CHAPTER V

SYNTHESIS AND MESOMORPHIC PROPERTIES OF

i) \([S]-\text{bis-}N-[4'-n\text{-alkoxybiphenyl-4''-(2-methylbutoxy)}\]
\text{salicylaldiminato})\text{copper(II)}

ii) \([S]-\text{bis-}N-[4'-n\text{-alkoxybiphenyl-4''-(2-chloro-4-}\]
\text{ethylpentanoyloxy)}\text{salicylaldiminato})\text{copper(II)}

iii) \([2S,3S]-\text{bis-}N-[4'-n\text{-alkoxybiphenyl-4''-(2-chloro-3-}\]
\text{ethylpentanoyloxy)}\text{salicylaldiminato})\text{copper(II)}

complexes, some palladium complexes and
their corresponding ligands
V.1. SURVEY OF THE MESOGENIC PROPERTIES EXHIBITED BY COORDINATION COMPOUNDS

Probably the first known thermotropic metal containing liquid crystals were the alkali metal salts of the carboxylic acids,\(^1\) which form classical lamellar phases characteristic of soaps, and the diaryl mercury derivatives,\(^1,2\) which form smectic phases. Since then, a variety of metal based materials exhibiting liquid crystalline phases have been made.

Coordination compounds consist of a central metal atom bonded to a specific number of ions or atoms or neutral molecules. Amongst the most widely studied coordination compounds are the complexes of \(\beta\)-diketones, which have been investigated with virtually every metal in the periodic table. Similarly, N-salicyldieneaniline derivatives can also coordinate with various metal ions to yield metal chelates. However not all metal chelates show liquid crystalline phases.

It is only in the last decade or so that metal containing liquid crystalline substances are being investigated in greater detail. There are various types of ligands that have been utilised for complexation. Bruce et al.\(^3\) have used mesogenic organic nitrile ligands to synthesise the first examples of a new range of metal-containing liquid crystal materials. The metal dithiolate complexes described by Giroud\(^4,5\) are of interest as only the nickel and platinum complexes exhibit nematic and smectic mesophases. Ghedini et al.\(^6\) prepared several palladium
complexes of the azobenzene esters in an attempt to make a systematic study of the coordination of mesogenic ligands to metals. Ohta et al.\textsuperscript{7} reported the first long chain substituted bis-β-diketonato copper(II) complex, which was synthesised in an attempt to investigate mesomorphism in such transition metal complexes.

β-Diketones and N-salicylideneaniline derivatives are the most widely used ligands for preparing the metal chelates. The first transition metal complex exhibiting a mesophase was reported by Giroud and Billard.\textsuperscript{8} This complex, viz., bis(p-n-decylbenzoyl) methanatocopper(II) has a two-fold molecular symmetry and the mesophase has a lamellar structure. Ohta et al.\textsuperscript{9} have synthesised a number of copper β-diketonates, and based on optical and X-ray studies have identified the mesophases as 'discotic lamellar' phases. Giroud et al.\textsuperscript{10} have also obtained a hexagonal columnar mesophase \(D_h\) in some transition metal complexes. This happens to be the first observation of a columnar mesophase \(D_h\) in a compound consisting of a non-symmetrical surrounding of paraffin chains.

Several thousands of compounds are known to exhibit the nematic phase and all of them are diamagnetic. In 1986, Chandrasekhar et al.\textsuperscript{11} reported several bis[1-(p-n-decylbiphenyl) 3-(p-substituted phenyl)propane 1,3-dionato]copper(II) complexes \([V(i)]\) which exhibited a nematic phase. These constitute the first examples of paramagnetic nematic liquid crystals. Very recently many more such complexes have been prepared by Sadashiva
et al.,\textsuperscript{12} Muhlberger and Haase,\textsuperscript{13} Ohta et al.\textsuperscript{14} and Goodby et al.\textsuperscript{14} All these materials belong to the copper $\beta$-diketonate system. Many complexes with palladium have also been prepared which exhibit the nematic phase.

As mentioned earlier, N-salicylideneaniline derivatives have also been utilised to synthesise metal complexes exhibiting mesophases. The first representative compounds V(ii) of this type were reported by Ovchinnikov et al.\textsuperscript{15} Caruso et al.\textsuperscript{16} and Marcos et al.\textsuperscript{17} have investigated several series of metallo-organic complexes containing copper(II) and palladium(II). These two have been used because of the square planar coordinate geometry which is typical for their atomic species. Mesomorphism has been observed in molecules containing a square planar complexed copper(II). The occurrence of nematic and smectic mesomorphism has been reported in such complexes. In fact Ghedini et al.\textsuperscript{18} have synthesised a number of N-salicylaldiminato copper(II) complexes and have examined the X-ray diffraction pattern of monodomain samples. Hoshino et al.\textsuperscript{20} have characterised a homologous series of 3-hydroxy 4-[[4-ethoxyphenyl]imino]methyl] phenyl-4-alkoxybenzoates and their copper(II) complexes. The copper(II) complexes exhibit enantiotropic nematic and smectic C phases over very wide temperatures.

Examples of complexes exhibiting an $S_\infty$ phase have been reported. Barbera et al.\textsuperscript{19} have synthesised ortho palladated imine complexes using chloro, bromo, thiocyanato and acetato groups. Except for the acetato bridged complexes, most of the
others are found to be mesogenic. The chloro-bridged complexes exhibit $S_C$ phase. Caruso et al.\textsuperscript{16} have studied the effect of varying the N-alkyl chain in the tetradecyloxy copper, bis[N-\{(4-[4-(tetradecyloxy)benzoyloxy])-2-hydroxyphenyl methylene]alkanamine]complexes \text{V(iii)}. They have observed that $S_C$ phase present in the N-methylated compound vanishes as the alkyl chain is lengthened and appears again first as a monotropic phase in the decyloxy and then as an enantiotropic phase from the dodecyloxy homologue onwards. X-ray diffraction spectra showed that the smectic layer separation is remarkably smaller for the tetra and pentadecyloxy homologues than the smectic periodicity measured for the N-methylated homologue. This indicates that, notwithstanding the phase homology, molecular packing within smectic layers must have undergone a significant change. Hoshino et al.\textsuperscript{19} have reported the crystal structure of bis[4-(4-butoxybenzoyloxy)-N-(4-n-hexylphenyl)salicylaldiminato]copper(II) complex \text{V(iv)}. The higher homologues of this series exhibit $S_C$ phase. From the X-ray data overall molecular shape was found to be lath-like rather than disc-like. They have also suggested a weak coordination of carbonyl oxygen to the copper centre of neighbouring molecule.

V.2 RESULTS AND DISCUSSION

Mesogenic compounds containing metal atoms have a potential to possess metallic properties in combination with the usual properties associated with liquid crystalline compounds. With a view to explore the possibilities of obtaining ferroelectric
phases in metal containing compounds, a number of copper and palladium complexes were synthesised. The ligands that have been used to synthesise these complexes are the salicylidene derivatives. The structures of the ligands and the complexes are shown in figures 1 and 2 respectively. As can be seen these contain \([S]-2\text{-methylbutyl}, [S]-2\text{-chloro-4\text{-methylpentanoyl}}\) and \([2S,3S]-2\text{-chloro-3\text{-methylpentanoyl}}\) optically active groups.

These compounds were synthesised according to the schemes shown in figures 3, 4, 5 & 6. Methylation of 4-hydroxybiphenyl using dimethyl sulphate and ethanolic sodium hydroxide followed by Friedel-Crafts acylation with acetyl chloride and anhydrous aluminium chloride in carbon disulphide afforded 4-acetyl-4'-methoxybiphenyl. This was demethylated with 48% hydrobromic acid in acetic acid to obtain 4-acetyl-4'-hydroxybiphenyl. Alkylation reactions with dodecyl, undecyl and decylbenzene sulphonates using potassium carbonate in acetone yielded the corresponding alkoxy products. These 4-acetyl-4'-alkoxybiphenyls were converted to the amines following the procedure of van der Veen et al.\(^2\) Thus, addition of sodium azide to a solution of 4-acetyl-4'-alkoxybiphenyl in 70% sulphuric acid and dichloromethane afforded the acetonilides, which on hydrolysis with ethanolic sodium hydroxide afforded 4-(4'-n-alkoxyphenyl)anilines.

2,4-Dihydroxybenzaldehyde was obtained from resorcinol following the procedure described by Vogel.\(^3\) Alkylation with \([S]-2\text{-methylbutylbenzene sulphonate}\) and potassium carbonate in acetone resulted in the undesired dialkylated product. Hence \([S]-\)
\[ H_{2n+1}C_nO\overset{\text{N=CH}}{\longrightarrow}OR^* \]

\[ n = 10, 11 \text{ or } 12 \]

\[ R^* = \overset{\text{CH}_2}{\longrightarrow}\overset{\text{CH}}{\longrightarrow}\overset{\text{CH}_2}{\longrightarrow}\overset{\text{CH}_3}{\longrightarrow} \]

\[ \text{5 (a)} \]

\[ \overset{\text{O}}{\longrightarrow}\overset{\text{C}}{\longrightarrow}\overset{\text{CH}}{\longrightarrow}\overset{\text{CH}_2}{\longrightarrow}\overset{\text{CH}-\text{CH}_3}{\longrightarrow} \]

\[ \text{Cl} \]

\[ \text{5 (b)} \]

\[ \overset{\text{O}}{\longrightarrow}\overset{\text{C}}{\longrightarrow}\overset{\text{CH}}{\longrightarrow}\overset{\text{CH}}{\longrightarrow}\overset{\text{CH}_2}{\longrightarrow}\overset{\text{CH}_3}{\longrightarrow} \]

\[ \text{Cl} \]

\[ \text{5 (c)} \]

FIGURE 1
$M = \text{Cu or Pd} \quad ; \quad n = 10, 11 \text{ or } 12$

$R^* = \begin{array}{c}
\text{CH}_2 - \text{*CH - CH}_2 - \text{CH}_3 \\
\text{CH}_3
\end{array} \quad 5\ (d)$

$\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array} - \text{C - *CH - CH}_2 - \text{CH - CH}_3 \\
\text{CH}_3 \quad \quad 5\ (e)$

$\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array} - \text{C - *CH - *CH - CH}_2 - \text{CH}_3 \\
\text{CH}_3 \quad \quad 5\ (f)$

FIGURE 2
FIGURE 3

(cont'd.)
FIGURE 3
$\text{H}_2n+1\text{CnO}-\text{NH}_2 + \text{H-C-O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$

$\text{EtOH/AcOH (1 drop)}$

$\text{H}_2n+1\text{CnO}-\text{N=C-O-CH}_2\text{-CH}_2\text{-CH}_3$

$n = 10, 11 \text{ or } 12$

$\text{EtOH/AcOH (1 drop)}$

$\text{H}_2n+1\text{CnO}-\text{N=C-O-CH}_2\text{-CH}_2\text{-CH}_3$

$n = 10, 11 \text{ or } 12$

$\text{EtOH/AcOH (1 drop)}$

$\text{H}_2n+1\text{CnO}-\text{N=C-O-CH}_2\text{-CH}_2\text{-CH}_3$

$n = 10, 11 \text{ or } 12$

\text{FIGURE 4}
\[ \text{H}_2\text{n+1CnO} \text{N=C} \text{O-CH}_2\text{-CH}_2\text{-CH}_3 \]

\[ \text{THF} \]

\[ \text{CuCl}_2\cdot2\text{H}_2\text{O/ EtOH} \]

\[ \text{H}_2\text{n+1CnO} \text{N=C} \text{O-M-O} \text{CH}_2\text{-CH}_2\text{-CH}_3 \]

\[ \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3 \]

\[ \text{C}=\text{N-O-CH}_2\text{-CH}_2\text{-CH}_3 \]

\[ \text{M}=\text{Cu}; \text{ } n=10,11 \text{ or } 12 \]

**FIGURE 5**

(contd.)
5(e) \( M = Cu \); \( n = 10, 11 \) or 12
\[ \text{H}_{25}\text{C}_{12}\text{O} - \text{N} \equiv \text{C} - \text{OR}^* \]

\[ \text{PdCl}_2, \text{K}_2\text{CO}_3 \]

\[ \text{CH}_3\text{CN} \]

\[ \text{H}_{25}\text{C}_{12}\text{O} - \text{N} \equiv \text{C} - \text{OR}^* \]

\[ \text{R}^* = \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \quad (5.\ d.\ 4) \]

\[ \text{Cl} \quad \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_3 \quad (5.\ e.\ 4) \]

\[ \text{Cl} \quad \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} - \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_3 \quad (5.\ f.\ 4) \]

\[ \text{Cl} \quad \text{CH}_3 \]

**FIGURE 6**
2-methylbutyl iodide and potassium carbonate in acetone was used to obtain the desired monoalkylated product, viz., [S]-4'-(2-methylbutoxy)-2'-hydroxybenzaldehyde. Esterification of the optically active acids with 2,4-dihydroxybenzaldehyde following the procedure of Hassner and Alexanian resulted in the desired monoesters, viz., [S]-4'-(2-chloro-4-methylpentanoyloxy)-2'-hydroxybenzaldehyde and [2S,3S]-4'-(2-chloro-3-methylpentanoyloxy)-2'-hydroxybenzaldehyde. Schiff's bases were prepared by refluxing the aldehydes with corresponding 4-(4'-n-alkoxyphenyl)-anilines using a drop of acetic acid as a catalyst.

Copper complexes 5(d) were obtained by treating the potassium salt of the Schiff's base 5(a) in tetrahydrofuran with copper(II) chloride dihydrate in ethanol at room temperature. However, in case of the copper complexes 5(e) and 5(f) anhydrous conditions had to be maintained. Thus, refluxing the Schiff's bases 5(b) and 5(c) with anhydrous copper(II) acetate and anhydrous potassium carbonate in dry acetonitrile afforded the desired copper complexes 5(e) and 5(f). All the palladium complexes were obtained by refluxing the Schiff's bases with anhydrous potassium carbonate and palladium chloride in acetonitrile.

4-Acetyl-4'-dodecyloxybiphenyl and 4-acetyl-4'-decyloxybiphenyl are reported to exhibit $S_E$ phase. 4-Acetyl-4'-undecyloxybiphenyl was also found to exhibit $S_E$ phase, the transition temperatures being $C_{109.0}$ $S_E 128.8$ I. 4-(4'-n-alkoxyphenyl)acetanilides were also found to exhibit a smectic phase.
The thermal range of the smectic phase for these compounds is found to be between 6°C and 9°C.

The transition temperatures of the Schiff's bases 5(a), 5(b) and 5(c) are given in tables 1, 2 and 3 respectively. All the Schiff's bases exhibit smectic polymorphism. In addition to $S_A$ and $S_{C^*}$ phases some additional higher order smectic phases are also observed.

The transition temperatures of the complexes 5(d), 5(e) and 5(f) are given in tables 4, 5 and 6 respectively. All the complexes are enantiotropic mesomorphic. The complexes exhibit enantiotropic $S_A$ phase. An $S_{C^*}$ phase is also observed in copper complexes having $[S]-2$-methylbutoxy 5(d) and $[S]-2$-chloro-4-methylpentanoyloxy 5(e) groups.

All the Schiff's bases as well as the complexes decompose as they go to the isotropic phase.

As is seen in table 1, $[S]-N-[2'-hydroxy-4'-(2$-methylbutoxy)benzylidene]$-4''-n$-alkoxyphenylanilines 5(a) exhibit four smectic phases. The thermal range of $S_A$ phase is about 6°C. $S_A$ phase shows a fan shaped focal conic texture. The range of $S_{C^*}$ phase for these compounds is about 60°C. Two more smectic phases are observed below $S_{C^*}$ phase. The textures of these phases are shown in plates V1 & V2. $[S]-N-[2'-Hydroxy-4'-(2$-chloro-4-methylpentanoyloxy)benzylidene]$-4''-n$-alkoxyphenylanilines 5(b) exhibit three smectic phases. The thermal range of $S_A$ and $S_{C^*}$ phases for these
Plate V.1: The Schlieren texture of $S_1$ phase of the compound 5.a.1 at 142°C. (x300)

Plate V.2: The mosaic texture of $S_2$ phase of the compound 5.a.3 at 120°C (x300).
Table 1

Transition temperatures (°C) and heats of transition (Kcals/mole) of

\[
\text{H}_{2n+1} \text{CnO} \raisebox{1ex}{\text{N=CH}} \O \text{O-CH}_{2}\text{CH-CH}_{2}\text{-CH}_{3} \quad \text{5(a)}
\]

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<th>Compound number</th>
<th>n</th>
<th>C</th>
<th>S₂</th>
<th>S₁</th>
<th>S_{C^*}</th>
<th>S_A</th>
<th>I</th>
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<tr>
<td>5.a.1</td>
<td>10</td>
<td>92.5</td>
<td>132.5</td>
<td>154.5</td>
<td>218.0</td>
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<td>(3.1)</td>
<td>(0.4)</td>
<td>(0.3)</td>
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<td>5.a.2</td>
<td>11</td>
<td>89.0</td>
<td>129.5</td>
<td>152.5</td>
<td>214.0</td>
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<td>(5.3)</td>
<td>(0.4)</td>
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<td>5.a.3</td>
<td>12</td>
<td>88.5</td>
<td>129.0</td>
<td>152.5</td>
<td>213.5</td>
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<td>(3.3)</td>
<td>(0.4)</td>
<td>(0.2)</td>
</tr>
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Table 2

Transition temperatures (°C) and heats of transition (Kcals/mole) of

\[
\text{H}_{2n+1}\text{CnO} - \text{O} - \text{N} = \text{CH} - \text{O} - \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_3
\]

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<tr>
<th>Compound number</th>
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<th>(S_1)</th>
<th>(S_{C^*})</th>
<th>(S_A)</th>
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<td>5.b.1</td>
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<td>118.0</td>
<td>(5.6)</td>
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<td>114.0</td>
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<td>(0.08)</td>
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<td>5.b.2</td>
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<td>108.0</td>
<td>(8.04)</td>
<td>206.0</td>
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<td>120.0</td>
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<td>5.b.3</td>
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<td>.</td>
<td>106.5</td>
<td>(8.8)</td>
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<td>121.0</td>
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Table 3

Transition temperatures (°C) and heats of transition (Kcals/mole) of

\[ H_{2n+1}CnO\_\text{N}^{\text{\textbullet}}\text{CH}^{\text{\textbullet}}\text{O}^{\text{\textbullet}}\text{C}^{\text{\textbullet}}\text{\textbullet}^{\text{\textbullet}}\text{CH}^{\text{\textbullet}}\text{CH}\_\text{CH}_2\_\text{CH}_3 \]

<table>
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<th>Compound number</th>
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<th>n</th>
<th>C</th>
<th>( S_2 )</th>
<th>( S_1 )</th>
<th>( S_{C^*} )</th>
<th>( S_A )</th>
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Table 4

Transition temperatures (°C) and heats of transition (Kcals/mole) of complexes 5(d)

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<th>Compound number</th>
<th>M</th>
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<th>C₁</th>
<th>C</th>
<th>S_C⁺</th>
<th>S_A</th>
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<td>5.d.1</td>
<td>Cu</td>
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### Table 5

Transition temperatures (°C) and heats of transition (Kcals/mole) of complexes 5(e)

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Table 6

Transition temperatures (°C) and heats of transition (Kcals/mole) of complexes 5(f)

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<th>C₁</th>
<th>C</th>
<th>S_A</th>
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compounds are about 25°C and 65°C respectively.

In the case of [2S,3S]-N-[2'-hydroxy-4'-(2-methyl-3-chloro pentanoyloxy)benzyldene]-4"-n-alkoxyphenylanilines four smectic phases are observed. The thermal ranges of $S_A$ and $S_{C*}$ phases are about 30°C and 75°C respectively. The Schlieren texture of $S_{C*}$ phase becomes clearer in the higher order smectic phases. It is seen that in all the Schiff's bases $S_{C*}$ phase is a predominant phase with a wider range than the other phases. The higher order smectic phases have not been identified.

[S]-bis-N-[4'-n-alkoxybiphenyl-4"-(2-methylbutoxy)salicyl aldiminato]copper(II) complexes 5(d) exhibit only $S_A$ and $S_{C*}$ phases. The thermal range of $S_A$ phase is about 70°C. The decyloxy homologue 5.d.1 shows a monotropic $S_{C*}$ phase while the other two are enantiotropic. Compound 5.d.3 (n=12) melts at 174°C and has a $S_{C*}$ phase range of 16°C. The $S_{C*}$ phase shows a schlieren texture.

The copper complexes having [S]-2-chloro-4-methylpentanoyloxy group (5.e.1 to 5.e.3) exhibit an enantiotropic $S_A$ phase and a monotropic $S_{C*}$ phase. The $S_A$-$S_{C*}$ transition temperatures are only 3-5°C below the melting points. The thermal range of $S_A$ phase is about 75°C. In compounds 5.e.2 and 5.e.3, $S_{C*}$ phase does not crystallise till about 90°C when cooled at a rate of 10°C/minute.

Copper complexes having [2S,3S]-2-chloro-3-methylpentanoyloxy group 5(f) exhibit only $S_A$ phase. The range of $S_A$ phase increases on ascending the homologous series. All the palladium complexes (5.d.4, 5.e.4 and 5.f.4) exhibit only $S_A$ phase with a fan shaped focal-conic texture. The melting and the clearing points of these
Plate V.3: The Schlieren texture of $S_{C_6}$ phase of the complex 5.d.3 at 180°C. (x300)
complexes are considerably higher than the corresponding homologues of the copper complexes.

The Schiff's bases 5(b) and 5(c) are isomeric as also the complexes 5(e) and 5(f). The structural difference involved is only a change in the position of the methyl group on pentanoyloxy chain. This also results in an additional chiral centre. In case of the Schiff's bases 5(b) and 5(c), it is seen that an additional smectic phase exists in the latter, which has two chiral centres. The melting points show a considerable reduction in compounds belonging to this series. However, the clearing points do not show much variation. The $S_{C^*}$-$S_A$ transition temperatures also do not change much. The range of $S_{C^*}$ phase is wider by about 10$^\circ$C for the compounds with two chiral centres [5(c)]. The copper complexes 5(e) exhibit a monotropic $S_{C^*}$ phase which is absent in the corresponding isomers 5(f). The melting points of the copper complexes belonging to the series 5(f) are 36$^\circ$C to 48$^\circ$C higher than the corresponding copper complexes of series 5(e). The clearing points too, are higher by about 30$^\circ$C in copper complexes of series 5(f). However, the differences are reduced in case of the palladium complexes 5.e.4 and 5.f.4.

The only other example of a metallomesogen exhibiting $S_{C^*}$ phase has been reported by Espinet et al.\textsuperscript{23} very recently. This is perhaps the first ferroelectric liquid crystal containing a transition metal in it. The structure of this compound is shown in figure 7. From spectroscopic studies they have shown that this compound consists of a mixture of trans-$\Lambda$.R,R (34%), trans-$\Lambda$.RR (34%)
and cis-RR(32%) isomers. $S_{C^*}$ phase is observed in this compound from $102^\circ C$ to $119^\circ C$.

Introduction of a lateral hydroxyl group in a Schiff's base is known to increase the clearing points and the overall smectic mesophase range. A tendency to stabilise $S_C$ phase more than the other phases has also been observed.$^{23,24}$ Otterholm et al.$^{26}$ have investigated the mesomorphic behaviour of $[S]-4'-(2$-methylbutyl), $[S]-4'-(4$-methylhexyl) and $[S]-4'-(6$-methyloctyl)resorcylinene 4-alkylanilines. Most members of these series exhibit an unusually high propensity to show $S_{C^*}$ phases. The lateral hydroxyl group strongly promotes the occurrence of $S_{C^*}$ phase. This has been explained by considering coplanarity of the aromatic rings, the intramolecular bonding leading to a pseudo three ring system and intermolecular hydrogen bonding which can develop in the tilt direction and stabilise the tilt of $S_{C^*}$ phase. However, the infrared spectra data do not indicate the presence of intermolecular hydrogen bonds and therefore the coplanarity of the benzene rings seems to be a major factor influencing smectic thermal stability in case of these Schiff's bases with a lateral hydroxyl group.

In conclusion, it is believed that copper complexes 5(d) and 5(e) synthesised by the author represent the first examples of paramagnetic ferroelectric liquid crystals.
V.I. EXPERIMENTAL

4-Methoxybiphenyl

4-Hydroxybiphenyl (51.0 g, 0.3 mol) was placed in a 500 ml three-necked flask equipped with a pressure equalising separatory funnel, mechanical stirrer and a reflux condenser. A solution of sodium hydroxide (12.8 g, 0.32 mol) in water (128 ml) and ethanol (100 ml) was added to it. This mixture was stirred and cooled in an ice-bath to about 10°C. Dimethyl sulphate (37.8 g, 0.3 mol) was added dropwise to it over a period of forty minutes. After completion of addition, the reaction mixture was refluxed for one hour and a clear solution was obtained. On cooling, the precipitated product was filtered, washed with water, dried and crystallised from ethanol (54.2 g, 80%). m.p. 89.0°C. (Reported27 m.p. 91.0°C).

4-Acetyl-4'-methoxybiphenyl

In a 500 ml three-necked flask fitted with a mercury sealed stirrer, a pressure equalising funnel and a reflux condenser connected to water trap through anhydrous calcium chloride guard tube, a mixture of 4-methoxybiphenyl (18.4 g, 0.1 mol), anhydrous aluminium chloride (18.7 g, 0.14 mol) and carbon disulphide (175 ml) was placed. This was stirred, cooled in an ice-bath and freshly distilled acetyl chloride (7.8 g, 0.1 mol) was added dropwise to it. After the addition was complete the reaction mixture was stirred at 35°C for five hours and then refluxed for one hour. After removal of carbon disulphide the syrupy residue
was poured on to a mixture of ice and concentrated hydrochloric acid. The solid formed was filtered and boiled with ether (50 ml) for fifteen minutes and the ethereal solution was decanted off. This operation was repeated thrice and then the ether insoluble portion was crystallised from isopropanol (14.7 g, 65%) m.p. 157.0°C. (Reported²⁸ m.p. 156.5°C).

4-Acetyl-4'-hydroxybiphenyl

A mixture of 4-acetyl-4'-methoxybiphenyl (10.0 g, 0.044 mol), hydrobromic acid (48%, 75 ml) and acetic acid (125 ml) was refluxed for sixteen hours. It was then poured into ice-cold water and the precipitate formed was filtered, washed thoroughly with water and dried. The crude product so obtained was crystallised from ethanol (8.9 g, 95%). m.p. 146.0°C. (Reported²⁹ m.p. 146-147.5°C).

n-Dodecylbenzenesulphonate

Benzenesulphonyl chloride (19.4 g, 0.11 mol) was added dropwise to a stirred ice-cold solution of n-dodecanol (18.6 g, 0.1 mol) in pyridine (16 ml) and left overnight. It was then poured on to a mixture of ice and concentrated hydrochloric acid and extracted with ether (3x100 ml). The combined ethereal solution was washed with water (3x100 ml), dried (Na₂SO₄) and the solvent removed. The residual liquid so obtained was used as such without further purification (30.7 g, 94%).
4-Acetyl-4'-n-dodecyloxybiphenyl

A mixture of 4-acetyl-4'-hydroxybiphenyl (2.60 g, 0.0123 mol), n-dodecylbenzene sulphonate (3.26 g, 0.01 mol) and potassium carbonate (2.4 g, 0.0174 mol) was refluxed in acetonitrile (30 ml) for seventeen hours with stirring. The reaction mixture was then poured into ice-cold water and extracted with chloroform (3x50 ml). The combined chloroform solution was washed with water (3x100 ml) and dried (Na₂SO₄). The residue obtained on removal of the solvent was chromatographed on silica gel and eluted with 20% chloroform-petroleum ether (b.p. 60-80°C) mixture. The solvent was removed from the eluate and the solid residue so obtained was crystallised from isopropanol (3.0 g, 80%). m.p. 108.0°C. (Reported²⁹ m.p. 108.5°C).

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

4-Acetyl-4'-n-decyloxybiphenyl

Yield, 74%; m.p. 104.0°C. (Reported³⁰ m.p. 103.0°C)

4-Acetyl-4'-n-undecyloxybiphenyl

Yield, 80%; m.p. 109°C; ν_max (nujol): 2900, 2850, 1680, 1600, 1500, 1460, 1360, 1285, 1200, 1030 and 820 cm⁻¹.

[Found: C, 82.13; H, 9.32% C²⁵H₃₄O₂ requires C, 81.97; H, 9.29%].
4-(4'-n-Dodecylxyloxyphenyl)acetalnilide

This was prepared following the procedure of van der Veen et al.\textsuperscript{21} Thus, sodium azide (0.7 g, 0.011 mol) was added in small portions to a vigorously stirred mixture of 4-acetyl-4'-n-dodecylxyloxybiphenyl (3.8 g, 0.01 mol) and 70% sulphuric acid (15 ml). Dichloromethane (10 ml) was also added to inhibit any frothing. After the addition was complete the reaction mixture was poured into ice-cold water and extracted with dichloromethane (3x40 ml). The combined organic solution was washed with water (5x60 ml), dried (Na\textsubscript{2}SO\textsubscript{4}) and the solvent removed. The crude product so obtained was crystallised from benzene (3.2 g, 81%). m.p. 165.5\textdegreeC; (C 165.5 S 171.0 I); $\nu_{\text{nujol}}^\text{max}$: 3300, 2900, 2850, 1660, 1600, 1500, 1460, 1380, 1260, 1040 and 810 cm\textsuperscript{-1}.

[Found: C,78.94; H,9.44; N,3.11%] \hspace{1cm} C\textsubscript{26}H\textsubscript{37}NO\textsubscript{2} requires C,78.99; H,9.37; N,3.5%].

The physical data of the cognate preparations of other 4-(4'-n-alkoxyphenyl)acetalnilides are given below.

4-(4'-n-Decylxyloxyphenyl)acetalnilide

Yield, 78%; m.p: 167.0\textdegreeC (C 167.0 S 174.0 I); $\nu_{\text{nujol}}^\text{max}$: 3300, 2900, 2850, 1660, 1610, 1500, 1460, 1380, 1260, 1030 and 810 cm\textsuperscript{-1}.

[Found: C,78.53; H,9.00; N,3.47%] \hspace{1cm} C\textsubscript{24}H\textsubscript{33}NO\textsubscript{2} requires C,78.47; H,8.99; N,3.81%].
4-(4'-n-Undecyloxyphenyl)acetanilide

Yield, 78%; m.p. 147.0°C (C 147.0 ± 156.0 I); \( v_{\text{nujol}}^{\text{max}} \) 3300, 2900, 2850, 1660, 1610, 1500, 1460, 1380, 1260 and 800 cm\(^{-1}\)

[Found: C, 78.37; H, 9.52; N, 3.26\%; \( \text{C}_{25}\text{H}_{35}\text{NO}_2 \) requires C, 78.74; H, 9.19; N, 3.67\%].

4-(4'-n-Dodecyloxyphenyl)aniline

This was prepared following the procedure of van der Veen et al.\(^{21}\). Thus, a mixture of 4-(4'-n-dodecyloxyphenyl)acetanilide (13.0 g, 0.033 mol), sodium hydroxide (27.5 g, 0.68 mol), ethanol (55 ml) and water (17 ml) was refluxed for six hours. Ethanol was removed under reduced pressure and the residue was poured into ice-water. This was extracted with benzene (4x100 ml) and the combined benzene solution was washed with water (3x100 ml) and dried (\( \text{Na}_2\text{SO}_4 \)). The residue obtained upon removal of the solvent was crystallised from benzene. (10.5 g, 90\%). m.p. 103.0°C; \( v_{\text{nujol}}^{\text{max}} \): 3400, 3200, 1610, 1500, 1460, 1380, 1260 and 820 cm\(^{-1}\).

[Found: C, 81.29; H, 9.53; N, 3.68\%; \( \text{C}_{24}\text{H}_{35}\text{NO} \) requires C, 81.58; H, 9.91; N, 3.97\%].

The physical data of the cognate preparations of other 4-(4'-n-alkoxyphenyl)anilines are given below.

4-(4'-n-Decyloxyphenyl)aniline

Yield, 88\%. m.p. 110.0°C; \( v_{\text{nujol}}^{\text{max}} \): 3350, 3200, 2900, 2850, 1600,
1500, 1460, 1380, 1270, 1030 and 810 cm\textsuperscript{-1}.

\[ \text{([Found: C, 80.98; H, 9.33; N, 4.18\% C\textsubscript{22}H\textsubscript{31}NO requires C, 81.23; H, 9.54; N, 4.31\%])} \]

4-(4'-n-Undecyloxyphenyl)aniline

\[ \text{Yield, 87\%; m.p. 100.0^\circ\text{C}; \nu_{\text{max}}^\text{nujol}: 3400, 3200, 2925, 2875, 1610, 1500, 1460, 1380, 1260 and 820 cm\textsuperscript{-1}.} \]

\[ \text{([Found: C, 81.09; H, 9.58; N, 4.32\% C\textsubscript{23}H\textsubscript{33}NO requires C, 81.41; H, 9.73; N, 4.13\%])} \]

2,4-Dihydroxybenzaldehyde

This was prepared following the procedure described by Vogel.\textsuperscript{31} Thus, in a 500 ml three-necked flask fitted with a mercury sealed stirrer, a wide inlet tube extending nearly to the bottom of the flask and a reflux condenser carrying anhydrous calcium chloride guard tube was placed a mixture of resorcinol (20.0 g, 0.18 mol), anhydrous zinc cyanide (40.0 g, 0.34 mol) and sodium dried ether (175 ml). A rapid stream of hydrogen chloride gas was passed into it while stirring. The zinc cyanide gradually disappeared with the formation of a cloudy solution. Further passage of hydrogen chloride resulted in the separation of imine hydrochloride, after which hydrogen chloride was passed more slowly and the stirring continued for a further period of thirty minutes. The ether was decanted and the solid material was crystallised using minimum quantity of water (23.5 g, 94\%). m.p. 135.0^\circ\text{C}. (Reported\textsuperscript{31} m.p. 135-136^\circ\text{C}).
A mixture of 2,4-dihydroxybenzaldehyde (3.4 g, 0.025 mol), [S]-2-methylbutyl iodide (5.3 g, 0.027 mol), anhydrous potassium carbonate (5.0 g, 0.36 mol) and dry acetone (50 ml) was refluxed for thirty hours. Acetone was removed under reduced pressure and the residue was poured into cold water and extracted with ether (3x50 ml). The combined ethereal solution was washed with water (3x100 ml) and dried (Na₂SO₄). The residue obtained after removal of the solvent was chromatographed on silica gel and eluted with 60% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate yielded the pure product as a viscous liquid (3.3 g, 65%). \([\alpha]_{D}^{25} = -12.2 (c=2 \text{ in } \text{CHCl}_3)\); \(\nu_{\text{max}}^{\text{neat}}: 2950, 2800, 2700, 1660, 1620, 1600, 1500, 1460, 1380, 1200, 1120 \text{ and } 810 \text{ cm}^{-1};\)

\(\delta: 0.71-2.07 (m, 9H, 2\times \text{CH}_3, \text{CH} \text{ and CH}), 3.82 (d, 2H, \text{OCH}_2), 6.14-7.57 (m, 3H, \text{ArH}), 9.7 (s, 1H, \text{CHO}), 11.46 (s, 1H, \text{-OH}).\)

[Found: C, 69.55; H, 7.86% \(\text{C}_{12}\text{H}_{16}\text{O}_3\) requires C, 69.23; H, 7.69%].

[S]-4'-(2-Chloro-4-methylpentanoyloxy)-2'-hydroxybenzaldehyde

This was prepared following the esterification procedure of Hassner and Alexanian. Thus, a mixture of 2,4-dihydroxybenzaldehyde (3.45 g, 0.025 mol), [S]-2-chloro-4-methylpentanoic acid (3.46 g, 0.023 mol), N,N-dicyclohexylcarbodiimide (5.15 g, 0.025 mol) and 4-pyrrolidinopyridine was stirred at room temperature in dry chloroform (100 ml) for twelve hours. The dicyclohexylurea formed was filtered off. The filtrate was washed with 5%
acetic acid (2 x 60 ml), water (3 x 60 ml) and dried (Na₂SO₄). The residue obtained on removal of the solvent was chromatographed on silica gel and eluted with 70% chloroform-petroleum ether (b.p. 60-80°C) mixture. On removal of solvent from the eluate, a viscous liquid was obtained. (3.7 g, 60%). [α]D²⁵ = -13.04 (c = 2 in CHCl₃); νmax neat 2950, 2875, 2700, 1680, 1580, 1460, 1370, 1260, 1200, 1190 and 800 cm⁻¹; δ: 0.64-2.0 (m, 9H, 2 x CH₃, CH₂ and CH), 4.12 (t, 1H, -OCHCl), 6.32-8.0 (m, 3H, ArH), 9.72 (s, 1H, -CHO), 10.32 (s, 1H, -OH).

[Found: C, 57.98; H, 5.92% C₁₃H₁₅ClO₄ requires C, 57.67; H, 5.54%].

[2S,3S]-4′-(2-Chloro-3-methylpentanoyloxy)-2′-hydroxybenzaldehyde

Following a procedure similar to the one described above, esterification of [2S,3S]-2-chloro-3-methylpentanoic acid with 2,4-dihydroxybenzaldehyde in presence of N,N-dicyclohexyl carbodiimide and 4-pyrrolidinopyridine afforded the desired monoester. Yield, 62%; [α]D²⁵ = -13.7 (c = 2 in CHCl₃); νmax neat 2975, 2800, 2700, 1680, 1600, 1500, 1460, 1360, 1260, 1180 and 840 cm⁻¹; δ: 0.66-2.32 (m, 9H, 2 x CH₃, CH₂ and CH), 4.19 (d, 1H, -CHCl), 6.34-8.19 (m, 3H, ArH), 9.7 (s, 1H, -CHO), 10.34 (s, 1H, -OH).

[Found: C, 57.25; H, 5.18% C₁₃H₁₅ClO₄ requires C, 57.67; H, 5.54%].
[S]-N-[2'-Hydroxy-4'-(2-methylbutoxy)benzyldiene]-4'-n-dodecyloxyphenylaniline (5.a.3)

A mixture of 4-[4'-n-dodecyloxyphenyl]aniline (0.337 g, 0.001 mol), [S]-4'-(2-methylbutoxy)-2'-hydroxybenzaldehyde (0.208 g, 0.001 mol) and a drop of acetic acid was refluxed in ethanol (20 ml) for four hours. It was then cooled and the precipitated solid filtered off, washed with cold ethanol, dried and crystallised repeatedly from butan-2-one (0.515 g, 95%). m.p. 88.5°C; \([\alpha]_{D}^{25} = +6.93 (c = 2 \text{ in CHCl}_3); \) \(v_{\text{max}}^{\text{nujol}}:2900,2850,1630,1600,1500,1460,1380,1280,1200\) and 820 cm\(^{-1}\); \(\delta:0.85-2.04 (m, 32\text{H},3\times\text{CH}_3,11\times\text{CH}_2\text{ and }\text{CH}),3.69-4.16 (m,4\text{H},-\text{OCH}_2),6.27-8.5 (m,9\text{H},\text{ArH and -N=CH-}),13.58 (s,1\text{H},-\text{OH}).

[Found: C,79.43;H,9.35;N,2.26% \(C_{36}H_{49}NO_3\) requires C,79.56;H,9.02;N,2.58%].

The physical data of the cognate preparations of other [S]-N-[2'-hydroxy-4'-(2-methylbutoxy)benzyldiene]-4'-n-alkoxyphenylanilines [5(a)] are given below.

[S]-N-[2'-Hydroxy-4'-(2-methylbutoxy)benzyldiene]-4'-n-decyloxyphenylaniline (5.a.1)

Yield, 90%; m.p. 92.5°C; \([\alpha]_{D}^{25} = +6.28 (c = 2 \text{ in CHCl}_3); \) \(v_{\text{max}}^{\text{nujol}}:2900,2850,1620,1600,1500,1460,1380,1280,1205\) and 830 cm\(^{-1}\); \(\delta:0.73-2.04 (m,28\text{H},3\times\text{CH}_3,9\times\text{CH}_2\text{ and }\text{CH}),3.62-4.12 (m,4\text{H},-\text{OCH}_2),6.23-8.35 (m,9\text{H},\text{ArH and -N=CH-}),13.19 (s,1\text{H},-\text{OH}).

[Found: C,79.05;H,8.84;N,2.51% \(C_{34}H_{45}NO_3\) requires C,79.22;H,8.74;N,2.72%].
[S]-N-[2'-Hydroxy-4'(2-methylbutoxy)benzylidene]-4'-n-undecyloxyphenylaniline (5.a.2)

Yield, 92%; m.p. 89.0°C; [α]D^25 = +6.49 (c=2 in CHCl₃); v\text{nujol} \text{max}: 2900, 2850, 1630, 1600, 1500, 1460, 1380, 1280, 1190 and 820 cm\(^{-1}\); δ: 0.81-2.04 (m, 30H, 3xCH₃, 10xCH₂ and CH), 3.61-4.17 (m, 4H, -OCH₂), 6.35-8.38 (m, 9H, ArH and -N=CH⁻), 14.07 (s, 1H, -OH).

[Found: C, 79.23; H, 8.56; N, 2.30% C\text{₃₄H₄₇NO₃} \text{requires} C, 79.47; H, 8.88; N, 2.65%].

[S]-N-[2'-Hydroxy-4'(2-chloro-4-methylpentanoyloxy)benzylidene]-4'-n-dodecyloxyphenylaniline (5.b.3)

Following a procedure similar to the one described for compound 5.a.3, 4-(4'-n-dodecyloxyphenyl)aniline was condensed with [S]-4'-2-chloro-4-methylpentanoyloxy)-2'-hydroxybenzaldehyde to afford the desired Schiff's base 5.b.3.

Yield, 88%; m.p. 106.5°C; [α]D^25 = -4.23 (c=2 in CHCl₃); v\text{nujol} \text{max}: 2900, 2850, 1750, 1630, 1600, 1500, 1460, 1380, 1280, 1200, 1180 and 820 cm\(^{-1}\); δ: 0.89-2.18 (m, 32H, 3xCH₃, 11xCH₂ and CH), 3.86-4.82 (m, 3H, ArOCH₂ and CHCl), 6.73-8.77 (m, 9H, ArH and -N=CH⁻), 13.75 (s, 1H, -OH).

[Found: C, 73.45; H, 8.03; N, 2.12% C\text{₃₇H₄₆ClNO₄} \text{requires} C, 73.33; H, 7.93; N, 2.31%].

The physical data of the cognate preparations of other [S]-N-[2'-hydroxy-4'(2-chloro-4-methylpentanoyloxy)benzylidene]-4'-n-alkoxyphenylanilines [5(b)] are given below.
[S]-N-[2'-Hydroxy-4'-(2-chloro-4-methylpentanoyloxy)benzylidene]
-4''-n-decyloxyphenylalaniline (5.b.1)

Yield, 90%; m.p. 118.0°C; [α]D25 = -4.07 (c=2 in CHCl₃); νmax
2950, 2850, 1750, 1620, 1600, 1500, 1460, 1380, 1270, 1200, 1175 and 820 cm⁻¹;
δ: 0.84-2.09 (m, 28H, 3xCH₃, 9xCH₂ and CH), 3.82-4.71 (m, 3H, ArOCH₂ and
CHCl), 6.67-8.75 (m, 9H, ArH and -N=CH-), 13.58 (s, 1H, -OH).

[Found: C, 72.83; H, 7.76; N, 1.98% ]
C₃₅H₴₂ClNO₄ requires
C, 72.73; H, 7.62; N, 2.40%].

[S]-N-[2'-Hydroxy-4'-(2-chloro-4-methylpentanoyloxy)benzylidene]
-4''-n-undecyloxyphenylalaniline (5.b.2)

Yield, 90%; m.p. 108.0°C; [α]D25 = -4.28 (c=2 in CHCl₃); νmax
2950, 2850, 1750, 1620, 1600, 1500, 1460, 1380, 1270, 1200, 1180 and 820
cm⁻¹; δ: 0.82-2.12 (m, 30H, 3xCH₃, 10xCH₂ and CH), 3.84-4.71 (m, 3H,
ArOCH₂ and CHCl), 6.61-8.75 (m, 9H, ArH and -N=CH-), 13.37 (s, 1H, -OH).

[Found: C, 73.31; H, 7.86; N, 2.21% ]
C₃₆H₴₄ClNO₄ requires
C, 73.03; H, 7.78; N, 2.37%].

[2S,3S]-N-[2'-Hydroxy-4'-(2-chloro-3-methylpentanoyloxy)benzylidene]
-4''-n-dodecyloxyphenylalaniline (5.c.3)

Following a procedure similar to the one described for
compound 5.a.3, the desired Schiff's base 5.c.3 was obtained as a
condensation product of 4'-(4''-n-dodecyloxyphenyl)aniline and
[2S,3S]-4'-(2-chloro-3-methylpentanoyloxy)-2'-hydroxybenzaldehyde.
Yield, 92%; m.p. 89.0°C; [α]D25 = +2.42 (c=2 in CHCl₃); νmax

$^1$H NMR spectrum of the compound 5.c.3.
and 820 cm\(^{-1}\); \(\delta: 0.85-2.0\) (m, 32H, 3xC\(\_n\) and CH), 3.86-4.61 (m, 3H, ArOCH\(_2\) and CHCl), 6.61-8.56 (m, 9H, ArH and -N=CH-), 13.77 (s, 1H, -OH).

[Found: C, 73.65; H, 8.05; N, 2.14\%] \(C_{37}H_{46}ClNO_4\) requires C, 73.33; H, 7.93; N, 2.31\%].

The physical data of cognate preparations of other \([2S,3S]-N-[2'-hydroxy-4'-\{(2-chloro-3-methylpentanoyloxy) benzylidene\}-4'-n-alkoxyphenylanilines [5(c)] are given below.

\([2S,3S]-N-[2'-Hydroxy-4'-\{(2-chloro-3-methylpentanoyloxy) benzylidene\}-4'-n-decyloxyphenylaniline (5.c.1)

Yield, 89\%; m.p. 81.0\(^{\circ}\)C; \([\alpha]_{D}^{25} = +2.75\) (c=2 in CHCl\(_3\)); \(\nu_{\text{max}}^\text{nujol}: 2950, 2850, 1760, 1620, 1600, 1500, 1460, 1360, 1270, 1205\) and 820 cm\(^{-1}\); 
\(\delta: 0.85-2.35\) (m, 32H, 3xC\(\_n\) and CH), 3.37-4.81 (m, 3H, ArOCH\(_2\) and CHCl), 6.62-8.65 (m, 9H, ArH and -N=CH-), 13.4 (s, 1H, -OH).

[Found: C, 72.65; H, 7.76; N, 2.28\%] \(C_{35}H_{42}ClNO_4\) requires C, 72.73; H, 7.62; N, 2.40\%].

\([2S,3S]-N-[2'-Hydroxy-4'-\{(2-chloro-3-methylpentanoyloxy) benzylidene\}-4'-n-undecyloxyphenylanilnine (5.c.2)

Yield, 90\%; m.p. 85.5\(^{\circ}\)C; \([\alpha]_{D}^{25} = +2.72\) (c=2 in CHCl\(_3\)); \(\nu_{\text{max}}^\text{nujol}: 2900, 2850, 1760, 1620, 1600, 1500, 1460, 1380, 1280, 1200\) and 820 cm\(^{-1}\); 
\(\delta: 0.82-2.14\) (m, 30H, 3xC\(\_n\), 10xCH\(_2\) and CH), 3.84-4.82 (m, 3H, ArOCH\(_2\) and
Found: C, 72.92; H, 7.78; N, 2.00%  
C_{36}H_{44}ClNO_{4} requires  
C, 73.03; H, 7.78; N, 2.37%.

[S]-bis-N-[4'-n-Dodecyloxybiphenyl-4"-(2-methylbutoxy)  
salicylaldiminato]copper(II) (5.d.3)

Powdered potassium hydroxide (0.05 g, 0.00088 mol) was added  
to a solution of [S]-N-[2'-hydroxy-4'-[(2-methylbutoxy)benzylidene]-  
4"-n-dodecyloxyphenylalanine (5.a.3) (0.4 g, 0.00074 mol) in  
tetrahydrofuran (10 ml) and stirred till all of it dissolved. To  
this potassium salt, a solution of copper(II) chloride dihydrate  
(0.075 g, 0.00044 mol) in ethanol (5 ml) was added. This mixture  
was stirred at room temperature for one hour. The precipitated  
copper complex was filtered, dissolved in chloroform (25 ml),  
washed with water (5x15 ml) and dried (Na_{2}SO_{4}). The residue  
obtained after removal of the solvent was repeatedly crystallised  
from butan-2-one (0.45 g, 90%). m.p. 114.0^\circ C;  
[\alpha]_{D}^{25} = -61.29 (c=0.02  
in CHCl_{3}); \lambda_{\text{max}}^{\text{CHCl}_{3}}(\varepsilon): 388(44450), 311(61200), 259(48300),  
v_{\text{nujol}}^{\text{max}}: 2900, 2850, 1610, 1590, 1520, 1500, 1460, 1380, 1240, 1200 and 800 cm^{-1}.  

Found: C, 74.80; H, 8.44; N, 2.38%  
C_{72}H_{96}CuN_{2}O_{6} requires  
C, 75.29; H, 8.37; N, 2.44%]

The physical data of the cognate preparations of other [S]-  
bis-N-[4'-n-alkoxybiphenyl-4"-(2-methylbutoxy)salicylaldiminato]  
copper(II) [5(d)] complexes are given below.
[S]-bis-N-[4'-n-Decyloxybiphenyl-4''-(2-methylbutoxy) salicylaldiminato]copper(II) (5.d.1)

Yield, 88%; m.p. 141.0°C; \( [\alpha]_D^{25} = -65.04 (c=0.02 \text{ in CHCl}_3) \);
\( \lambda_{\text{max}}^{\text{CHCl}_3} (\epsilon): 384(34850), 312(46200), 259(36550), \nu_{\text{max}}^{\text{nujol}}: 2900, 2850, 1605, 1590, 1520, 1515, 1460, 1380, 1240, 1200 \) and 800 cm\(^{-1}\).

[Found: C,74.92; H,8.20; N,2.08% \( \text{C}_{68}H_{88}CuN_2O_6 \) requires C,74.76; H,8.06; N,2.51%].

[S]-bis-N-[4'-n-Undecyloxybiphenyl-4''-(2-methylbutoxy) salicylaldiminato]copper(II) (5.d.2)

Yield, 90%; m.p. 108.0°C; \( [\alpha]_D^{25} = -63.12 (c=0.02 \text{ in CHCl}_3) \);
\( \lambda_{\text{max}}^{\text{CHCl}_3} (\epsilon): 391(41800), 308(52400), 259(44650), \nu_{\text{max}}^{\text{nujol}}: 2900, 2850, 1610, 1590, 1500, 1460, 1380, 1270, 1200 \) and 800 cm\(^{-1}\).

[Found: C,74.92; H,8.39; N,2.57% \( \text{C}_{70}H_{92}CuN_2O_6 \) requires C,75.03; H,8.22; N,2.50%].

[S]-bis-N-[4'-n-Dodecyloxybiphenyl-4''-(2-chloro-4-methyl pentanoyloxy)salicylaldiminato]copper(II) (5.e.3)

A stirred mixture of [S]-N-[2'-hydroxy-4'-(2-chloro-4-methyl pentanoyloxy)benzylidene]-4''-n-dodecyloxyphenylalaniline (5.b.3) (0.52 g, 0.0008 mol), anhydrous potassium carbonate (0.236 g, 0.0012 mol), anhydrous copper (II) acetate (0.073 g, 0.0004 mol) and dry acetonitrile (15 ml) was heated at 80°C for four hours. It was then cooled and the precipitate formed filtered, dried, dissolved in chloroform (25 ml), washed with water (5x15 ml) and
dried (Na₂SO₄). The solid residue obtained on removal of the solvent was crystallised repeatedly from butan-2-one (0.45 g, 89%); m.p. 119.0°C; [α]_D^{25} = -27.27 (c=0.01 in CHCl₃); λ_{max} CHCl₃ (ε) 390 (32350), 309 (40400), 279 (49050), v_{nujol} max: 2900, 2800, 1740, 1600, 1520, 1460, 1370, 1240 and 800 cm⁻¹.

[Found: C, 69.62; H, 7.61; N, 1.90%] C₇₄H₇₄Cl₂CuN₂O₈ requires C, 69.78; H, 7.39; N, 2.20%].

The physical data of the cognate preparations of other [S]-bis-N-[4'-n-alkoxybiphenyl-4"-(2-chloro-4-methylpentanoyloxy) salicylaldiminato]copper(II) [5(e)] complexes are given below.

[S]-bis-N-[4'-n-Decyloxybiphenyl-4"-(2-chloro-4-methyl pentanoyloxy) salicylaldiminato]copper(II) (5.e.1)

Yield, 92%; m.p. 116.0°C; [α]_D^{25} = -35.7 (c = 0.01 in CHCl₃); λ CHCl₃ (ε): 388 (35250), 309 (43750), 279 (54750), v_{nujol} max: 2900, 2800, 1750, 1600, 1520, 1460, 1380, 1240 and 800 cm⁻¹.

[Found: C, 68.88; H, 7.36; N, 2.25%] C₇₀H₇₆Cl₂CuN₂O₈ requires C, 69.05; H, 7.07; N, 2.30%].

[S]-bis-N-[4'-n-Undecyloxybiphenyl-4"-(2-chloro-4-methyl pentanoyloxy) salicylaldiminato]copper(II) (5.e.2)

Yield, 90%; m.p. 118.0°C; [α]_D^{25} = -31.58 (c=0.015 in CHCl₃); λ CHCl₃ (ε): 391 (27800), 307 (34800), 279 (43100), v_{nujol} max: 2900, 2800, 1740, 1600, 1510, 1460, 1370, 1230 and 800 cm⁻¹.

[Found: C, 69.89; H, 7.33; N, 2.18%] C₇₂H₉₀Cl₂CuN₂O₈ requires C, 69.42; H, 7.23; N, 2.25%].
[2S,3S]-bis-N-[4'-n-Dodecyloxybiphenyl-4''-(2-chloro-3-methyl pentanoyloxy)salicylaldiminato]copper(II) (5.f.3)

Following a procedure similar to the one described for the compound 5.e.3, complexation of [2S,3S]-N-[2'-hydroxy-4'-(2-chloro-3-methylpentanoyloxy)benzylidene]-4''-n-dodecyloxyphenyl-aniline (5.c.3) using copper(II) acetate afforded the title compound 5.f.3.

Yield, 86%; m.p. 101.0°C; [α]D²⁵ = -18.5 (c = 0.02 in CHCl₃); λmax CHCl₃ (ε): 391 (31050), 308 (38100), 278 (47200), νmax nujol: 2900, 2850, 1750, 1610, 1530, 1500, 1460, 1380, 1240, 1195, 1180 and 800 cm⁻¹.

[Found: C, 69.89; H, 7.33; N, 2.18%]. C₇₄H₉₄Cl₂CuN₂O₈ requires C, 69.78; H, 7.39; N, 2.20%].

The physical data of the cognate preparations of other [2S,3S]-bis-N-[4'-n-alkoxybiphenyl-4''-(2-chloro-3-methylpentanoyloxy) salicylaldiminato]copper(II) complexes [5(f)] are given below.

[2S,3S]-bis-N-[4'-n-Decyloxybiphenyl-4''-(2-chloro-3-methyl pentanoyloxy)salicylaldiminato]copper(II) (5.f.1)

Yield, 89%; m.p. 118.0°C; [α]D²⁵ = -13.11 (c = 0.02 in CHCl₃); λmax CHCl₃ (ε): 391 (32200), 309 (40200), 280 (49900), νmax nujol: 2900, 2850, 1755, 1650, 1535, 1500, 1460, 1380, 1240, 1200, 1180 and 820 cm⁻¹.

[Found: C, 68.88; H, 7.36; N, 2.25%]. C₇₀H₈₆Cl₂CuN₂O₈ requires C, 69.05; H, 7.07; N, 2.30%].
[S,3S]-bis-N-[4'-n-Undecyloxybiphenyl-4"-(2-chloro-3-methyl pentanoyloxy)salicylaldiminato]copper(II) (5.f.2)

Yield, 88%; m.p. 111.0°C; $[\alpha]_{D}^{25} = +15.23$ (c = 0.02 in CHCl$_3$); 
$\lambda_{\text{max}}^{\text{CHCl}}$(e):391(30650),308(38050),279(48050), $\nu_{\text{max}}^{\text{nujol}}$:2900,2850,1750,1610,1590,1530,1500,1460,1380,1240,1200,1175 and 800 cm$^{-1}$.

[Found: C,69.89;H,7.33;N,2.18%  C$_{72}$H$_{90}$Cl$_2$CuN$_2$O$_8$ requires C,69.42;H,7.23;N,2.25%].

[S]-bis-N-[4'-n-Dodecyloxybiphenyl-4"-(2-methylbutoxy)
salicylaldiminato]palladium(II) (5.d.4)

A stirred mixture of [S]-N-[2'-hydroxy-4"-(2-methylbutoxy) benzylidene]-4"-n-dodecyloxyphenylaniline (5.a.3) (0.109 g, 0.0002 mol), anhydrous potassium carbonate (0.059 g, 0.0004 mol), palladium chloride (0.018 g, 0.0001 mol) and acetonitrile (15 ml) was heated at 80°C in an oil bath for five hours. The reaction mixture was then cooled, the precipitate filtered, dried, dissolved in chloroform (25 ml), washed with water (5x15 ml) and dried (Na$_2$SO$_4$). The residue obtained on removal of the solvent was crystallised repeatedly from butan-2-one (0.110 g, 88%), m.p. 236.0°C; $[\alpha]_{D}^{25} = +20.23$ (c = 0.5 in CHCl$_3$); $\lambda_{\text{max}}^{\text{CHCl}}$(e):402(17850),302(64450),265(76700); $\nu_{\text{max}}^{\text{nujol}}$:2900,2850,1600,1580,1520,1500,1460,1420,1380,1250,1200 and 800 cm$^{-1}$; $\delta$:0.96-2.0(m,64H,6xCH$_3$,22xCH$_2$ and 2xCH),3.35(d,4H,OCH$_2$),4.0(t,4H,OCH$_2$), 5.63(s.2H,ArH). 6.15(d. 2H,ArH),6.85-7.78(m,20H,ArH and -N=CH-).

[Found: C,72.36;H,8.19;N,2.00%  C$_{72}$H$_{96}$N$_2$O$_6$Pd requires C,72.58;H,8.06;N,2.35%].
$^{1}H$ NMR spectrum of the compound.
Following a procedure similar to the one described for the compound 5.d.4, complexation of [S]-N-[2'-hydroxy-4'-(2-chloro-4-methylpentanoyloxy)benzylidene]-4'-n-dodecyloxyphenylaniline (5.b.3) using palladium chloride afforded the title compound. Yield, 86%; m.p. 204.0°C; $[\alpha]_{D}^{25} = -3.9$ (c=0.5 in CHCl$_3$); $\lambda_{\text{max}}^{\text{CHCl}_3}$(c): 408(19600), 291(35150), 254(57950); $\nu_{\text{nujol}}$: 2900, 2850, 1750, 1600, 1530, 1500, 1460, 1380, 1245, 1180 and 800 cm$^{-1}$; $\delta$ 0.74-2.0(m, 6H, 6xCH$_3$, 22xCH$_2$ and 2xCH), 4.0(t, 4H, OCH$_2$), 4.22(t, 2H, CHCl), 5.89(s, 2H, ArH), 6.83-7.82(m, 20H, ArH and 2x-CH=N-).

[Found: C, 67.79; H, 7.23; N, 2.01% C$_{74}$H$_{94}$Cl$_2$N$_2$O$_8$Pd requires C, 67.48; H, 7.14; N, 2.13%].

[2S,3S]-N-bis-[4'-n-Dodecyloxydiphenyl-4'--(2-chloro-3-methyl pentanoyloxy)benzylidene]-4'-n-dodecyloxyphenylaniline (5.c.3) using palladium chloride afforded the title compound. Yield, 90%; m.p. 230.0°C; $[\alpha]_{D}^{25} = +1.53$ (c=0.5 in CHCl$_3$); $\lambda_{\text{max}}^{\text{CHCl}_3}$(c): 411(10700), 290(38000), 253(63300); $\nu_{\text{nujol}}$: 2900, 2850, 1760, 1610, 1530, 1500, 1460, 1380, 1240, 1200, 1180 and 820 cm$^{-1}$; $\delta$: 0.67-2.0 (m, 6H, 6xCH$_3$, 22xCH$_2$ and 2xCH), 3.91-4.7(m, 6H, OCH$_2$ and CHCl), 5.91(s, 2H, ArH), 6.3(d, 2H, ArH), 6.58-8.16(m, 20H, ArH and 2x-CH=N-).

[Found: C, 67.85; H, 7.44; N, 1.87% C$_{74}$H$_{94}$Cl$_2$N$_2$O$_8$Pd requires C, 67.48; H, 7.14; N, 2.13%].
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