 , $5 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.71–7.7 (m, 8H, ArH), 8.4 (s, 1H, OH).

[Found: C, 80.39; H, 8.54% $\text{C}_{19}\text{H}_{24}\text{O}_2$ requires
C, 80.28; H, 8.45%].

4-n-Octyloxy-4'-hydroxybiphenyl

Yield, 45%; m.p. 152.0°C; $\nu_{\text{max}}^{\text{nujol}}$: 3270, 2920, 2850, 1610, 1505, 1460, 1380, 1250, 1140 and 810 cm^{-1} ; δ : (acetone d_6): 0.68–1.66 (m, 15H, CH_3 , 6 $\times$ CH_2), 4.0 (t, 2H, OCH_2), 6.72–7.61 (m, 8H, ArH), 8.38 (s, 1H, OH).

[Found: C, 80.14; H, 8.77% $\text{C}_{20}\text{H}_{26}\text{O}_2$ requires
C, 80.53; H, 8.72%].

4-n-Nonyloxy-4'-hydroxybiphenyl

Yield, 46%; m.p. 150.5°C; $\nu_{\text{max}}^{\text{nujol}}$: 3370, 2920, 2850, 1615, 1500, 1460, 1380, 1275, 1130, 1040 and 810 cm^{-1} ; δ : (acetone d_6): 0.82–1.5 (m, 17H, CH_3 , 7 $\times$ CH_2), 4.0 (t, 2H, OCH_2), 6.8–7.62 (m, 8H, ArH), 8.34 (s, 1H, OH).

[Found: C, 80.99; H, 9.08% $\text{C}_{21}\text{H}_{28}\text{O}_2$ requires
C, 80.77; H, 8.97%].

4-n-Decyloxy-4'-hydroxybiphenyl

Yield, 45%; m.p. 139.0°C; $\nu_{\text{max}}^{\text{nujol}}$: 3300, 2920, 2850, 1615, 1505, 1460, 1380, 1270, 1130, 1030 and 810 cm^{-1} ; δ : (acetone d_6): 0.82–1.67 (m, 19H, CH_3 , 8 $\times$ CH_2), 3.99 (t, 2H, OCH_2), 6.68–7.6 (m, 8H, ArH), 8.0 (s, 1H, OH).

[Found: C, 80.77; H, 9.10% $\text{C}_{22}\text{H}_{30}\text{O}_2$ requires
C, 80.98; H, 9.20%].

4-n-Undecyloxy-4'-hydroxybiphenyl

Yield, 50%; m.p. 148.0°C; $\nu_{\text{max}}^{\text{nujol}}$: 3370, 2920, 2850, 1610, 1505, 1460, 1380, 1275, 1130, 1050 and 810 cm^{-1} .; δ : (acetone d_6): 0.8-1.82 (m, 21H, CH_3 , 9x CH_2), 4.0 (t, 2H, OCH_2), 6.79-7.61 (m, 8H, ArH), 8.33 (s, 1H, OH).

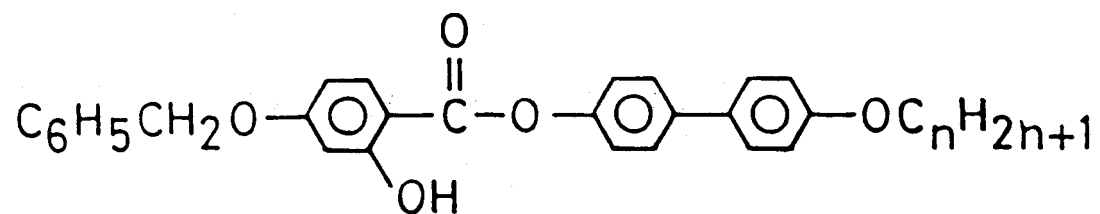
[Found: C, 81.52; H, 9.57% $\text{C}_{23}\text{H}_{32}\text{O}_2$ requires
C, 81.18; H, 9.41%].

4"-n-Dodecyloxybiphenyl 4-benzyloxy-2-hydroxybenzoate

This was prepared following the esterification procedure of Hassner and Alexanian.³² Thus, a mixture of 4-benzyloxy-2-hydroxybenzoic acid (2.44 g, 0.01 mol), 4-n-dodecyloxy-4'-hydroxybiphenyl (3.89 g, 0.011 mol), N,N-dicyclohexylcarbodiimide (2.26 g, 0.011 mol), 4-pyrrolidinopyridine (0.15 g, 0.001 mol) and dry dichloromethane (50 ml) was stirred at room temperature for two hours. N,N-Dicyclohexyl urea formed was filtered and the filtrate was washed with 5% acetic acid (3x25 ml), water (3x30 ml) and dried (Na_2SO_4). On removal of dichloromethane a solid residue was obtained which was chromatographed on silica gel and eluted with 25% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate afforded a white solid which was crystallised from ethyl acetate (3.8 g, 65%); m.p. 110.5°C; $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1680, 1580, 1510, 1480, 1380, 1280, 1190, 1090, 1010 and 805 cm^{-1} ; δ : 0.69-2.0 (m, 23H, CH_3 , 10x CH_2), 4.0 (t, 2H, OCH_2), 5.04 (s, 2H, PhCH_2OAr), 6.39-8.02 (m, 16H, ArH), 10.7 (s, 1H, OH).

[Found: C, 78.82; H, 7.60% $\text{C}_{38}\text{H}_{44}\text{O}_5$ requires
C, 78.62; H, 7.59%].

Table 4

Transition temperatures ($^{\circ}\text{C}$) of

n	C	S	N	I
6	. 128.0	-	. 189.0	.
7	. 126.0	-	. 186.0	.
8	. 109.0	(. 108.5)	. 185.5	.
9	. 111.5	. 120.5	. 181.5	.
10	. 108.5	. 126.0	. 178.5	.
11	. 110.0	. 132.0	. 175.0	.
12	. 110.5	. 139.0	. 173.5	.

The physical data of the cognate preparations of other 4"-n-alkoxybiphenyl 4-benzyloxy-2-hydroxybenzoate are given below.

4"-n-Hexyloxybiphenyl 4-benzyloxy-2-hydroxybenzoate

Yield, 62%; m.p. 128.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1680, 1580, 1510, 1480, 1380, 1290, 1090, 1010 and 810 cm^{-1} ; δ : 0.81–2.02 (m, 11H, CH_3 , $4\times\text{CH}_2$), 4.0 (t, 2H, OCH_2), 5.12 (s, 2H, OCH_2), 6.44–8.12 (m, 16H, ArH), 10.28 (s, 1H, OH).

[Found: C, 77.56%; H, 6.48% $\text{C}_{32}\text{H}_{32}\text{O}_5$ requires
C, 77.42%; H, 6.45%].

4"-n-Heptyloxybiphenyl 4-benzyloxy-2-hydroxybenzoate

Yield, 44%; m.p. 126.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 2920, 2850, 1680, 1630, 1580, 1500, 1460, 1380, 1280, 1180, 1070 and 805 cm^{-1} ; δ : 0.74–2.0 (m, 13H, CH_3 , $5\times\text{CH}_2$), 4.0 (t, 2H, OCH_2), 5.12 (s, 2H, OCH_2), 6.5–8.08 (m, 16H, ArH), 10.68 (s, 1H, OH).

[Found: C, 78.01%; H, 6.70% $\text{C}_{33}\text{H}_{34}\text{O}_5$ requires
C, 77.64%; H, 6.67%].

4"-n-Octyloxybiphenyl 4-benzyloxy-2-hydroxybenzoate

Yield, 47%; m.p. 108.5°C ; $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1680, 1625, 1580, 1500, 1480, 1380, 1280, 1160, 1070 and 810 cm^{-1} ; δ : 0.8–2.0 (m, 15H, CH_3 , $6\times\text{CH}_2$), 3.93 (t, 2H, OCH_2), 5.09 (s, 2H, OCH_2), 6.37–8.08 (m, 16H, ArH),

10.7(s, 1H, OH).

[Found: C, 77.73; H, 6.97% C₃₄H₃₆O₅ requires
C, 77.86; H, 6.87%].

4"-n-Nonyloxybiphenyl 4-benzyloxy-2-hydroxybenzoate

Yield, 47%; m.p. 111.5°C; $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1675, 1620, 1580, 1500, 1460, 1380, 1260, 1070 and 805 cm⁻¹; δ : 0.7-2.0(m, 17H, CH₃, 7xCH₂), 4.0(t, 2H, OCH₂), 5.15(s, 2H, OCH₂), 6.37-8.12(m, 16H, ArH), 10.71(s, 1H, OH).

[Found: C, 78.07; H, 7.12% C₃₅H₃₈O₅ requires
C, 78.07; H, 7.06%].

4"-n-Decyloxybiphenyl 4-benzyloxy-2-hydroxybenzoate

Yield, 45%; m.p. 108.5°C; $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2800, 1680, 1580, 1500, 1480, 1375, 1280, 1060, 1010 and 800 cm⁻¹; δ : 0.69-2.04(m, 19H, CH₃, 8xCH₂), 3.96(t, 2H, OCH₂), 5.06(s, 2H, OCH₂), 6.37-8.04(m, 16H, ArH), 10.59(s, 1H, OH).

[Found: C, 78.38; H, 7.31% C₃₆H₄₀O₅ requires
C, 78.26; H, 7.25%].

4"-n-Undecyloxybiphenyl 4-benzyloxy-2-hydroxybenzoate

Yield, 46%; m.p. 110.0°C; $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1680, 1580, 1510, 1480, 1380, 1290, 1180, 1090, 1010 and 810 cm⁻¹; δ : 0.71-2.02(m, 21H, CH₃,

9xCH₂), 4.1 (t, 2H, OCH₂), 5.25 (s, 2H, OCH₂), 6.65–8.33 (m, 16H, ArH), 11.0 (s, 1H, OH).

[Found: C, 78.38; H, 7.53% C₃₇H₄₂O₅ requires
C, 78.44; H, 7.44%].

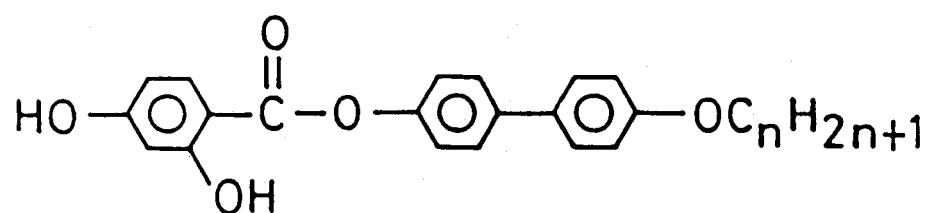
4"-n-Dodecyloxybiphenyl 2,4-dihydroxybenzoate

4 mixture of 4"-n-dodecyloxybiphenyl 4-benzyloxy-2-hydroxy benzoate (5.8 g, 0.01 mol) dissolved in 1,4-dioxan (50 ml) and 5% Pd/C catalyst (2.9 g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was filtered and dioxan removed by distillation under reduced pressure. The residual product so obtained was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised from benzene (4.5 g, 92%). m. p. 162.0°C; $\nu_{\max}^{\text{nujol}}$: 3550, 3200, 2900, 2850, 1680, 1620, 1605, 1500, 1460, 1380, 1280, 1215, 1185, 1060 and 800 cm⁻¹; δ (CDCl₃ + DMSO-d₆): 0.73–2.0 (m, 23H, CH₃, 10xCH₂), 4.0 (t, 2H, OCH₂), 6.36–8.0 (m, 11H, ArH), 8.54 (s, 2H, OH).

[Found: C, 75.46; H, 7.79% C₃₁H₃₈O₅ requires
C, 75.92; H, 7.75%].

The physical data of the cognate preparations other 4"-n-alkoxybiphenyl 2,4-dihydroxybenzoates are given below.

Table 5

Transition temperatures ($^{\circ}\text{C}$) of

n	C	N	I
6	. 174.0	(. 164.0)	.
7	. 173.0	(. 167.0)	.
8	. 176.5	(. 169.0)	.
9	. 173.0	(. 163.0)	.
10	. 173.0	(. 167.0)	.
11	. 165.5	(. 162.0)	.
12	. 162.0	(. 167.0)	.

4"-n-Hexyloxybiphenyl 2,4-dihydroxybenzoate

Yield, 95%; m.p. 174.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3500, 3200, 2920, 2850, 1675, 1635, 1500, 1460, 1380, 1270, 1185, 1065 and 805 cm^{-1} ; $\delta(\text{CDCl}_3 + \text{DMF}-d_6)$: 0.85–2.1 (m, 11H, CH_3 , $4 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.25–8.22 (m, 11H, ArH), 10.67 (s, 2H, OH).

[Found: C, 73.62; H, 6.55% $\text{C}_{25}\text{H}_{26}\text{O}_5$ requires
C, 73.89; H, 6.40%].

4"-n-Heptyloxybiphenyl 2,4-dihydroxybenzoate

Yield, 94%; m.p. 173.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3500, 3200, 2920, 2850, 1680, 1630, 1605, 1500, 1460, 1380, 1275, 1165, 1065 and 805 cm^{-1} ; $\delta(\text{CDCl}_3 + \text{DMSO}-d_6)$: 0.8–2.08 (m, 13H, CH_3 , $5 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.28–8.0 (m, 11H, ArH), 10.5 (s, 2H, OH).

[Found: C, 74.53; H, 6.32% $\text{C}_{26}\text{H}_{28}\text{O}_5$ requires
C, 74.28; H, 6.67%].

4"-n-Octyloxybiphenyl 2,4-dihydroxybenzoate

Yield, 92%; m.p. 176.5°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3400, 3250, 1660, 1620, 1600, 1500, 1460, 1380, 1280, 1200, 1185 and 805 cm^{-1} ; $\delta(\text{CDCl}_3 + \text{DMSO}-d_6)$: 0.68–2.0 (m, 15H, CH_3 , $6 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.32–8.1 (m, 11H, ArH), 10.56 (s, 2H, OH).

[Found: C, 74.67; H, 6.94% $\text{C}_{27}\text{H}_{30}\text{O}_5$ requires
C, 74.65; H, 6.98%].

4"-n-Nonyloxybiphenyl 2,4-dihydroxybenzoate

Yield, 90%; m.p. 173.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3300, 3200, 2900, 2850, 1680, 1620, 1600, 1500, 1460, 1380, 1260, 1180 and 800 cm^{-1} ; $\delta(\text{CDCl}_3 + \text{DMSO}-d_6)$: 0.94–2.0 (m, 17H, CH_3 , $7 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.34–8.0 (m, 11H, ArH), 10.54 (s, 2H, OH).

[Found: C, 74.56; H, 7.24% $\text{C}_{28}\text{H}_{32}\text{O}_5$ requires
C, 75.00; H, 7.14%].

4"-n-Decyloxybiphenyl 2,4-dihydroxybenzoate

Yield, 95%; m.p. 173.0°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3300, 3150, 2900, 2850, 1680, 1605, 1500, 1480, 1370, 1275, 1210, 1170, 1065 and 805 cm^{-1} ; $\delta(\text{CDCl}_3 + \text{DMSO}-d_6)$: 0.71–2.05 (m, 19H, CH_3 , $8 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.34–8.05 (m, 11H, ArH), 10.55 (s, 2H, OH).

[Found: C, 75.21; H, 7.41% $\text{C}_{29}\text{H}_{34}\text{O}_5$ requires
C, 75.32; H, 7.36%].

4"-n-Undecyloxybiphenyl 2,4-dihydroxybenzoate

Yield, 94%; m.p. 165.5°C ; $\nu_{\text{max}}^{\text{nujol}}$: 3550, 3150, 2900, 2850, 1680, 1605, 1500, 1460, 1380, 1280, 1165, 1060 and 800 cm^{-1} ; $\delta(\text{CDCl}_3 + \text{DMSO}-d_6)$: 0.77–2.0 (m, 21H, CH_3 , $9 \times \text{CH}_2$), 4.0 (t, 2H, OCH_2), 6.38–8.04 (m, 11H, ArH), 10.54 (s, 2H, OH).

[Found: C, 76.18; H, 7.69% $\text{C}_{30}\text{H}_{36}\text{O}_5$ requires
C, 75.63; H, 7.56%].

[S]-4"-n-Dodecyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-
2-hydroxybenzoate (4.a.7)

This was prepared following the esterification procedure of Hassner and Alexanian.³² Thus, a mixture of [S]-2-chloro-3-methylbutanoic acid (0.136 g, 0.001 mol), 4"-n-dodecyloxybiphenyl 2,4-dihydroxybenzoate (0.539 g, 0.0011 mol), N,N-dicyclohexylcarbodiimide (0.226 g, 0.0011 mol), 4-pyrrolidinopyridine (0.015 g, 0.0001 mol) and dry dichloromethane (25 ml) was stirred at room temperature for one hour. N,N-Dicyclohexyl urea formed was filtered and the filtrate was washed with 5% acetic acid (2x10 ml), water (5x15 ml), dried (Na_2SO_4) and the solvent removed by distillation. The residue obtained was chromatographed on silica gel and eluted with 30% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate afforded a white solid which was repeatedly crystallised from ethanol (0.4 g, 64%) m.p. 80.8°C; $[\alpha]_D^{25} = +1.65$ (c=1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol}}$: 2920, 2850, 1760, 1680, 1595, 1500, 1460, 1380, 1290, 1165, 1070 and 800 cm^{-1} ; δ : 0.78-2.66 (m, 30H, 3x CH_3 , 10x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.36 (d, 1H, CHCl), 6.68-8.2 (m, 11H, ArH), 10.66 (s, 1H, OH).

[Found: C, 70.61; H, 7.55% $\text{C}_{36}\text{H}_{45}\text{ClO}_6$ requires
C, 70.99; H, 7.39%].

The physical data of the cognate preparations of other [S]-4"-n-alkoxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-2-hydroxybenzoates [4(a)] are given below.

[S]-4"-n-Hexyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-
2-hydroxybenzoate (4.a.1)

Yield, 65%; m.p. 82.0°C; $[\alpha]_D^{25} = +2.02$ (c=1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol}}$.
2900, 2850, 1760, 1680, 1620, 1595, 1500, 1460, 1380, 1290, 1160 and 805
 cm^{-1} ; δ : 0.66-2.61 (m, 18H, $3 \times \text{CH}_3$, $4 \times \text{CH}_2$ and CH), 4.0 (t, 2H, OCH_2), 4.34
(d, 1H, CHCl), 6.7-8.3 (m, 11H, ArH), 10.5 (s, 1H, OH).

[Found: C, 68.90; H, 6.39% $\text{C}_{30}\text{H}_{33}\text{ClO}_6$ requires
C, 68.64; H, 6.29%].

[S]-4"-n-Heptyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-
2-hydroxybenzoate (4.a.2)

Yield, 62%; m. p. 103.5°C; $[\alpha]_D^{25} = +2.08$ (c = 1 in CHCl_3);
 $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1760, 1680, 1620, 1500, 1460, 1380, 1290, 1160 and 805
 cm^{-1} ; δ : 0.76-2.61 (m, 20H, $3 \times \text{CH}_3$, $5 \times \text{CH}_2$ and CH), 4.0 (t, 2H, OCH_2), 4.36
(d, 1H, CHCl), 6.67-8.25 (m, 11H, ArH), 10.65 (s, 1H, OH).

[Found: C, 68.75; H, 6.68% $\text{C}_{31}\text{H}_{35}\text{ClO}_6$ requires
C, 69.08; H, 6.50%].

[S]-4"-n-Octyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-
2-hydroxybenzoate (4.a.3)

Yield, 60%; m. p. 103.5°C; $[\alpha]_D^{25} = +2.17$ (c = 1 in CHCl_3);
 $\nu_{\text{max}}^{\text{nujol}}$: 2925, 2850, 1760, 1690, 1620, 1595, 1500, 1460, 1380, 1285, 1170 and

805 cm^{-1} ; δ : 0.65–2.66 (m, 22H, 3 $\times$ CH₃, 6 $\times$ CH₂ and CH), 4.0 (t, 2H, OCH₂), 4.33 (d, 1H, CHCl), 6.69–8.27 (m, 11H, ArH), 10.65 (s, 1H, OH).

[Found: C, 69.28; H, 6.80% C₃₂H₃₇ClO₆ requires
C, 69.50; H, 6.69%].

[S]-4"-Nonyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-
2-hydroxybenzoate (4.a.4)

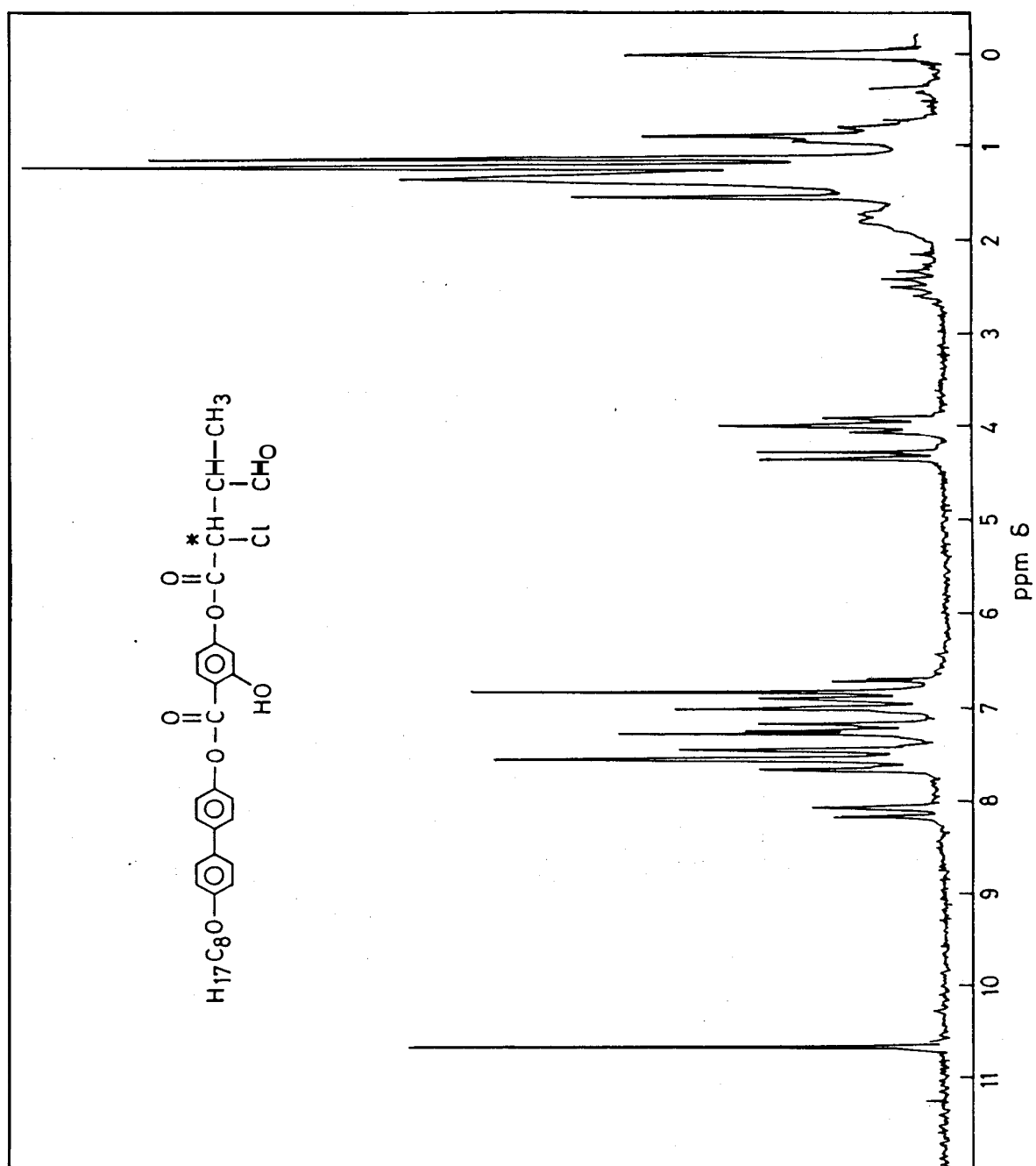
Yield, 64%; m. p. 80.5°C; $[\alpha]_D^{25} = +1.90$ (c = 1 in CHCl₃);
 $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1760, 1680, 1620, 1605, 1500, 1460, 1380, 1260, 1200, 1160
and 800 cm^{-1} ; δ : 0.69–2.67 (m, 24H, 3 $\times$ CH₃, 7 $\times$ CH₂ and CH), 4.0 (t, 2H, OCH₂), 4.34 (d, 1H, CHCl), 6.67–8.25 (m, 11H, ArH), 10.69 (s, 1H, OH).

[Found: C, 70.07; H, 6.80% C₃₃H₃₉ClO₆ requires
C, 69.90; H, 6.88%].

[S]-4"-Decyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-
2-hydroxybenzoate (4.a.5)

Yield, 64%; m. p. 79.5°C; $[\alpha]_D^{25} = +1.73$ (c = 1 in CHCl₃);
 $\nu_{\text{max}}^{\text{nujol}}$: 2920, 2850, 1765, 1680, 1600, 1500, 1460, 1380, 1290, 1165, 1070 and
805 cm^{-1} ; δ : 0.76–2.67 (m, 26H, 3 $\times$ CH₃, 8 $\times$ CH₂ and CH), 4.0 (t, 2H, OCH₂), 4.29 (d, 1H, CHCl), 6.59–8.22 (m, 11H, ArH), 10.63 (s, 1H, OH).

[Found: C, 70.19; H, 7.18% C₃₄H₄₁ClO₆ requires
C, 70.28; H, 7.06%].



¹H NMR spectrum of the compound 4.a.3.

[S]-4"-n-Undecyloxybiphenyl 4-(2-chloro-3-methylbutanoyloxy)-2-hydroxybenzoate (4.a.6)

Yield, 65%; m. p. 80.0°C; $[\alpha]_D^{25} = +1.68$ (c = 1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol}}$: 2920, 2850, 1765, 1680, 1595, 1500, 1460, 1380, 1290, 1165, 1070 and 805 cm^{-1} ; δ : 0.75-2.63 (m, 28H, 3x CH_3 , 9x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.33 (d, 1H, CHCl), 6.69-8.27 (m, 11H, ArH), 10.69 (s, 1H, OH).

[Found: C, 70.39; H, 7.39% $\text{C}_{35}\text{H}_{43}\text{ClO}_6$ requires
C, 70.65; H, 7.23%].

[S]-4"-n-Dodecyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoate (4.b.7)

This was prepared following a procedure similar to the one described for the compound 4.a.7. Thus, [S]-2-chloro-4-methylpentanoic acid was esterified with 4"-n-dodecyloxybiphenyl 2,4-dihydroxybenzoate in presence of N-N-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine to obtain the title compound.

Yield, 64%; m. p. 93.5°C; $[\alpha]_D^{25} = -7.43$ (c=1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1760, 1680, 1600, 1500, 1460, 1380, 1260, 1160 and 785 cm^{-1} . δ : 0.74-2.08 (m, 32H, 3x CH_3 , 11x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.52 (t, 1H, CHCl), 6.47-8.23 (m, 11H, ArH), 10.63 (s, 1H, OH).

[Found: C, 70.92; H, 7.69% $\text{C}_{37}\text{H}_{47}\text{ClO}_6$ requires
C, 71.32; H, 7.55%].

The physical data of the cognate preparations of other [S]-4"-n-alkoxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoates [4(b)] are given below.

[S]-4"-n-Hexyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoate (4.b.1)

Yield, 60%; m.p. 99.0 °C; $[\alpha]_D^{25} = -7.82$ (c=1 in CHCl₃); $\nu_{\max}^{\text{nujol}}$: 2920, 2850, 1760, 1680, 1600, 1500, 1460, 1380, 1280, 1170, 1060 and 805 cm⁻¹; δ : 0.66-2.04 (m, 22H, 3xCH₃, 6xCH₂ and CH), 4.0 (t, 2H, OCH₂), 4.44 (t, 1H, CHCl), 6.58-8.22 (m, 11H, ArH), 10.66 (s, 1H, OH).

[Found: C, 69.45; H, 6.33% C₃₁H₃₅ClO₆ requires
C, 69.08; H, 6.50%].

[S]-4"-n-Heptyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoate (4.b.2)

Yield, 62%; m.p. 85.5 °C; $[\alpha]_D^{25} = -7.82$ (c = 1 in CHCl₃); $\nu_{\max}^{\text{nujol}}$: 2920, 2850, 1765, 1680, 1595, 1500, 1460, 1380, 1285, 1651 070 and 805 cm⁻¹; δ : 0.73-2.11 (m, 22H, 3xCH₃, 6xCH₂ and CH), 4.0 (t, 2H, OCH₂), 4.53 (t, 1H, CHCl), 6.57-8.28 (m, 11H, ArH), 10.7 (s, 1H, OH).

[Found: C, 69.80; H, 7.10% C₃₂H₃₇ClO₆ requires
C, 69.50; H, 6.69%].

[S]-4"-n-Octyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoate (4.b.3)

Yield, 60%; m. p. 88.5 °C; $[\alpha]_D^{25} = -7.80$ (c = 1 in CHCl₃); $\nu_{\max}^{\text{nujol}}$: 2920, 2850, 1760, 1680, 1595, 1505, 1460, 1380, 1285, 1170, 1065 and

805 cm^{-1} ; δ : 0.61–2.06 (m, 24H, 3x CH_3 , 7x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.48 (t, 1H, CHCl), 6.59–8.27 (m, 11H, ArH), 10.67 (s, 1H, OH).

[Found: C, 69.50; H, 7.01% $\text{C}_{33}\text{H}_{39}\text{ClO}_6$ requires
C, 69.90; H, 6.88%].

[S]-4"-n-Nonyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoate (4.b.4)

Yield, 64%; m. p. 79.0°C; $[\alpha]_{\text{D}}^{25} = -7.85$ (c = 1 in CHCl_3);
 $\nu_{\text{max}}^{\text{nujol}}$: 2920, 2850, 1760, 1680, 1600, 1500, 1460, 1380, 1260, 1170, 1070 and
805 cm^{-1} ; δ : 0.74–2.11 (m, 26H, 3x CH_3 , 8x CH_2 and CH), 4.0 (t, 2H, OCH_2),
4.74 (t, 1H, CHCl), 6.67–8.28 (m, 11H, ArH), 10.74 (s, 1H, OH).

[Found: C, 70.50; H, 7.38% $\text{C}_{34}\text{H}_{41}\text{ClO}_6$ requires
C, 70.28; H, 7.06%]

[S]-4"-n-Decyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoate (4.b.5)

Yield, 64%; m. p. 88.5°C; $[\alpha]_{\text{D}}^{25} = -7.78$ (c = 1 in CHCl_3);
 $\nu_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1760, 1680, 1620, 1600, 1500, 1460, 1380, 1280, 1175 and
805 cm^{-1} ; δ : 0.71–2.07 (m, 28H, 3x CH_3 , 9x CH_2 and CH), 4.0 (t, 2H, OCH_2),
4.46 (t, 1H, CHCl), 6.6–8.23 (m, 11H, ArH), 10.52 (s, 1H, OH).

[Found: C, 70.90; H, 7.40% $\text{C}_{35}\text{H}_{43}\text{ClO}_6$ requires
C, 70.65; H, 7.25%]

[S]-4"-n-Undecyloxybiphenyl 4-(2-chloro-4-methylpentanoyloxy)-2-hydroxybenzoate (4.b.6)

Yield, 63%; m. p. 87.5°C; $[\alpha]_D^{25} = -7.7$ (c = 1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol}}: 2900, 2850, 1760, 1680, 1620, 1600, 1500, 1460, 1380, 1280, 1100$ and 810 cm^{-1} ; $\delta: 0.75-2.07$ (m, 30H, $3 \times \text{CH}_3$, $10 \times \text{CH}_2$ and CH), 4.03 (t, 2H, OCH_2), 4.60 (t, 1H, CHCl), 6.83-8.45 (m, 11H, ArH), 10.68 (s, 1H, OH).

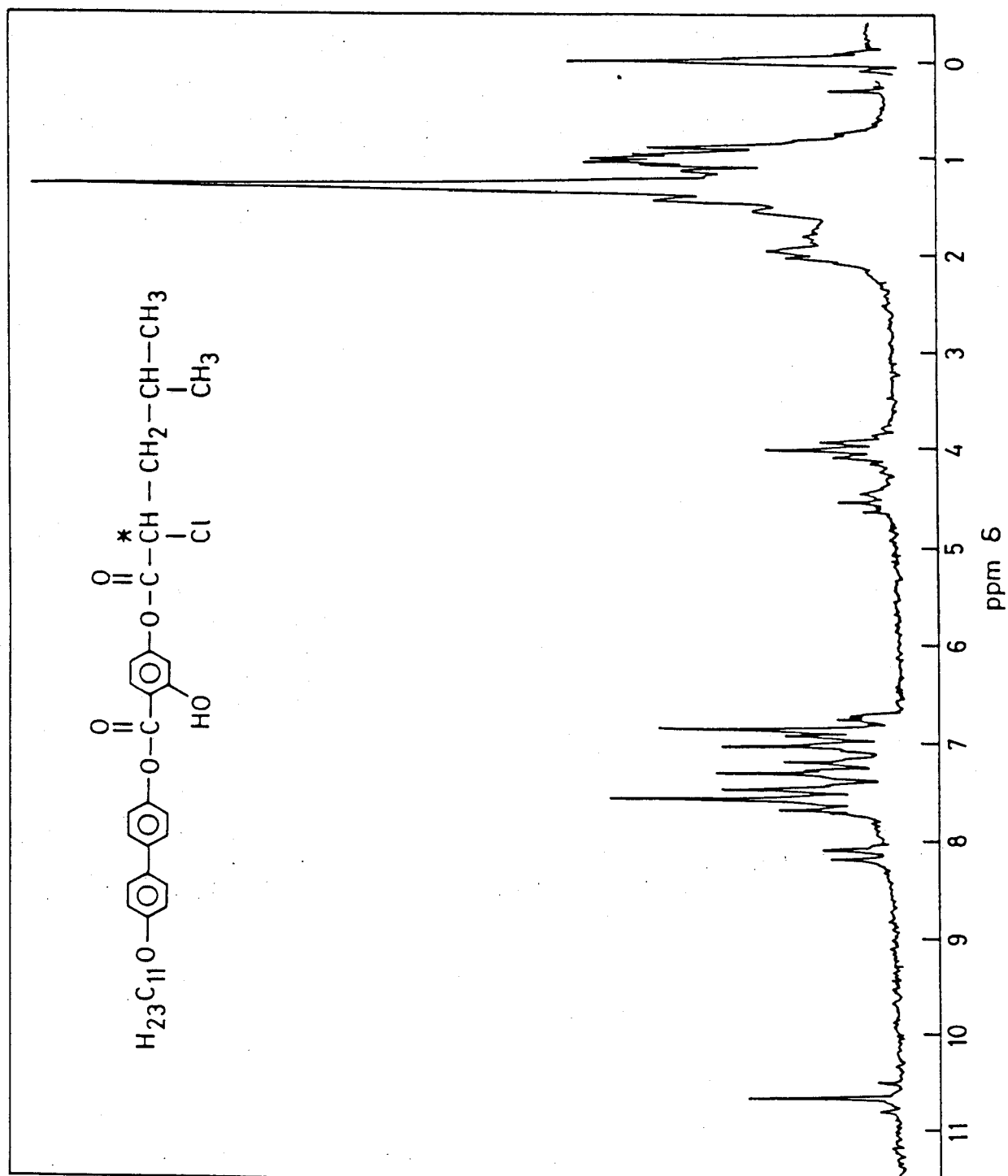
[Found: C, 70.60; H, 7.47% $\text{C}_{36}\text{H}_{45}\text{ClO}_6$ requires
C, 70.99; H, 7.39%]

[2S,3S]-4"-n-Dodecyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoate (4.c.7)

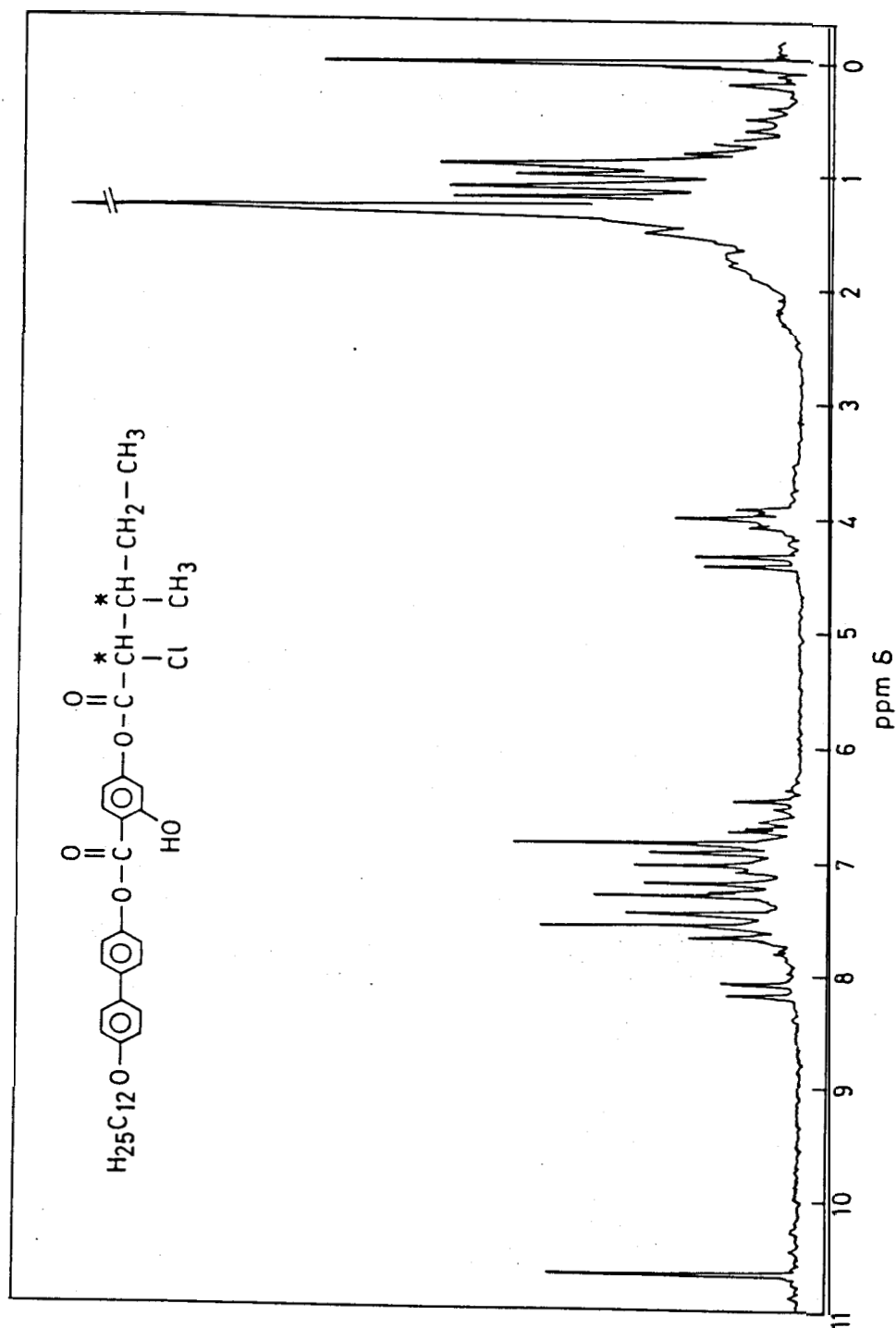
This was prepared following a procedure similar to the one described for 4.a.7. Thus [2S,3S]-2-chloro-3-methylpentanoic acid was esterified with 4"-n-dodecyloxybiphenyl 2,4-dihydroxybenzoate in presence of N,N-dicyclohexylcarbodiimide and 4-pyrrolidino-pyridine to obtain the title compound.

Yield, 64%; m. p. 67.5°C; $[\alpha]_D^{25} = +1.48$ (c = 1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol}}: 2900, 2850, 1760, 1680, 1620, 1600, 1500, 1460, 1380, 1260, 1085$ and 800 cm^{-1} ; $\delta: 0.62-2.0$ (m, 32H, $3 \times \text{CH}_3$, $11 \times \text{CH}_2$ and CH), 4.0 (t, 2H, OCH_2), 4.37 (d, 1H, CHCl), 6.4-8.26 (m, 11H, ArH), 10.69 (s, 1H, OH).

[Found: C, 71.50; H, 7.67% $\text{C}_{37}\text{H}_{47}\text{ClO}_6$ requires
C, 71.32; H, 7.54%]



¹H NMR spectrum of the compound 4.b.6.



¹H NMR spectrum of the compound 4.c.7.

The physical data of the cognate preparations of other [2S,3S]-4"-n-alkoxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoates [4(c)] are given below.

[2S,3S]-4"-n-Hexyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoate (4.c.1)

Yield, 68%; m.p. 64.0°C; $[\alpha]_D^{25} = +3.69$ (c=1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol.}}$ 2925, 2850, 1765, 1680, 1620, 1595, 1500, 1460, 1380, 1290, 1165 and 805 cm^{-1} ; δ : 0.8-2.44 (m, 22H, 3x CH_3 , 6x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.4 (d, 1H, CHCl), 6.64-8.28 (m, 11H, ArH), 10.68 (s, 1H, OH).

[Found: C, 69.46; H, 6.92% $\text{C}_{31}\text{H}_{35}\text{ClO}_6$ requires
C, 69.08; H, 6.50%]

[2S,3S]-4"-n-Heptyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoate (4.c.2)

Yield. 64%; m.p. 95.0°C; $[\alpha]_D^{25} = +3.53$ (c=1 in CHCl_3); $\nu_{\text{max}}^{\text{nujol.}}$ 2925, 2850, 1765, 1695, 1620, 1590, 1500, 1460, 1380, 1260, 1165 and 805 cm^{-1} ; δ : 0.61-2.0 (m, 22H, 3x CH_3 , 6x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.36 (d, 1H, CHCl), 6.61-8.25 (m, 11H, ArH), 10.61 (s, 1H, OH).

[Found: C, 69.18; H, 6.85% $\text{C}_{32}\text{H}_{37}\text{ClO}_6$ requires
C, 69.50; H, 6.69%]

[2S,3S]-4"-n-Octyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoate (4.c.3)

Yield, 68%; m.p. 58.0°C; $[\alpha]_D^{25} = +2.73$ (c=1 in CHCl_3); $v_{\text{max}}^{\text{nujol}}$: 2925, 2850, 1765, 1695, 1620, 1600, 1500, 1460, 1380, 1290, 1165 and 803 cm^{-1} ; δ : 0.8-2.0 (m, 24H, 3x CH_3 , 7x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.44 (d, 1H, CHCl), 6.67-8.25 (m, 11H, ArH), 10.65 (s, 1H, OH).

[Found: C, 69.81; H, 7.04% $\text{C}_{33}\text{H}_{39}\text{ClO}_6$ requires
C, 69.90; H, 6.88%]

[2S,3S]-4"-n-Nonyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoate (4.c.4)

Yield, 66%; m. p. 59.0°C; $[\alpha]_D^{25} = +2.26$ (c = 1 in CHCl_3); $v_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1760, 1680, 1620, 1605, 1500, 1460, 1380, 1260, 1085 and 800 cm^{-1} ; δ : 0.7-2.0 (m, 26H, 3x CH_3 , 8x CH_2 and CH), 4.0 (t, 2H, OCH_2), 4.37 (d, 1H, CHCl), 6.65-8.28 (m, 11H, ArH), 10.69 (s, 1H, OH).

[Found: C, 70.37; H, 7.29% $\text{C}_{34}\text{H}_{41}\text{ClO}_6$ requires
C, 70.28; H, 7.06%]

[2S,3S]-4"-n-Decyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoate (4.c.5)

Yield, 63.5%; m.p. 68.0°C; $[\alpha]_D^{25} = +2.05$ (c = 1 in CHCl_3); $v_{\text{max}}^{\text{nujol}}$: 2900, 2850, 1760, 1680, 1620, 1600, 1500, 1460, 1380, 1280, 1065 and 800 cm^{-1} ; δ : 0.81-2.0 (m, 28H, 3x CH_3 , 9x CH_2 and CH), 4.0 (t, 2H, OCH_2),

4.4 (d, 1H, CHCl), 6.57–8.24 (m, 11H, ArH), 10.68 (s, 1H, OH).

[Found: C, 70.35; H, 7.36% $C_{35}H_{43}ClO_6$ requires
C, 70.65; H, 7.25%]

[2S,3S]-4"-n-Undecyloxybiphenyl 4-(2-chloro-3-methylpentanoyloxy)-2-hydroxybenzoate (4.c.6)

Yield, 65%; m.p. 65.5°C; $[\alpha]_D^{25} = +1.76$ (c=1 in $CHCl_3$); ν_{max}^{nujol} : 2900, 2850, 1760, 1680, 1620, 1605, 1500, 1460, 1380, 2850 and 800 cm^{-1} ; 6: 0.68–2.34 (m, 30H, 3xCH₃, 10xCH₂ and CH), 4.0 (t, 2H, OCH₂), 4.4 (d, 1H, CHCl), 6.64–8.28 (m, 11H, ArH), 10.66 (s, 1H, OH).

[Found: C, 70.75; H, 7.54% $C_{36}H_{45}ClO_6$ requires
C, 70.99; H, 7.39%]

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