# Chapter 6

# Synthesis and mesomorphic properties of N-(2-hydroxy-4-n-alkyloxybenzylidene)-4"-n-dodecylphenylanilines and their copper(II), palladium(II) and nickel(II) complexes

## 6.1 Survey of the liquid crystalline properties exhibited by transition metal complexes of salicylideneamine derivatives

Schiff's bases derived from substituted salicylaldehydes are versatile ligands which form (N-O) chelates with many metals.[1] The first mesogenic salicylideneamine copper(II) complexes (6.a), were reported by Ovchinnikov et *al.*[2] These exhibited enantiotropic smectic phases. Since then, a number of different metallomesogens using salicylideneamine derivatives as ligands have been reported. In many of these cases the ligands themselves were also found to be mesogenic.

Many examples of mesogenic copper(II) and palladium(II) complexes have been reported. They mainly show smectic mesophases. Ghedini et *al.*[3] have reported a number of N-salicylaldiminato copper(II) complexes. Hoshino et *al.*[4] have synthesised a homologous series of 3-hydroxy-4-[{(4-ethoxyphenyl)imino}methyl]phenyl-4-n-alkoxybenzoates and their copper(II) complexes. They have also determined the single crystal structure by X-ray analysis for one of the copper(II) complexes (6.b). From the X-ray data, the overall molecular shape was found to be lath-like. Also, a weak axial interaction involving a neighbouring carbonyl oxygen to the copper centre in the crystalline state was observed. In this series of copper(II) complexes, lower homologues exhibited enantiotropic nematic and higher ones enantiotropic smectic C phases.

Caruso et *al.*[5] have reported the synthesis and liquid crystalline properties of some bis[N-4-(n-alkoxyphenyl)-4'-(n-alkoxysalicylaldiminato)]copper(II) complexes, and a homologous series of bis[N-4-(n-alkanoyloxyphenyl)-4'-( n-alkanoyloxysalicylaldiminato)]copper(II) and some corresponding palladium(II) complexes. All these complexes were found to be smectogenic. They also observed that the transition

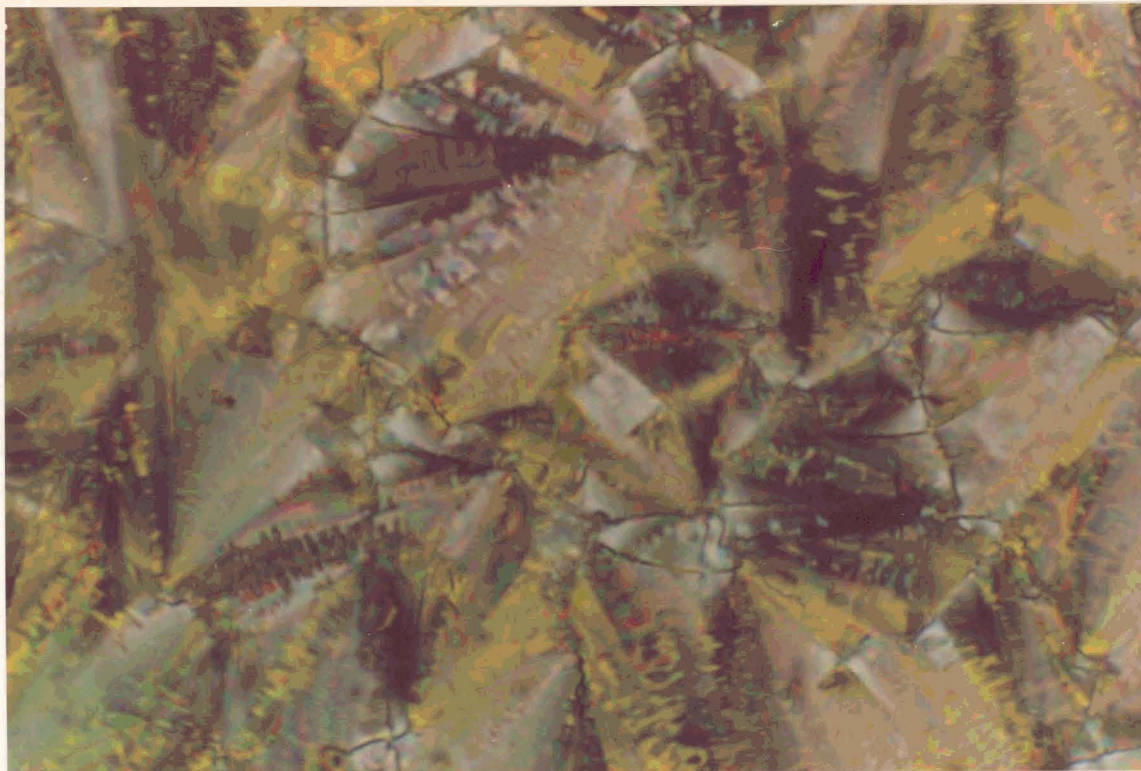$R = C_nH_{2n+1}$
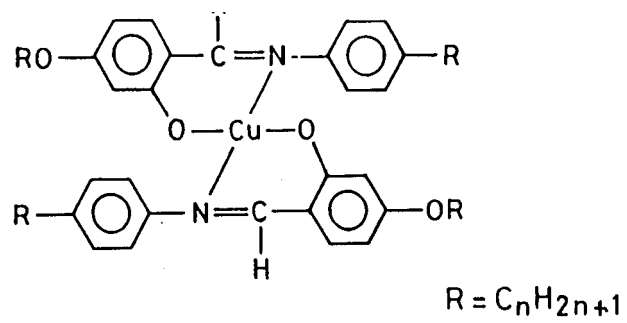
6.a
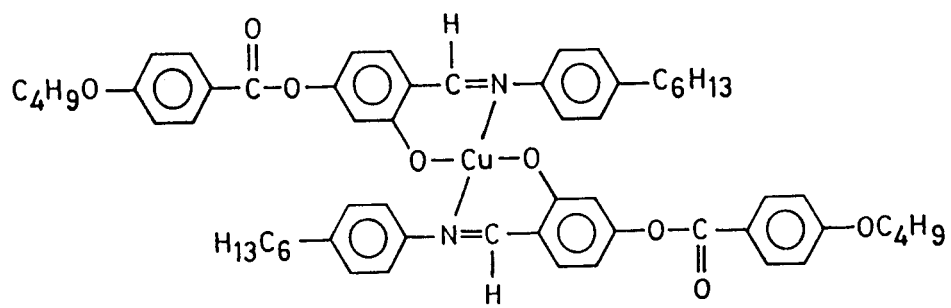
6.b

**Plate 6.1:** The paramorphotic broken focal-conic texture of the mesophase $(S_1)$

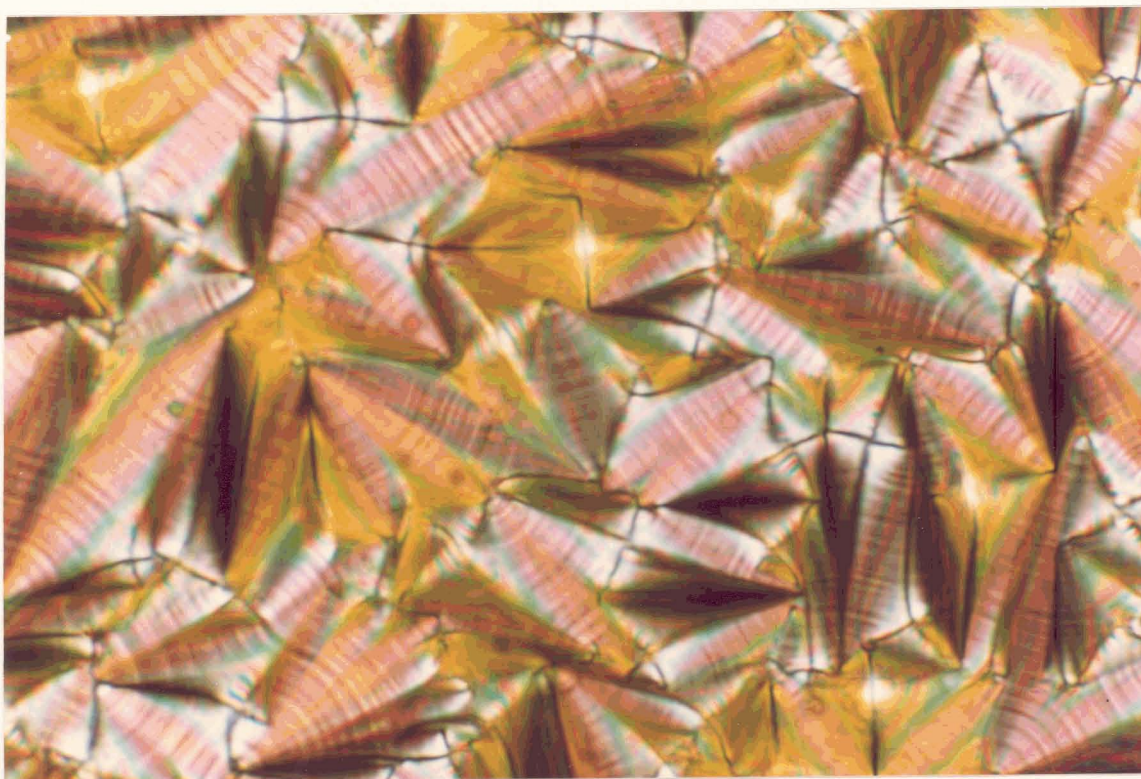of compound 6.e.6 at 121.0°C.



**Plate 6.2:** The focal-conic texture with concentric arcs of the mesophase

$(S_2$, probably $S_E)$ of compound 6.e.5 at 68.0°C.

temperatures of palladium(II) complexes were comparatively higher than the corresponding copper(II) complexes. Caruso *et al.*[6] have also studied the effect of variation in the length of N-alkyl chain, on the mesomorphic behaviour of a series of bis[N-[{4 -[4 -(tetradecyloxy)benzoyloxy]}2 -hydroxyphenyl methylene ]alkanamino]-copper(II) complexes (6.c). They observed that,, smectic C phase present in the N-methylated compound disappeared as the alkyl chain was lengthened. It reappeared first as a monotropic phase in the decyloxy and then as an enantiotropic phase from the dodecyloxy homologue onwards. Their X-ray diffraction studies indicated that, the smectic layer separation was remarkably smaller for the tetra- and pentadecyloxy homologues than the smectic periodicity measured for the N-methylated homologue. This implies that, molecular packing within smectic layers must have undergone a significant change.
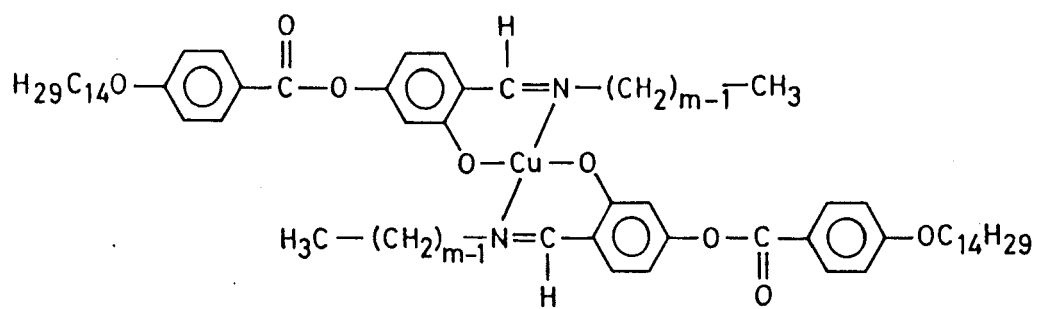
Roviello *et al.*[7] have studied the crystal structure of a mesogenic copper(II) square-planar complex, *viz.*, bis[N -4- (n-hexyloxyphenyl) -4' -(n-heptyloxysalicylald-iminato)]copper(II). Their observations explain as to why the liquid crystalline phases of this and related compounds are not discotic. The formation of a cylindrical pile of molecules having flexible tails arranged with two fold symmetry, requires their packing to be close but rotationally disordered around the cylinder axis. The considerable rotation of the phenyl groups with respect to the salicylaldiminato-copper groups, leads to an uneven increase in the thickness of the molecular cores; this appears to be the major obstacle for the formation of a discotic mesophase. Marcos et *al.*[8] have investigated several series of copper(II) complexes derived from salicylideneamine derivatives.

'Very few mesogenic nickel complexes of salicylidenearnine derivatives are known in literature. Marcos *et al.*[9] have reported a scries of nickel(II) arid copper(II)
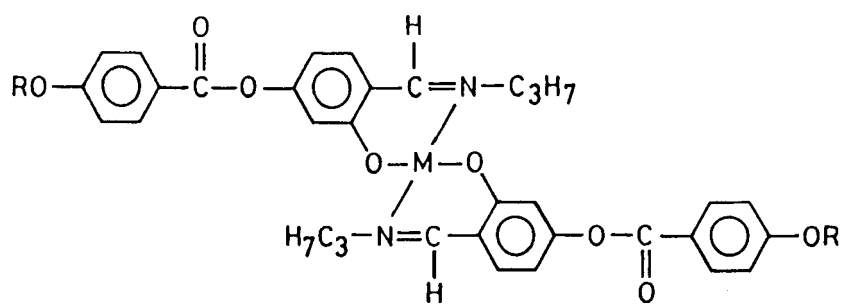
complexes. They exhibited enantiotropic nematic mesophase over a very wide temperature range, with fairly low melting points. They concluded from their studies that, nickel(II) complexes have higher thermal stability of the mesophase than the corresponding copper(II) complexes, but the latter have lower melting points. Preliminary X-ray experiments showed that both nickel(II) and copper(II) complexes behave differently when oriented by a magnetic field. ESR studies of these indicated that the nematic phase was paramagnetic in copper(II) complexes, while it was diamagnetic in nickel(II) complexes.[9]

Other salicylideneamines have also been used for the synthesis of mesogenic copper and nickel complexes. Paschke et al.[10] have synthesised a series of copper(II) and nickel(II) complexes using disalicylidene-ethylenediamine as ligands. All of them exhibited high melting smectic **A** mesophases. The related complexes with the N-methylalkyloxysalicylideneamine ligands were riot mesogenic. Hoshino et al.[11] have reported a series of nickel and oxovanadium complexes of N-salicylidene-n-propylamine derivatives (6.d). All the nickel(II) complexes exhibited enantiotropic nematic phases over a moderate range of temperature. Corresponding oxovanadium(IV) complexes were also nematogenic, but the thermal stability of the nematic phases was much lower as indicated by their clearing temperatures being depressed by 51°C on the average.

Galyametdinov et al.[12] have investigated a number of salicylaldiminato metallomesogeris containing different metal atoms, viz., Zn, Co, Ni, Cu, VO and I'd. Among these zinc, cobalt and nickel complexes showed no mesomorphic behaviour whereas copper, vanadyl and palladium complexes showed smectic mesophases. The absence of mesophases for the nickel and cobalt complexes was ascribed to the tetrahedral geometry of the metal; the copper and palladium centres are square planar,

$$H_{29}C_{14}O - \text{[benzene]} - \overset{\overset{O}{\parallel}}{C} - O - \text{[benzene]} - \overset{\overset{H}{|}}{C} = N - (CH_2)_{m-1} - CH_3$$

6.c



$R = C_nH_{2n+1}$

while the vanadyl unit is square pyramidal.[13] Galyametdinov et *al.*[14] have also reported a mesogenic iron(III) complex exhibiting a srnectic A phase with paramagnetic properties. Recently there is a report[15] on mesogenic properties of a series of salicylideneaminato platinum(II) and oxovanadium(IV) complexes. All these complexes predominantly showed smectic A and smectic C phases.

Caruso et *al.*[16] have synthesised and studied the mesogenic properties of bis[N-[[4-[4-(alkoxybenzoyloxy)]]2-hydroxy]methylene]alkanamino] complexes of Cu(II), Pd(II) and Ni(II). They studied the influence of alkoxy and alkanamine groups on the nature and stability of the mesophase. They found, with some exception, that smectic C mesomorphism was favoured as the chain length increased. They also observed that the nematic phase stability was higher for palladium and nickel complexes than for the copper containing homologues. Barbera et *al.*[17] have reported the X-ray diffraction data of some mesogenic copper, nickel and vanadyl complexes. They found that, for a given ligand linked to different metal atoms (Cu, Ni, VO), the nature of this central atom influenced mainly the magnetic susceptibilies of tlie mesophases. They also observed that with different ligands, which keep the close neighbourhood of the metal atom unchanged, the apparent length of the mesogenic unit was longer for short ligands than for longer ones. This was explained by taking into account tlie global shape of tlie different complexes.

Campillos *et al.*[18] have reported the synthesis and mesogenic behaviour of copper(II) complexes derived from polar Schiff's bases, *viz.*, Schiff's bases containing CN, F, CF$_3$ etc. groups. The ligands exhibited smectic C, smectic A and nematic phases, whereas the complexes showed only srnectic A and nematic phases. Optical investigations carried out with one of the complexes showed that the nematic phase was uniaxial. Bayle et *al.*[19] have reported a series of copper, nickel and

palladium complexes of N-(4-(4'-n- alkoxybenzoyloxy)salicylidene)-4-n-butylaniline and N-(4-(4'-n- hexadecyloxybenzoyloxy)salicylidene)-4-n-alkoxyaniline. Here, copper and palladium derivatives exhibited nematic phase over a large temperature range but surprisingly they found that the corresponding nickel complexes were non-mesogenic. Levelut[20] has studied the molecular organisation in some metallo-organic mesophases. The global molecular shape was derived from the usual X-ray diffraction experiments. A comparison of the organisation of molecules in the complexes and ligands indicated that the structural features of the mesophases depend on the nature of the metal bridge, the length and the nature of the ligand.

## 6.2    Results and Discussion

The survey indicated that a biphenyl moiety was not utilised and we undertook a study of complexes containing such a group. With this in view and to study the influence of different transition metal atoms on the mesophases formed in such complexes, a series of N-(2-hydroxy-4-n-alkyloxybenzylidene)-4''-n-dodecylphenylanilines (6.e) and their copper(II) (6.f), palladium(II) (6.g) and nickel(II) (6.h) complexes were synthesised. The ligands (6.e) used themselves were found to be mesogenic.

These compounds were prepared according to the general schemes shown in figures 6.1 and 6.2. 4-n-Dodecyl-4'-acetylbiphenyl was prepared following the procedure described in chapter 3. From this, 4-n-dodecyl-4'-aminobiphenyl was prepared following a procedure described by Van der Veen et al.[21] Thus, addition of sodium azide to a stirred solution of 4-n-dodecyl-4'-acetylbiphenyl in 80% sulphuric acid arid dichloromethane afforded the anilide which on hydrolysis with ethanolic sodium hydroxide gave 4-n-dodecyl-4'-aminobiphenyl.

2,4-Dihydroxybenzaldehyde was prepared from resorcinol by following a well
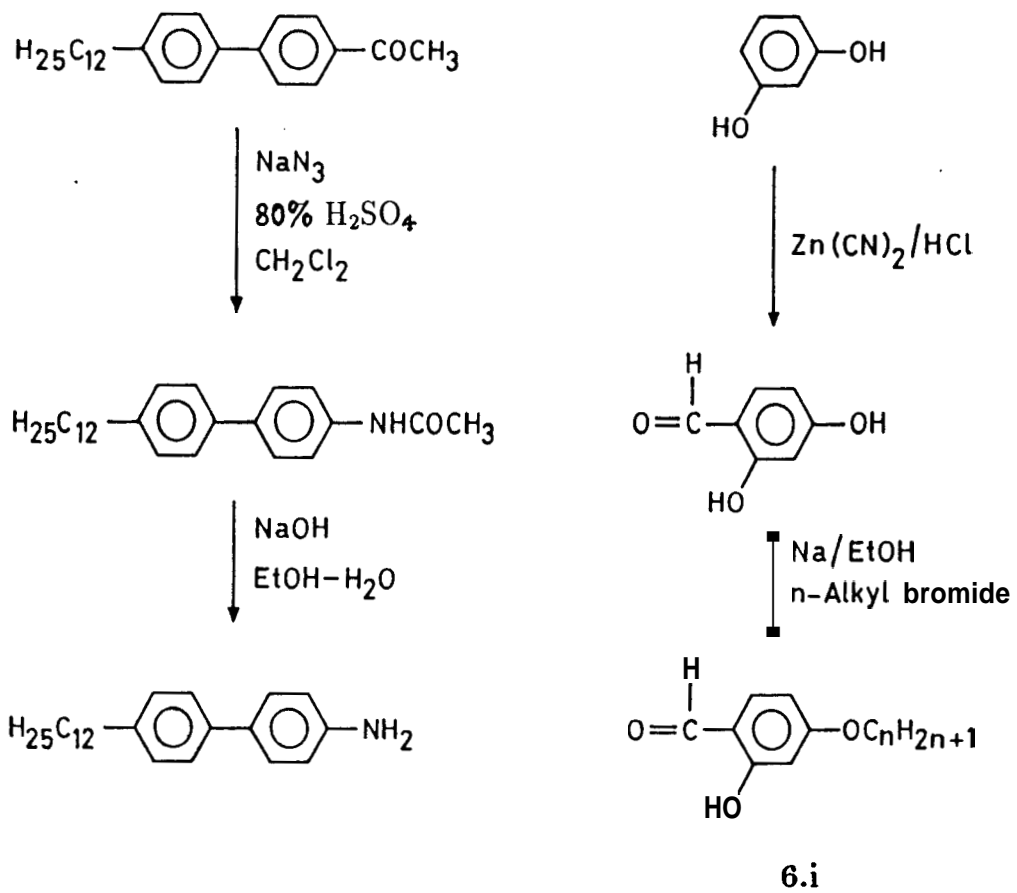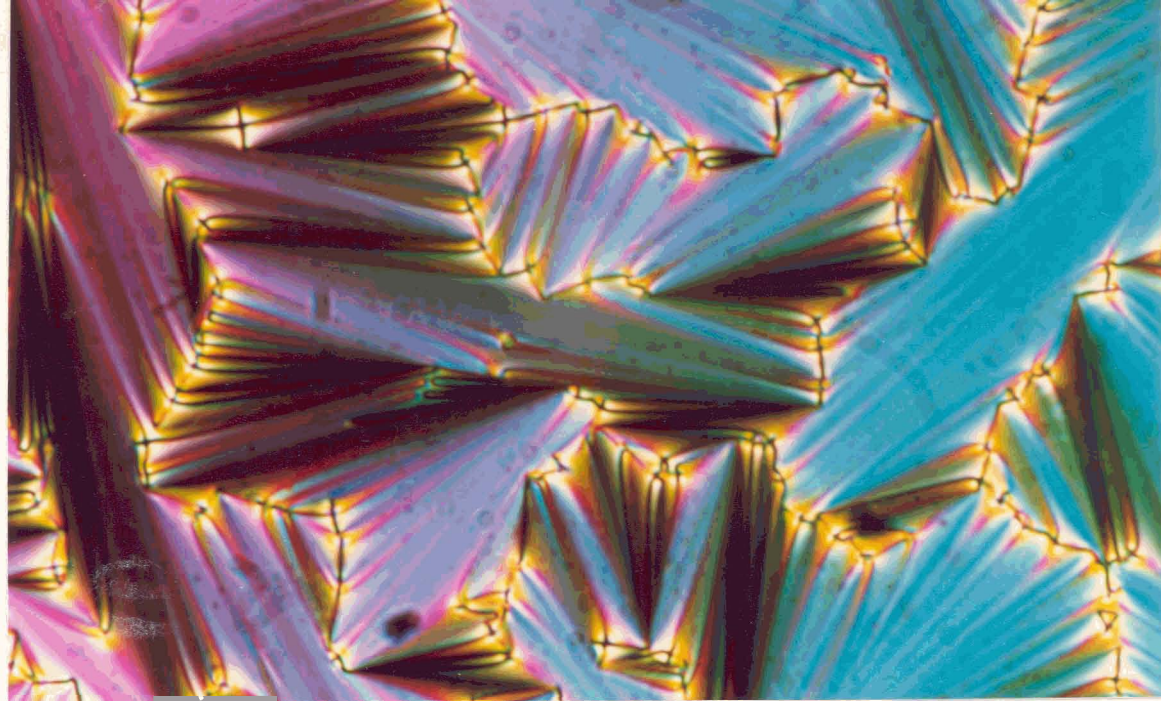
**Figure 6.1**

**Plate 6.3:** The focal-conic texture of smectic A phase of complex 6.f.9 at 230.0°C.
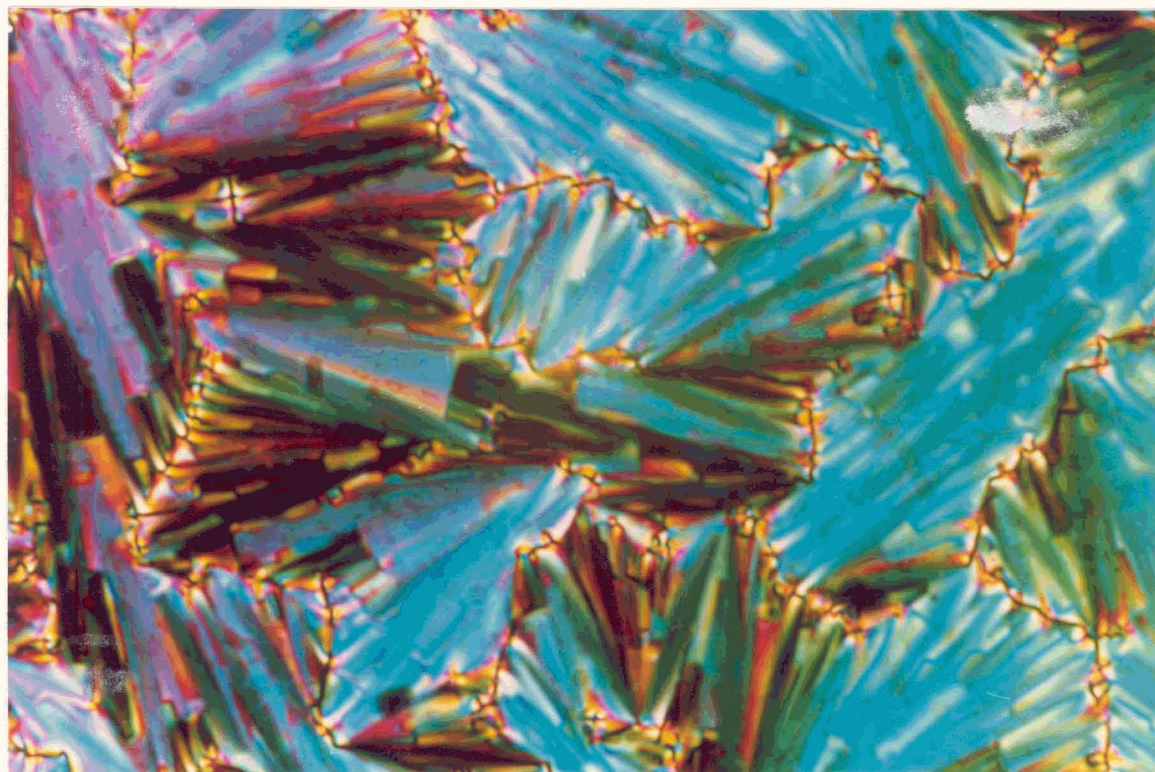


**Plate 6.4:** The broken focal-conic texture of srnectic *C* phase of complex 6.f.9 at 220.0°C.

$R = C_n H_{2n+1}$

$M = Cu$, 6.f

$= Pd$, **6.g**

$= Ni$, 6.h

**Figure 6.2**

known procedure.[22] Monoalkylation of this aldehyde was carried out using an appropriate n-alkyl bromide in the presence of sodium ethoxide in ethyl alcohol. Schiff's bases were prepared by refluxing 4-n-dodecyl-4'-aminobiphenyl with the appropriate 2-hydroxy-4-n-alkyloxybenzaldehydes (6.i), in ethyl alcohol using 1-2 drops of acetic acid as a catalyst.

Copper(II) complexes were obtained by treating the potassium salt of the corresponding Schiff's bases in tetrahydrofuran with cupric chloride dihydrate in ethyl alcohol at room temperature. The nickel(II) and palladium(II) complexes were prepared by refluxing the Schiff's bases with nickel acetate tetrahydrate and palladium chloride respectively, in dry acetonitrile using anhydrous potassium carbonate as a base.

The precursor of 4-n-dodecyl-4'-aminobiphenyl ie; 4-(4'-n-dodecylphenyl)acetanilide was found to exhibit a smectic phase with a mesophase range of 5.5°C. The transition temperatures and the thermodynamic data for the Schiff's base ligands, N-(2-hydroxy-4-n-alkyloxybenzylidene)-4''-n-dodecylphenylanilines (6.e), are given in table 6.1. All the compounds of this series are enantiotropic with fairly wide mesophase ranges. Except for the first homologue which melts above 100°C and exhibits a nematic phase over a 4°C range, the rest are all smectogenic in nature and have melting points below 100°C. For compounds n=2 to n=7, two smectic phases are seen. The higher temperature phase exhibits a focal-conic texture and is characterised as smectic **A** while the lower temperature phase shows a broken focal-conic texture and is characterised as smectic C. The enthalpy of this transition $(S_C \rightarrow S_A)$ was quite low and could not be measured for three homologues. Smectic **A** phase disappeares at n=8 and from n=8 to n=18, the smectic C phase goes over directly to the isotropic liquid. It is seen that the smectic C mesophase range

### Table 6.1

Transition temperatures (°C) and enthalpies (kcal/mol) of transitions for
**N-(2-hydroxy-4-n-alkyloxybenzylidene)-4″-n-dodecylphenylanilines,
6.e**

| Compound number | n | C | $S_2$ | $S_1$ | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|---|---|
| 6.e.1 | 1 | . 113.0 / *10.0* | - | - | - | . 216.5 / *0.40* | . 220.5 / *0.28* | . |
| 6.e.2 | 2[+] | . 98.0 / *4.25* | - | - | . 148.5 / *0.22* | . 230.0 / *1.46* | - | |
| 6.e.3 | 3 | . 91.0 / *8.33* | (. 87.5 ) / *0.37* | . 149.0 / *0.24* | . 171.5 / *0.07* | . 224.0 / *1.87* | - | |
| 6.e.4 | 4 | . 87.5 / *9.21* | (. 76.5 ) / *0.30* | . 148.0 / *0.21* | . 189.0* | . 222.5 / *1.94* | - | . |
| 6.e.5 | 5 | . 82.5 / *9.46* | (. 69.0 ) / *0.22* | . 145.0 / *0.27* | . 204.5* | . 219.5 / *1.96* | - | . |
| 6.e.6 | 6[+] | . 81.0 / *4.51* | (. 65.0 ) / *0.20* | . 145.0 / *0.56* | . 209.0 / *0.04* | . 218.0 / *1.94* | - | |
| 6.e.7 | 7 | . 83.5 / *13.28* | (. 62.0 ) / *0.15* | . 143.0 / *0.48* | . 210.0* | . 212.5 / *2.06* | - | . |
| 6.e.8 | 8[+] | . 76.5 / *4.05* | (. 58.0 ) / *0.13* | . 141.5 / *0.65* | . 208.5 / *2.19* | - | - | . |
| 6.e.9 | 9 | . 85.0 / *15.56* | (. 57.5 ) / *0.13* | . 140.0 / *0.37* | . 207.0 / *2.58* | - | - | . |
| 6.e.10 | 10 | . 79.5 / *12.55* | - | . 138.0 / *0.55* | . 203.5 / *2.87* | - | - | . |
| 6.e.11 | 11 | . 83.0 / *16.88* | - | . 136.5 / *0.65* | . 201.5 / *2.51* | - | - | . |
| 6.e.12 | 12 | . 80.5 / *16.99* | - | . 135.0 / *0.93* | . 199.5 / *2.82* | - | - | . |
| 6.e.13 | 18 | . 87.0 / *18.23* | - | . 128.5 / *0.23* | . 179.5 / *2.65* | - | - | . |

[+]Compounds 6.e.2, 6.e.6 arid 6.e.8 have crystal → crystal transitions at 74.5°C (2 9 kcal/mol), 74.5°C (2.0 kcal/mol) and 71.5°C (6.0 kcal/mol) respectively.

*Enthalpies could not be measured.

initially increases upto n=11 and then tends to decrease. Most of these compounds have a fairly wide smectic C mesophase range ($20°-65°$). For compounds from $n \geq 3$, a higher order smectic phase is obtained directly on melting. This mesophase range is between $50°-65°$ for most homologues. The texture of this mesophase obtained on cooling the smectic C phase shows a paramorphotic broken focal-conic texture (shown in plate 6.1). Though, this highly ordered phase ($S_1$) has not yet been identified, its distinctive features indicate that this could possibly be a smectic F phase. In addition to these enantiotropic mesophases, for compounds n=1 to n=9, a monotropic highly ordered smectic mesophase below $S_1$, is observed. This mesophase exhibits a focal-conic texture with concentric arcs (shown in plate 6.2) and has been designated as $S_2$ phase. From n=10 onwards this mesophase gets completely eliminated. The dsc thermogram for compound 6.e.5 is shown in figure 6.3.

A comparison of the mesomorphic properties of the above ligands with those of a similar series of 3 -hydroxy-4[(4 - ethoxyphenyl)iminomethyl]phenyl-4-alkoxybenzo-ates[4] indicate that the latter ester Schiff's bases which have more flexible parts exhibit fairly wide nematic phase ranges. This indicates that probably the biphenyl moiety in the present series of compounds helps in promoting smectic phases through efficient molecular packing. It is seen that the introduction of a lateral hydroxyl group in a Schiff's base affects the smectic polymorphism as well as the transition temperatures. A tendency to stabilise $S_C$ phase more than the other phases has also been observed.[23,24]

Figure 6.4 shows a plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for the Schiff's bases, 6.e. The curves for the like mesophase transitions follow the normal behaviour observed in a large number of
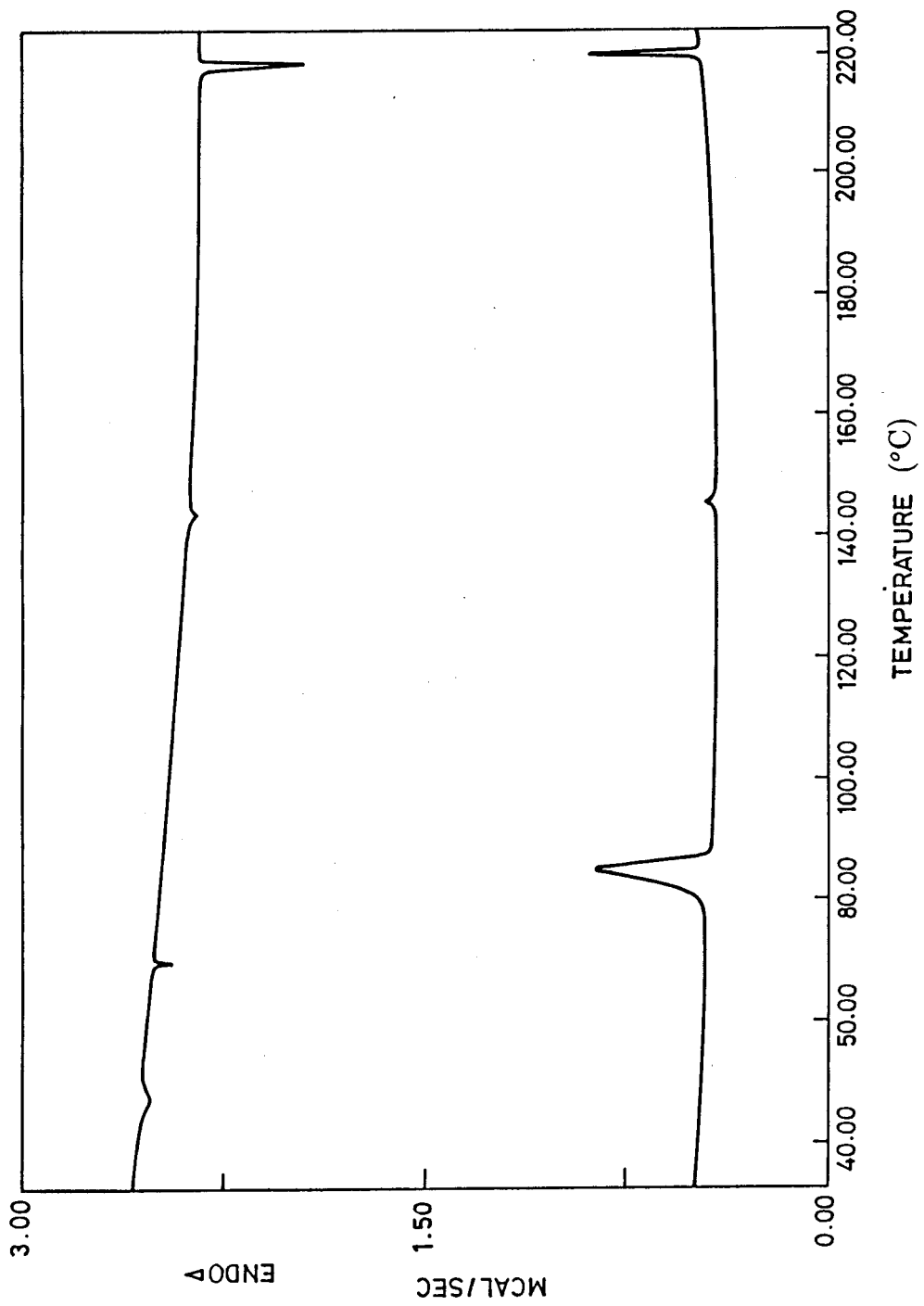
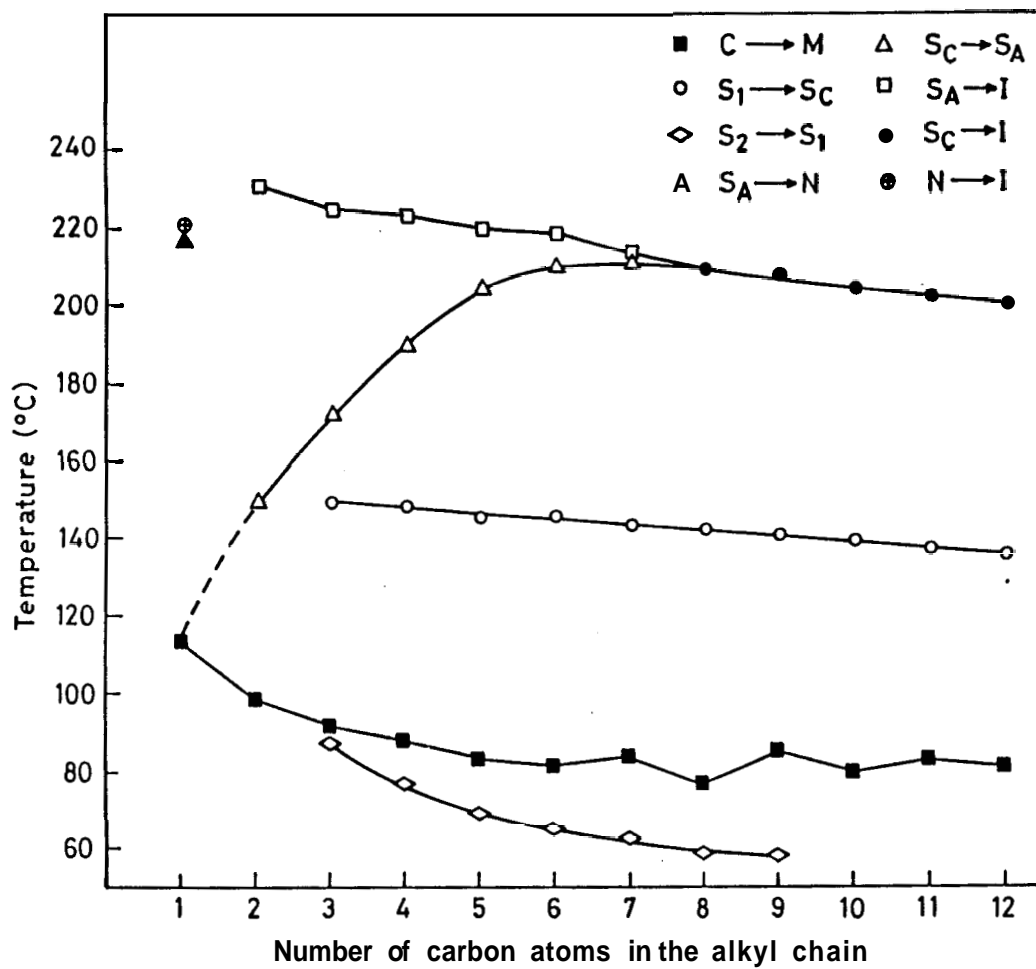Figure 6.3: The dsc thermogram for compound 6.e.5.

**Figure** 6.4: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 6.e.

homologous series. However, the points joining the $S_1$ to $S_C$ transitions lie on almost a straight line. This is rather unusual. It is also seen that the clearing points decrease gradually with increase in chain length.

The transition temperatures and enthalpies of transitions for the bis[N- (4″-n-dodecylbiphenyl)4-n-alkyloxysalicylaldiminato]copper(II) complexes (6.f), are given in table 6.2. These green complexes were obtained in crystalline form with fairly good yield. It is seen from the table that on introduction of a metal atom into the Schiff's base, the transition temperatures are elevated. However, the higher order smectic phases $S_1$ and $S_2$ are totally eliminated. The two smectic phases exhibit focal-conic and broken focal-conic textures as the temperature is lowered from the isotropic liquid and are characterised as smectic A and smectic C phases, respectively. The typical textures of these two phases are shown in plates 6.3 and 6.4, respectively. The complexes n=1 to n=4, exhibiting a smectic A phase, decompose before going to the isotropic phase.

A comparison of the mesomorphic properties of the present chelates with those of bis[4-(4-alkyloxybenzoyloxy)-N-(4-ethoxyphenyl)salicylaldiminato]copper(II) comp-lexes, $(CuL_2)^4$ reveals interesting features. By and large the mesophases observed in the ligands are retained upon complexation in both series. Though the metal chelates are more symmetric than the ligands from which they are derived, it is rather surprising that the higher order smectic phases $S_1$ and $S_2$ observed in the ligands are not seen in the chelates. While the smectic phase has been sup-pressed upon complexation in the present series of compounds, an opposite ef-fect was observed in $CuL_2$ series, wherein incorporation of a metal centre into the ligand lead to a more ordered mesophase of bis[4-(4-alkyloxybenzoyloxy)-N-(4-ethoxyphenyl)salicylaldiminato]copper(II) complexes.

Table 6.2

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for
bis[N-(4″-n-dodecylbiphenyl)-4-n-alkyloxysalicylaldiminato]copper(II),

**6.f**

| Compound number | n | $C_1$ | | C | $S_C$ | | $S_A$ | | I | |
|---|---|---|---|---|---|---|---|---|---|---|
| 6.f.1 | 1 | - | . | 182.0 / 13.86 | . | | . | | 282.0** | . |
| 6.f.2 | 2[+] | . | 146.5 / 6.08 | . | 174.0 / 12.28 | - | | . | | 290.0** | . |
| 6.f.3 | 3 | - | | . | 177.0 / 13.56 | . | | . | | 295.0** | . |
| 6.f.4 | 4 | . | 88.5 / 0.78 | . | 168.0 / 12.35 | . | | . | | 288.0** | . |
| 6.1.5 | 5[+] | . | 164.5 / 4.07 | . | 191.5 / 6.51 | . | | . | | 278.0** | . |
| 6.f.6 | 6 | . | 147.5 / 1.25 | . | 200.5 / 9.53 | - | | . | | 268.0 | . |
| 6.f.7 | 7 | . | 138.5 / 1.77 | . | 207.0 / 11.54 | - | 212.0* | . | | 263.0 / 3.11 | . |
| 6.f.8 | 8 | . | | . | 206.0 / 11.44 | . | 224.0' | . | | 255.5 / 3.11 | . |
| 6.f.9 | 9 | . | | . | 202.0 / 11.83 | . | 228.5' / 0.04 | . | | 248.0 / 2.45 | , |
| 6.f.10 | 10 | - | | . | 201.0 / 13.39 | . | 229.0 / 0.21 | . | | 243.5 / 2.33 | . |
| **6.f.11** | 11 | - | | . | 194.0 / 13.71 | . | 230.0 / 0.40 | . | | 242.0 / 3.96 | . |
| 6.f.12 | 12 | . | | . | 191.5 / 13.23 | . | 223.0 / 0.55 | . | | 232.0 / 2.13 | . |
| 6.f.13 | 18 | . | 69.0 / 2.53 | . | 181.5 / 16.92 | . | 207.5 / 0.38 | . | | 212.5 / 1.80 | . |

[+]Compounds 6.f.2 and 6.f.5 have a crystal → crystal transition at 87.0°C (0.2 kcal/mol)
and 84.5°C (0.21 kcal/mol) respectively.

*Enthalpies could not be measured.

**These cornpounds decompose before going to isotropic phase.

Figure 6.5 shows a graphic comparison of the transition temperatures versus the number of carbon atoms in the alkyl chain for the copper(II) complexes, 6.f. Here again, the usual pattern obtained by joining like transition points is seen. As mentioned earlier, the first four homologues thermally decompose before reaching clearing temperatures and hence these points have been joined by a dashed line.

The transition temperatures and enthalpies of transitions for bis[N-(4''-n-alkyl-oxysalicylaldiminato]palladium(II) chelates ( 6.g ) are given in table 6.3. These orange-yellow complexes were obtained as fine microcrystals in fairly good yield. For complexes n=1 to n=7, the clearing temperatures are >290°C and these start decomposing at this high temperature. All the homologues exhibit enantiotropic mesomorphism. For complexes n=1 to n=5 there is only smectic A phase and for n=6 onwards there is a smectic C phase below the smectic A phase. They show focal-conic and broken focal-conic textures for $S_A$ and $S_C$ phases, respectively. In addition to mesomorphism, all the complexes also show crystal $\rightarrow$ crystal transitions. All the transition temperatures are raised as a result of replacing copper with palladium as has been observed in other series of compounds.[7] Also these two metal atoms do not seem to affect the nature of the mesophases for some of the ligands. The enthalpies for $S_C \rightarrow S_A$ and $S_A \rightarrow I$ transitions of the palladium complexes are comparable to those of the corresponding copper cheiates.

Figure 6.6 shows a plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for the palladium(II) chelates, 6.g. As observed for copper chelates, the lower homologues of this series also thermally decompose and $S_A \rightarrow I$ transition points follow a general trend that has been seen for such transitions in many homologous series.

The transition temperatures and enthalpies of transitions for bis[N-(4''-n-alkyl-
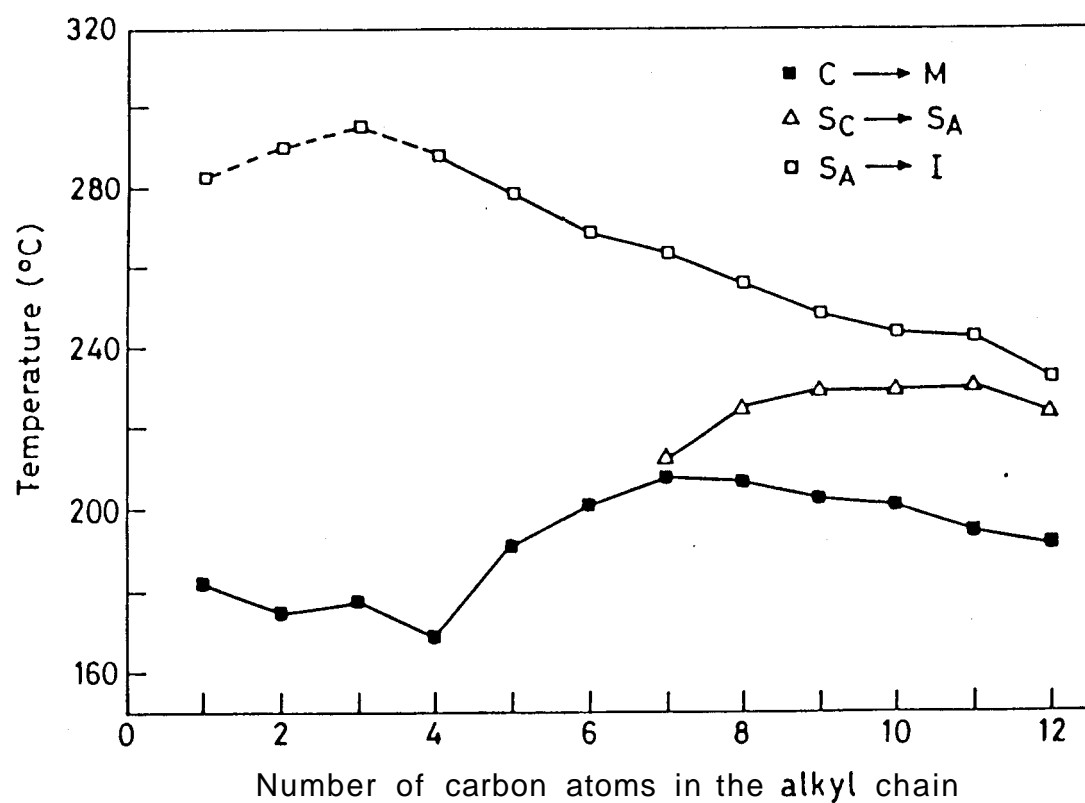
**Figure** 6.5: A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for series 6.f.

Table 6.3

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for
**bis[N-(4″-n-dodecylbiphenyl)-4-n-alkyloxysalicylaldiminato]palladium(II),**
**6.g**

| compound number | n | $C_1$ | | C | $S_C$ | | $S_A$ | | I |
|---|---|---|---|---|---|---|---|---|---|
| 6.g.1 | 1 | . | 132.0 *4.70* | . 185.0 *13.0* | . | | . | >290.0** | . |
| 6.g.2 | 2 | . | 160.0 *4.91* | . 197.5 *3.78* | - | | . | >290.0** | . |
| 6.g.3 | 3 | . | 158.5 *2.51* | . 203.5 *3.90* | . | | . | >290.0** | . |
| G.g.4 | 4+ | . | 173.0 *1.95* | . 207.5 *4.31* | . | | . | >290.0** | . |
| G.g.5 | 5 | . | 115.0 *8.78* | . 209.0 *8.74* | . | | . | >290.0** | . |
| 6.g.6 | 6 | . | 106.5 *6.77* | . 207.5 *8.60* | . | 228.5' | . | >290.0** | .· |
| 6.g.7 | 7 | . | 96.5 *3.82* | . 207.0 *8.70* | . | 250.0' | . | >290.0** | . |
| 6.g.8 | 8 | . | 94.0 *3.90* | . 206.5 *9.59* | . | 259.0' | . | 282.0 *2.06* | . |
| 6.g.9 | 9 | . | 80.5 *2.17* | . 201.0 *10.33* | . | 260.0* | . | 278.0 *1.76* | . |
| 6.g.10 | 10 | . | 65.0 *0.93* | . 197.0 *10.57* | . | 257.0 *0.30* | . | 268.0 *1.63* | . |
| 6.g.11 | 11 | . | 164.0 *0.47* | . 194.0 *10.66* | . | 254.5 *0.33* | . | 262.0 *1.47* | . |
| 6.g.12 | 12+ | . | 165.0 *1.58* | . 193.0 *12.96* | . | 253.0 *0.40* | . | 262.5 *1.65* | . |
| 6.g.13 | 18 | . | 150.5 *2.72* | . 172.5 *12.05* | . | 223.5' | . | 226.5 *2.17* | . |

+Compounds 6.g.3, 6.g.4 and 6.g.12 have a crystal → crystal transition at 112.0°C
(7.16 kcal/mol), 143.0°C (5.7 kcal/mol)and 54.0°C (0.5 kcal/mol) respectively.

*Enthalpies could not be measured.

**These compounds decompose before going to isotropic phase.
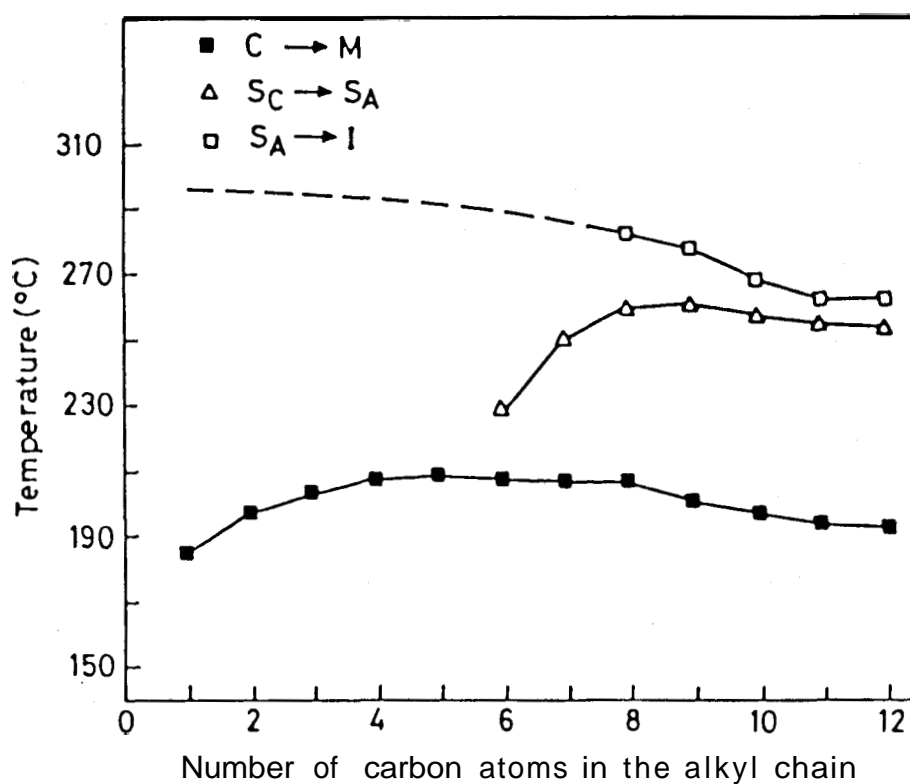
**Figure** 6.6: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 6.g. (The dotted line indicates the temperature beyond which observations could not be made due to thermal decomposition.)

oxysalicylaldiminato]nickel(II) chelates (6.h) are given in table 6.4. These complexes are obtained as greeriish microcrystals with low yield as compared to those obtained for copper(II) and palladium(II) complexes. All these nickel(II) chelates are thermally stable at their clearing temperatures unlike those of copper(II) and palladium(II) complexes. These nickel(II) chelates show smectic mesophases. For complexes, n=1 to n=4, they show only smectic A and for n=5 onwards they exhibit smectic C phase in addition to smectic A phase. They show focal-conic and broken focal-conic textures for smectic A and smectic C phases respectively. The enthalpy of this transition was quite low and could not be measured. All these complexes show crystal → crystal transitions. The dsc thermogram for compound 6.h.1 is shown in figure 6.7.

A comparison of the transition ternperatures of these copper(II), palladium(II) and nickel(II) complexes indicate that the nickel complexes have the lowest transition temperatures. This is in complete contrast to what has been observed by Marcos *et al.*[9] for a series of bis(N-$C_n H_{2n+1}$,4-decyloxybenzoyloxysalicylaldiminato)nickel(II) and copper(II) complexes. Bayle et *al.*[19] have reported a series of nickel, copper and palladium complexes of N-(4-(4'-n-alkoxybenzoyloxy)salicylidene)-4-n-butylaniline and N-(4 - (4'-n-hexadecyloxybenzoyloxy)salicylidene) -4- n-alkoxyaniline. It was found that copper and palladium derivatives were mesogenic and surprisingly the corresponding nickel complexes were non-mesogenic.

Figure 6.8 shows a graphic representation of the transition temperatures 'as a function of alkyl chain length for the nickel chelates, 6.h. As can be seen like transition points follow a smooth curve relationship.

In conclusion, the following points can be noted. A comparison of the meso-morphic properties of all tho compounds synthesised, indicate that the Schiff's base

Table 6.4

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for
bis[N-(4″-n-dodecylbiphenyl)-4-n-alkyloxysalicylaldiminato]nickel(II),
6.h

| compound number | n | $C_2$ | $C_1$ | C | $S_C$ | $S_A$ | I |
|---|---|---|---|---|---|---|---|
| 6.h.1 | 1 | - | . 119.0 <br> *5.09* | . 158.5 <br> *9.57* | | 240.5 <br> *3.0* | . |
| 6.h.2 | 2 | . 88.5 <br> *11.24* | . 122.0 <br> *4.98* | . 144.5 <br> *3.18* | - | . 269.0 <br> *4.34* | . |
| 6.h.3 | 3 | . 89.5 <br> *5.37* | . 108.0 <br> *10.5* | . 161.5 <br> *2.14* | | 261.0 <br> *4.32* | . |
| 6.h.4 | 4 | . 69.0 <br> *2.55* | . 94.5 <br> *8.15* | . 157.5 <br> *2.46* | - | . 262.5 <br> *3.89* | . |
| 6.h.5 | 5 | - | . 96.0 <br> *10.51* | . 152.0 <br> *0.55* | . 168.5* | . 245.5 <br> *3.80* | . |
| 6.h.6 | 6 | - | . 90.0 <br> *9.38* | . 160.0 <br> *1.38* | . 199.0* | . 243.5 <br> *4.03* | . |
| 6.h.7 | 7 | . 85.0 <br> *1.78* | 114.5 <br> *1.34* | . 176.5 <br> *3.53* | . 214.0* | . 240.5 <br> *3.05* | |
| 6.h.8 | 8 | . 126.5 <br> *0.28* | 151.5 <br> *1.64* | . 180.0 <br> *4.83* | . 222.0* | . 237.0 <br> *3.66* | . |
| 6.h.9 | 9 | . 74.0 <br> *1.49* | 95.0 <br> *2.78* | . 156.5 <br> *3.99* | . 220.5* | . 227.5 <br> *3.26* | |
| 6.h.10 | 10 | . 59.5 <br> *0.71* | 106.5 <br> *5.46* | . 157.0 <br> *2.80* | . 220.0 <br> *4.01* | - | |
| 6.h.11 | 11 | . 81.0 <br> *5.30* | 109.0 <br> *3.91* | . 140.0 <br> *4.45* | . 210.0 <br> *4.30* | - | . |
| 6.h.12 | 12 | . 70.0 <br> *5.30* | 114.5 <br> *3.91* | . 141.0 <br> *4.45* | . 196.5 <br> *3.12* | - | |
| 6.h.13 | 18 | - | 79.0 <br> *12.63* | . 122.5 <br> *1.03* | . 179.0 <br> *4.18* | - | . |

*Enthalpies could not be measured.
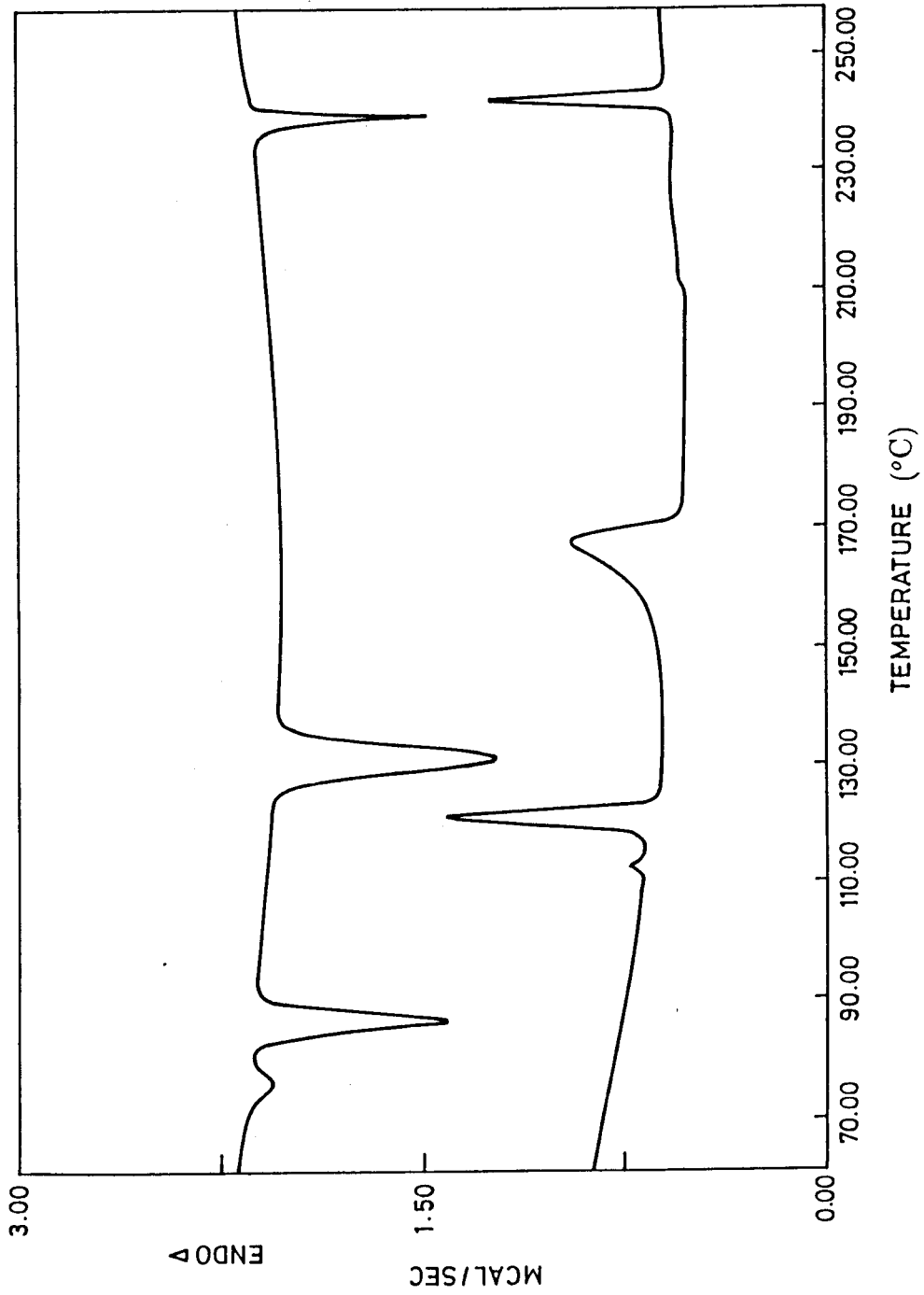
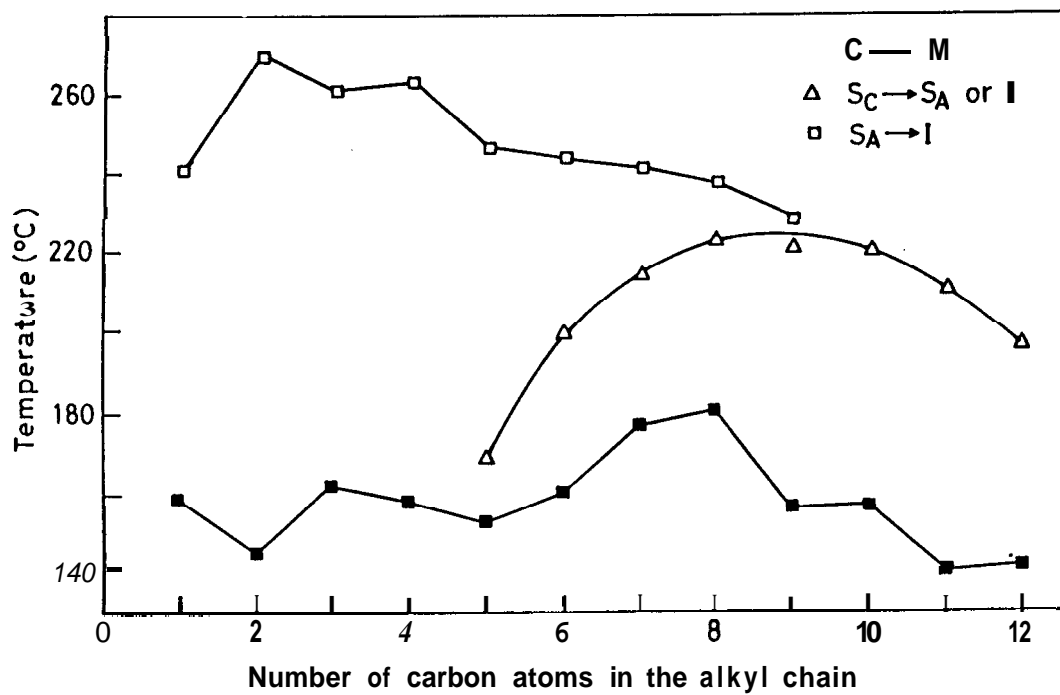Figure 6.7: The dsc thermogram for compound 6.h.1.

**Figure** 6.8: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 6.h.

ligands mainly exhibit smectic polymorphism. Introduction of a lateral hydroxyl group in a Schiff's base is known to increase the clearing points and the overall smectic mesophase range. Introduction of metal atoms like copper, palladium and nickel into such Schiff's base ligands do not seem to affect the mesophases of the resulting complexes though the transition temperatures are elevated. Basically they show srnectic A and smectic C phases. A comparison of these palladium, copper and nickel complexes shows that the nickel complexes have the lowest melting as well as clearing points and the palladium complexes have the highest transition temperatures. Nickel complexes are thermally more stable than the corresponding copper and palladium complexes.

## 6.3    Experimental

### 2,4-Dihydroxybenzaldehyde:

This was prepared following the well known procedure.[22] Thus, by using resorcinol (20.0 g, 0.18 mol) and powdered anhydrous zinc cyanide (40.0 g, 0.34 niol), 2,4-dihydroxybenzaldehyde (23.0 g, 94%), m.p. 134.5°C was obtained. (Reported[22] yield, 94 %, m.p. 135-136°C).

### 4-(4'-n-Dodecylphenyl)acetanilide:

This was prepared from 4-n-dodecyl-4'-acetylbiphenyl following a procedure similar to that described by Van der Veen et al.[21] 4-n-Dodecyl-4'-acetylbiphenyl (14.6 g, 0.04 mol), dichloromethane (5 nil), 80% sulphuric acid (13.5 ml) were taken in a two-necked round bottom flask, fitted with a mechanical stirrer. To this was added sodium azide (2.86 g, 0.044 niol) in small portions during four hours. After the addition was complete it was stirred for a further period of two hours to ensure completion of the reaction. The reaction mixture was poured into a beaker

containing crushed ice (500 g) and left overnight. The precipitate so obtained was filtered, washed with water until it was free of acid, and dried. This was washed with petroleum ether to remove the starting material and was finally crystallised using benzene.

Yield, 9.0 g, (59%), m.p. 149.5°C (C 149.5 S 155.0 I). IR $\nu_{max}$: 3310, 2900, 2850, 1660, 1600, 1500, 1470, 1370, 1265, 1010 and 810 cm$^{-1}$.

Anal. calcd. for $C_{26}H_{37}ON$,

          C, 82.30 ;   H, 9.76 ;   N, 3.69 %

   Found: C, 81.90 ;   H, 9.92 ;   N, 3.43 % .

**4-n-Dodecyl-4'-aminobiphenyl:**

This was prepared following a procedure described by Van der Veen et *al.*[21] Thus, a mixture of 4-n-dodecylphenyl-4'-acetanilide (9.0 g, 0.024 mol), sodium hydroxide (19.2 g, 0.48 mol) in ethyl alcohol (40 ml) and water (13 ml), was stirred and refluxed in a 250 ml round bottom flask for six hours. It was then cooled, poured into a beaker containing crushed ice (400 g) and extracted with chloroform ($3 \times 100$ ml).The combined chloroform solution was washed with water ($5 \times 100$ ml) and dried ($Na_2SO_4$). Removal of solvent and crystallisation of the crude product using hexane gave the required **4-n-dodecyl-4'-arninobiphenyl.**

Yield, 6.5 g, (81%); m.p. 79.0°C; IR $\nu_{max}$: 3430, 3300, 2900, 2850, 1610, 1508, 1460, 1380, 1260 and 820 cm$^{-1}$; NMR $\delta$: 0.8 (t, 3H, -C$\underline{H}_3$), 1.2–2.0 (m, 20H, $10 \times$-C$\underline{H}_2$), 2.6 (t, 2H, arC$\underline{H}_2$), 3.7 (s, 2H, -N$\underline{H}_2$), 6.6–7.5 (m, 8H, ar$\underline{H}$).

2-Hydroxy-4-n-dodecyloxybenzaldehy de:

Sodium (0.83 g, 0.036 mol) was dissolved in absolute ethyl alcohol (150 ml) in a 250 ml round bottom flask fitted with a reflux condenser carrying a calcium

chloride guard tube. To this was added 2,4-dihydroxybenzaldehyde (5.0 g, 0.036 mol), followed by n-dodecylbromide (9.1 g, 0.036 mol). Then, it was stirred and refluxed for a period of thirtyeight hours. Excess ethyl alcohol was removed by distillation and the residue was poured into a beaker containing crushed ice (400 g) and acidified with concentrated hydrochloric acid. This was extracted with ether (3×50 ml), the combined ether solution was washed with water (5x50 ml) and dried ($Na_2SO_4$). The solvent was removed and the residue was chromatographed to obtain a colourless product. This was crystallised using ethyl alcohol to give pure 2-hydroxy-4-n- dodecyloxybenzaldehyde. Yield, 3.0 g, (27%); m.p. 39.5°C.

`All the required 2-hydroxy-4-n-alkyloxybenzaldehydes were prepared following the above procedure (described for 2-Hydroxy-4-n-dodecyloxybenzaldehyde) and were characterised by their physical constants as well as spectral data. The physical constants of these 2-hydroxy-4-n-alkyloxybenzaldehydes (6.i) are given in table 6.5.

### N-(2-Hydroxy-4-n-pentyloxybenzylidene)-4″-n-dodecylphenylaniline:

A mixture of 2-hydroxy-4-n-pentyloxybenzaldehyde (0.62 g, 0.3 mmol), ethyl alcohol (20 ml) and glacial acetic acid (a few drops) was refluxed in a 100 ml round bottom flask for four hours and cooled. The pale yellow precipitate so obtained was filtered off, washed with ethyl alcohol and dried. Crystallisation of the precipitate from butan-2-one gave crystals of the desired Schiff's base.

Yield, 1.1 g, (70%); m.p. 82.5°C; IR $\nu_{max}$: 2900, 2850, 1623, 1592, 1460, 1400, 1285, 1030, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 352 (31,100), 288 (15,600), 250 (19,200); NMR 6: 0.9 (t, 6H, 2×-C$\underline{H}_3$), 1.2–2.0 (m, 26H, 13×-C$\underline{H}_2$), 2.7 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.8 (m, 11H, ar$\underline{H}$), 8.6 (s, 1H, =C-$\underline{H}$), 13.75 (s, 1H, -O$\underline{H}$).

Table **6.5**

Physical constants for 2-hydroxy-4-n-alkyloxybenzaldehydes,

**6.i**

| n | Melting points (°C) | Boiling points (°C)/mm |
|---|---|---|
| 1 | **38.5** | |
| 2 | – | **108-110/1** |
| 3 | | **100-10310.5** |
| 4 | | **110-112/0.5** |
| 5 | | 125-128/0.5 |
| 6 | | **160-16311.5** |
| 7 | | 146-149/0.5 |
| 8 | | **157-16010.3** |
| 9 | **31.5** | |
| 10 | **29.0** | |
| 11 | **44.5** | |
| 18 | **59-61** | |

Anal. calcd. for $C_{36}H_{49}O_2N$,

        C, 81.97 ;    H, 9.29 ;    N, 2.65 %

   Found:  C, 81.96 ;   H, 9.44 ;    N, 2.51 % .

The physical data of the other N-(2-hydroxy-4-n-alkyloxybenzylidene)-4″-n-do-decylphenylanilines are given below:

### N-(2-Hydroxy-4-methyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 73%; m.p. 113.0°C; IR $\nu_{max}$: 2900, 2850, 1625, 1595, 1460, 1410, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (30,000), 286 (14,900), 252 (17,500); NMR δ: 0.85 (t, 3H, -C$\underline{H}_3$), 1.12–2.0 (m, 20H, 10×-C$\underline{H}_2$), 2.48–2.8 (t, 2H, arC$\underline{H}_2$), 3.8 (s, 3H, arOC$\underline{H}_3$), 6.4–7.8 (m, 11H, ar$\underline{H}$), 8.56 (s, 1H, =C-$\underline{H}$), 13.8 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{32}H_{41}O_2N$,

        C, 81.52 ;    H, 8.70 ;    N, 2.97 %

   Found:  C, 81.73 ;    H, 8.86 ;    N, 2.77 % .

### N-(2-Hydroxy-4-ethyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 71%; m.p. 98.0°C; IR $\nu_{max}$: 2900, 2850, 1625, 1590, 1460, 1405, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (31,000), 286 (14,800), 252 (17,800); NMR δ: 0.86 (t, 6H, 2×-C$\underline{H}_3$), 1.12–2.0 (m, 20H, 10×-C$\underline{H}_2$), 2.5–2.8 (t, 2H, arC$\underline{H}_2$), 3.9–4.3 (q, 2H, arOC$\underline{H}_2$), 6.4–7.7 (m, 11H, ar$\underline{H}$), 8.5 (s, 1H, =C-$\underline{H}$), 13.8 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{33}H_{43}O_2N$,

        C, 81.64 ;    H, 8.86 ;    N, 2.88 %

   Found:  C, 81.67 ;    H, 8.99 ;    N, 2.60 % .

## N-(2-Hydroxy-4-n-propyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 75%; m.p. 91.0°C; IR $\nu_{max}$: 2900, 2850, 1625, 1590, 1460, 1405, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 352 (31,500), 286 (15,100), 252 (18,000); NMR $\delta$: 0.95 (t, 6H, 2×-C$\underline{H}_3$), 1.12–2.0 (rn, 22H, 11×-C$\underline{H}_2$) 2.48–2.76 (t, 2H, arC$\underline{H}_2$), 3.84–4.12 (t, 2H, arOC$\underline{H}_2$), 6.4–7.76 (m, 11H, ar$\underline{H}$), 8.6 (s, 1H, =C-$\underline{H}$), 13.76 (s,1H, -O$\underline{H}$).

Anal. calcd. for $C_{34}H_{45}O_2N$,

C, 81.76 ;    H, 9.01 ;    N, 2.80 %

Found:  C, 81.94 ;    H, 9.16 ;    N, 2.77 % .

## N-(2-Hydroxy-4-n-butyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 69%; m.p. 87.5°C; IR $\nu_{max}$: 2900, 2800, 1625, 1590, 1460, 1400, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 352 (29,800), 287· (14,600), 251 (17,800); NMR $\delta$: 0.95 (t, 6H, 2×-C$\underline{H}_3$), 1.2–2.0 (m, 24H, 12×-C$\underline{H}_2$), 2.52–2.8 (t, 2H, arC$\underline{H}_2$), 3.8–4.12 (t, 2H, arOC$\underline{H}_2$), 6.4–7.72 (m, 11H, ar$\underline{H}$), 8.56 (s, 1H, =C-$\underline{H}$), 13.76 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{35}H_{47}O_2N$,

C, 81.87 ;    H, 9.16 ;    N, 2.72 %

Found:  C, 81.68 ;    H, 9.29 ;    N, 2.47 % .

## N-(2-Hydroxy-4-n-hexyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 73%; m.p. 81.0°C; IR $\nu_{max}$: 2900, 2850, 1625, 1595, 1465, 1410, 1285, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 352 (31,300), 287 (15,000), 250 (18,600); NMR $\delta$: 0.96 (t, 6H, 2×-C$\underline{H}_3$), 1.0–2.0 (rn, 28H, 14×-C$\underline{H}_2$), 2.6 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.75 (m, 1114, ar$\underline{H}$), 8.56 (s, 1H, =C-$\underline{H}$), 13.95 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{37}H_{51}O_2N$,

C, 82.07 ;    H, 9.42 ;    N, 2.58 %

Found: C, 81.93 ;    H, 9.59 ;    N, 2.18 % .

## N-(2-Hydroxy-4-n-heptyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 81%; m.p. 83.5°C; IR $\nu_{max}$: 2900, 2850, 1625, 1595, 1460, 1410, 1280, 1205, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 352 (32,300), 288 (15,400)) 250 (18,900); NMR 6: 0.92 (t, 6H, 2×-C$\underline{H}_3$), 1.1–2.0 (m, 30H, 15×-C$\underline{H}_2$), 2.64 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.76 (m, 11H, ar$\underline{H}$), 8.52 (s, 1H, =C-$\underline{H}$), 13.8 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{38}H_{53}O_2N$,

C, 82.16 ;    H, 9.54 ;    N, 2.52 %

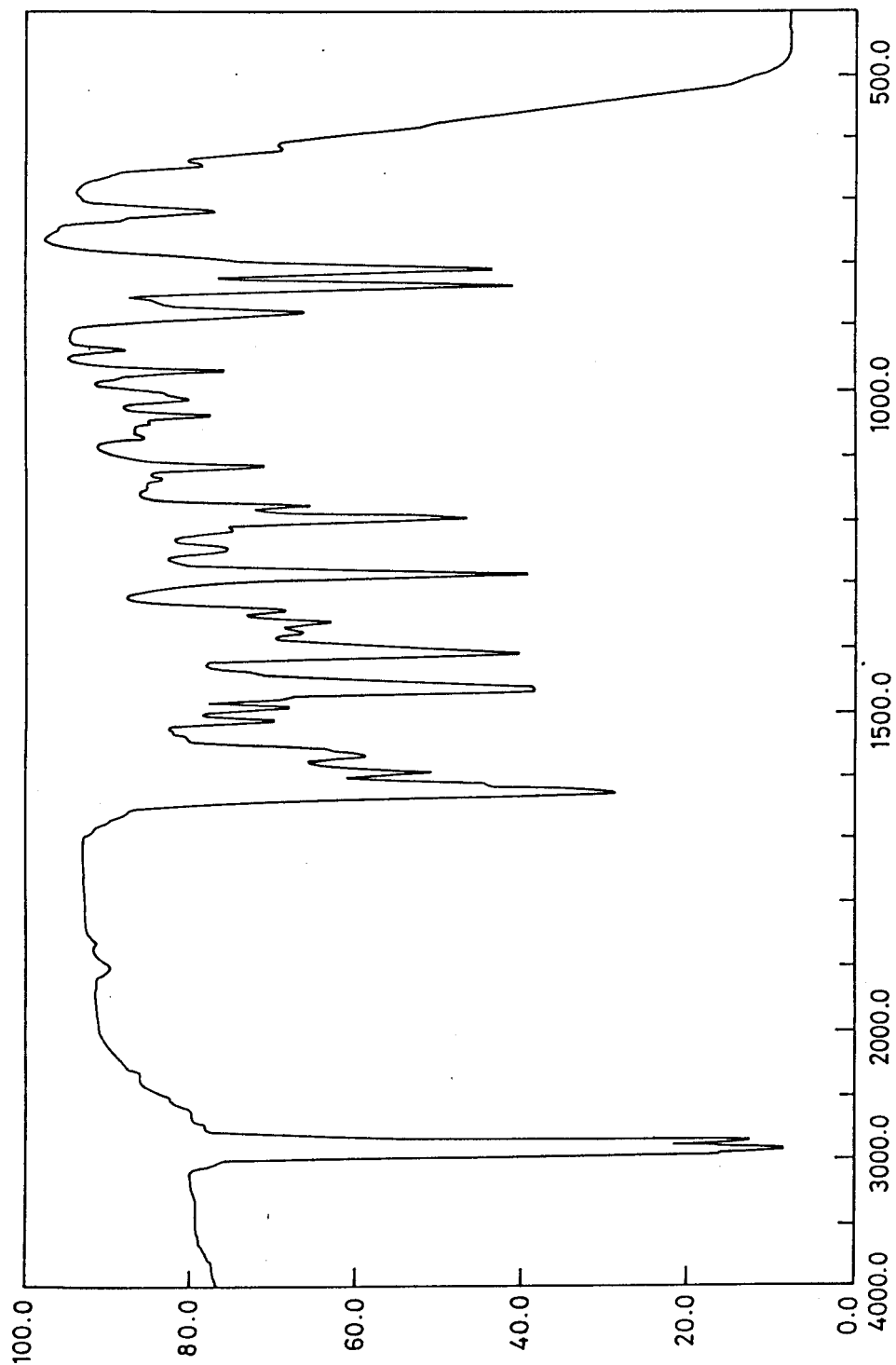Found: C, 82.05 ;    H, 9.70 ;    N, 2.14 % .

## N-(2-Hydroxy-4-n-octyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 77%; m.p. 76.5°C; IR $\nu_{max}$: 2910, 2860, 1630, 1600, 1465, 1410, 1285, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (32,000), 287 (15,500), 250 (19,300); NMR 6: 0.92 (t, 6H, 2×-C$\underline{H}_3$), 1.1–2.0 (m, 32H, 16×-C$\underline{H}_2$), 2.68 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.8 (m, 11H, ar$\underline{H}$), 8.6 (s, 1H, =C-$\underline{H}$), 13.8 (s, 1H, -O$\underline{H}$).
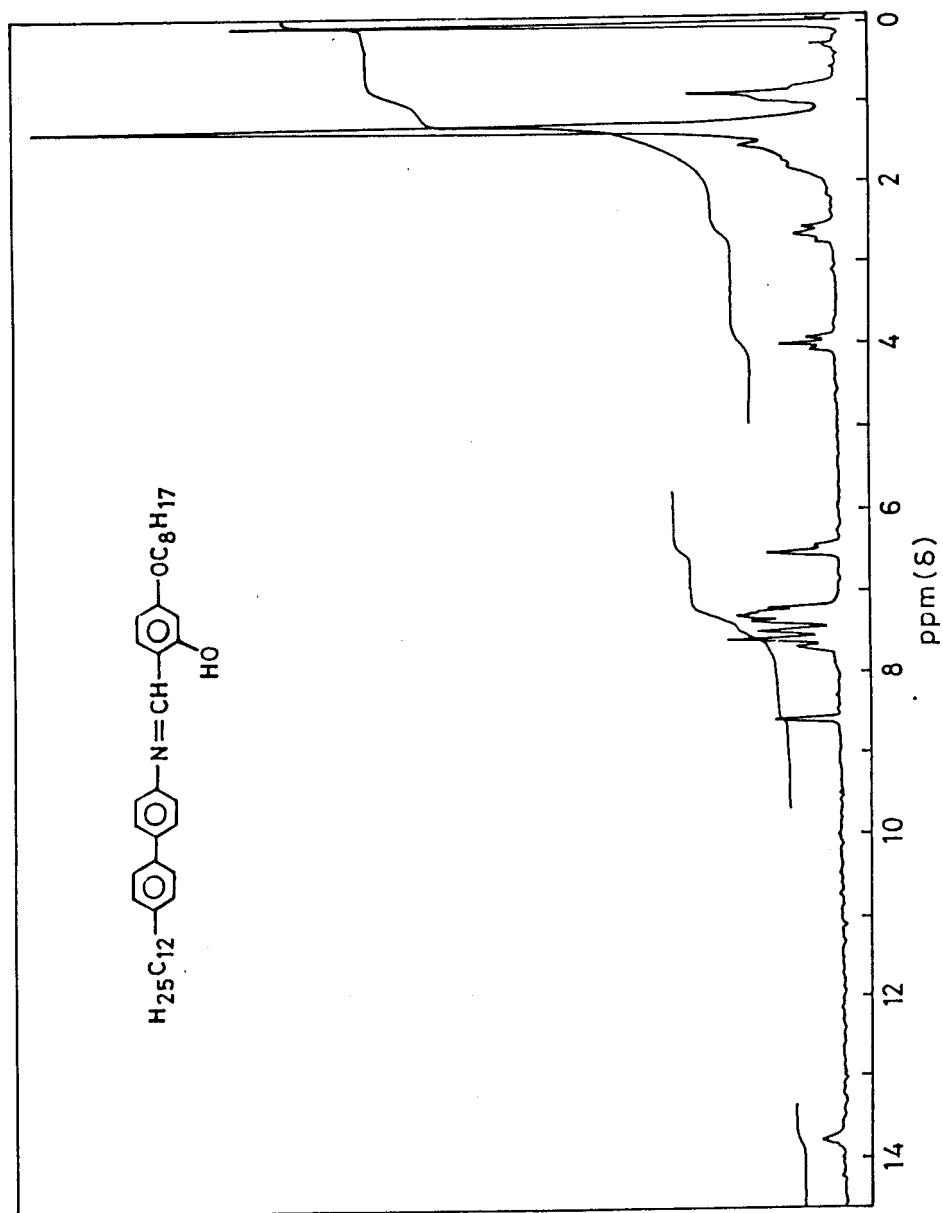
Anal. calcd. for $C_{39}H_{55}O_2N$,

C, 82.24 ;    H,9.66 ;    N, 2.46 %

Found: C, 82.04 ;    H,9.82 ;    N, 2.14 % .

IR spectrum for compound 6.e.7.

$^1$H NMR spectrum for compound 6.e.8.

## N-(2-Hydroxy-4-n-nonyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 80%; m.p. 85.0°C; IR $\nu_{max}$: 2900, 2860, 1630, 1600, 1460, 1410, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (31,100), 288 (15,800), 249 (19,600); NMR 6: 0.92 (t, 6H, 2×-C$\underline{H}_3$), 1.1–2.0 (m, 34H, 17×-C$\underline{H}_2$), 2.64 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.76 (m, 11H, ar$\underline{H}$), 8.56 (s, 1H, =C-$\underline{H}$), 13.76 (s, 1H, -O11).

Anal. calcd. for $C_{40}H_{57}O_2N$,

<div align="center">

C, 82.33 ;    H, 9.77 ;    N, 2.40 %

Found:  C, 82.54 ;    H, 9.93 ;    N, 2.09 % .

</div>

## N-(2-Hydroxy-4-n-decyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 86%; m.p. 79.5°C; IR $\nu_{max}$: 2900, 2860, 1630, 1600, 1470, 1410, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (31,200), 287·(14,800), 252 (17,700); NMR 6: 0.92 (t, 6H, 2×-C$\underline{H}_3$), 1.1–2.0 (m, 36H, 18×-C$\underline{H}_2$), 2.68 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.76 (m, 11H, ar$\underline{H}$), 8.6 (s, 1H, =C-$\underline{H}$), 13.8 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{41}H_{59}O_2N$,

<div align="center">

C, 82.41 ;    H, 9.88 ;    N, 2.34 %

Found:  C, 82.23 ;    H, 10.04 ;    N, 1.95 % .

</div>

## N-(2-Hydroxy-4-n-undecyloxybenzylidene)-4″-n-dodecylphenylaniline:

Yield, 84%; m.p. 83.0°C; IR $\nu_{max}$: 2900, 2850, 1630, 1600, 1460, 1410, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (32,500), 286 (15,800), 253 (18,800); NMR 6: 0.9 (t, 6H, 2×-C$\underline{H}_3$), 1.0–2.0 (rn, 38H, 19×-C$\underline{H}_2$), 2.6 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.76 (m, 11H, ar$\underline{H}$), 8.6 (s, 1H, =C-$\underline{H}$), 13.76 (s, 111, -O11).

Anal. calcd. for $C_{42}H_{61}O_2N$,

C, 82.48 ;    H, 9.98 ;    N, 2.29 %

Found: C, 82.69 ;    H, 10.16;   N, 1.93 % .

## N-(2-Hydroxy-4-n-dodecyloxybenzylidene)-4''-n-dodecylphenylaniline:

Yield, 79%; m.p. 80.5°C; IR $\nu_{max}$: 2900, 2850, 1630, 1600, 1460, 1410, 1290, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (c): 350 (32,000), 287 (15,100), 252 (18,100); NMR $\delta$: 0.86 (t, 6H, 2×-C$\underline{H}_3$), 1.1–2.0 (m, 40H, 20×-C$\underline{H}_2$), 2.6 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.68 (m, 11H, ar$\underline{H}$), 8.54 (s, 1H, =C-$\underline{H}$), 13.77 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{43}H_{63}O_2N$,

C, 82.56 ;    H, 10.08 ;    N, 2.24 %

Found: C, 82.61 ;    H, 10.26 ;    N, 1.87 % .

## N-(2-Hydroxy-4-n-octadecyloxybenzylidene)-4''-n-dodecylphenylaniline:

Yield, 83%; m.p. 87.0°C; IR $\nu_{max}$: 2910, 2850, 1630, 1600, 1460, 1410, 1280, 1200, 840 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (32,000)) 287 (16,400), 251 (19,600); NMR $\delta$: 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.1–2.0 (m, 52H, 26×-C$\underline{H}_2$), 2.6 (t, 2H, arC$\underline{H}_2$), 4.0 (t, 2H, arOC$\underline{H}_2$), 6.4–7.72 (m, 11H, ar$\underline{H}$), 8.56 (s, 1H, =C-$\underline{H}$), 13.76 (s, 1H, -O$\underline{H}$).

Anal. calcd. for $C_{49}H_{75}O_2N$,

C, 82.93 ;    H, 10.57 ;    N, 1.97 %

Found: C, 82.53 ;    H, 10.78 ;    N, 1.61 %

**Bis-[N-(4″-dodecylbiphenyl)-4-n-pentyloxysalicylaldiminato]copper(II):**

To a stirred mixture of N-(2-hydroxy-4-n-pentyloxybenzylidene)-4″-n-dodecyl-phenylaniline (0.53 g, 1 mmol), tetrahydrofuran (5 ml), powdered potassium hydroxide (0.056 g, 1 mmol) and ethyl alcohol (5 ml) was added a solution of cupric chloride dihydrate (0.085 g, 0.5 mmol) in ethyl alcohol (5 ml). The mixture became dark green and precipitation occurred immediately. This mixture was stirred for four hours at room temperature. Ethyl alcohol (20 ml) was added to this and the solid filtered off. This was dissolved in chloroform (75 ml), washed with water $(3 \times 50$ ml) and dried $(Na_2SO_4)$. Removal of solvent and crystallisation of the residue from butan-2-one afforded green crystals of the desired complex.

Yield, 0.32 g, (59%); m.p. 191.5°C; IR $\nu_{max}$: 2900, 2850, 1608, 1588, 1530, 1500, 1440, 1380, 1320, 1210, 830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 389 (40,400), 310 (56,800), 259 (39,600).

Anal. calcd. for $C_{72}H_{96}O_4N_2Cu$,

        C, 77.45 ;    H, 8.60 ;    N, 2.50 %

   Found:  C, 77.62 ;    H, 8.74 ;    N, 2.48 % .

The physical data of the other bis[N-(4″-n-dodecylbiphenyl)-4-n-alkyloxysalicy-laldiminato]copper(II) complexes are given below:

**Bis[N-(4″-n-dodecylbiphenyl)-4-methyloxysalicylaldiminato]copper(II):**

Yield, 68%; m.p. 182.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1588, 1530, 1500, 1440, 1380, 1320, 1210, 830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 389 (39,700), 309 (56,700), 258 (37,400).

Anal. calcd. for $C_{64}H_{80}O_4N_2Cu$,

C, 76.52 ; H, 7.97 ; N, 2.79 %

Found: C, 76.14 ; H, 8.08 ; N, 2.50 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-ethyloxysalicylaldiminato]copper(II):**

Yield, 70%; m.p. 174.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1500, 1440, 1380, 1320, 1210, 830 and 810 cm⁻¹; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 389 (41,100), 311 (57,700), 257 (42,700).

Anal. calcd. for $C_{66}H_{84}O_4N_2Cu$,

C, 76.77 ; H, 8.14 ; N, 2.71 %

Found: C, 76.77 ; H, 8.29 ; N, 2.50 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-propyloxysalicylaldiminato]copper(II):**

Yield, 64%; m.p. 177.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1500, 1440, 1380, 1320, 1210, 830 and 810 cm⁻¹; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 389 (40,200), 311 (57,900), 258 (42,000).

**Anal.** calcd. for $C_{68}H_{88}O_4N_2Cu$,

C, 77.01 ; H, 8.30 ; N, 2.64 %

Found: C, 76.80 ; H, 8.31 ; N, 2.59 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-butyloxysalicylaldiminato]copper(II):**

Yield, 58%; m.p. 168.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1500, 1440, 1370, 1320, 1210, 830 and 810 cm⁻¹; UV-Vis: $\lambda_{max}^{CHCl_3}$ (c): 387 (40,900), 311 (55,500), 257 (40,200).

Anal. calcd. for $C_{70}H_{92}O_4N_2Cu$,

C, 77.23 ;   H, 8.45 ;   N, 2.57 %

Found: C, 77.49 ;   H, 8.65 ;   N, 2.51 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-hexyloxysalicylaldiminato]copper(II):**

Yield, 61%; m.p. 200.5°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1490, 1440, 1380, 1320,1210,830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 388 (40,000), 310 (58,100), 259 (41,700).

Anal. calcd. for $C_{74}H_{100}O_4N_2Cu$,

C, 77.65 ;   H, 8.74 ;   N, 2.44 %

Found: C, 77.50 ;   H, 8.91 ;   N, 2.15 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-heptyloxysalicylaldiminato]copper(II):**

Yield, 56%; m.p. 207.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1490, 1440, 1380, 1320,1210,830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 390 (40,900), 310 (59,200)) 257 (45,100).

Anal, calcd. for $C_{76}H_{104}O_4N_2Cu$,

C, 77.84 ;   H, 8.87 ;   N, 2.39 %

Found: C, 78.16 ;   H, 9.06 ;   N, 2.34 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-octyloxysalicylaldiminato]copper(II):**

Yield, 61%; m.p. 206.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1490, 1440, 1380, 1320,1210,830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 389 (40,000), 310 (58,000), 258 (42,500).

Anal. calcd. for $C_{78}H_{108}O_4N_2Cu$,

<div align="center">

C, 78.02 ;   H, 9.0 ;   N, 2.33 %

Found: C, 77.82 ;  H, 9.17 ;   N, 2.05 % .

</div>

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-nonyloxysalicylaldiminato]copper(II):**

Yield, 60%; m.p. 202.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1490, 1440, 1380, 1320, 1210,830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (E): 390 (40,000), 311 (58,100)) 258 (41,100).

Anal. calcd. for $C_{80}H_{112}O_4N_2Cu$,

<div align="center">

C, 78.20 ;   H, 9.12 ;   N, 2.28 %

Found: C, 77.93 ;   H, 9.28 ;   N, 1.97 % .

</div>

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-decyloxysalicylaldiminato]copper(11) :**

Yield, 63%; m.p. 201.0°C; IR $\nu_{max}$: 2900, 2800, 1610, 1590, 1530, 1490, 1440, 1380, 1320, 1210, 830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 388 (40,300)) 310 (58,600), 257 (41,600).
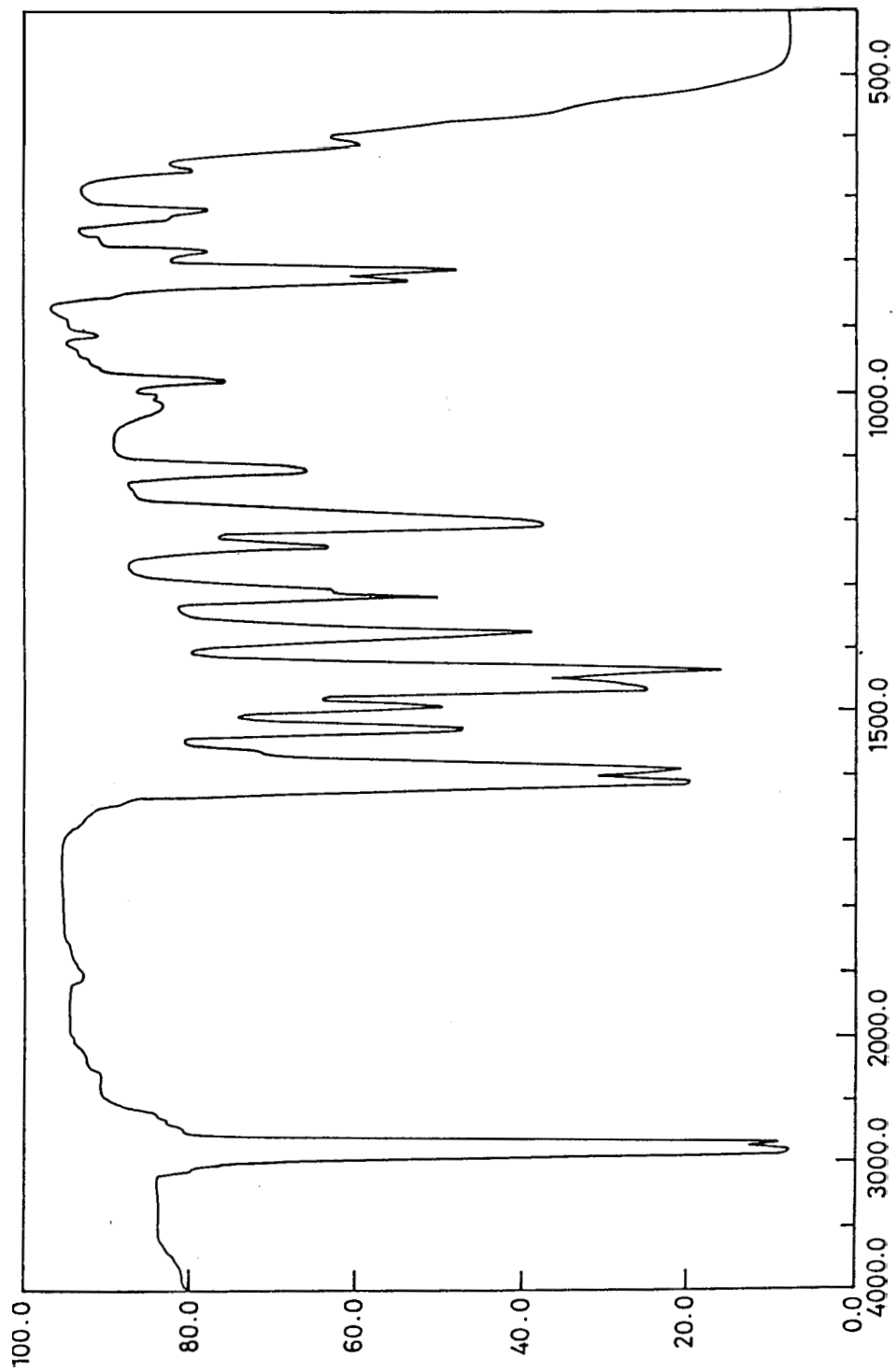
Anal. calcd. for $C_{82}H_{116}O_4N_2Cu$,

<div align="center">

C, 78.37 ;   H, 9.23 ;   N, 2.23 %

Found: C, 78.72 ;   H, 9.42 ;   N, 2.11 % .

</div>

**Bis[N -(4″-n -dodecylbiphenyl)-4 -n -undecyloxysalicylaldiminato]copper(II):**

Yield, 58%; m.p. 194.0°C; IR $\nu_{max}$: 2900, 2800, 1610, 1590, 1530, 1490, 1440, 1380, 1320,1210,830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 390 (40,400), 311 (58,300)) 258 (41,700).

IR spectrum for compound 6.f.10.

Anal. calcd. for $C_{84}H_{120}O_4N_2Cu$,

. C, 78.53 ; H, 9.34 ; N, 2.18 %

Found: C, 78.54 ; H, 9.37 ; N, 2.00 % .

## Bis[N -(4″-n -dodecylbiphenyl)-4 -n -dodecyloxysalicylaldiminato]copper(II):

Yield, 61%; m.p. 191.5°C; IR $\nu_{max}$: 2900, 2800, 1610, 1590, 1530, 1490, 1440, 1380, 1320,1210,830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 388 (40,800), 310 (58,600)) 257 (46,800).

Anal. calcd. for $C_{86}H_{124}O_4N_2Cu$,

C, 78.68 ; H, 9.45 ; N, 2.13 %

Found: C, 78.59 ; H, 9.58 ; N, 2.07 % .

## Bis[N -(4″-n -dodecylphenyl)-4 -n -octadecyloxysalicylaldiminato]copper(II):

Yield, 64%; m.p. 181.5°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1530, 1490, 1440, 1380, 1320,1210,830 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (e): 388 (40,100), 309 (57,900), 257 (43,400).

Anal. calcd. for $C_{98}H_{148}O_4N_2Cu$,

C, 79.48 ; H, 10.0 ; N, 1.89 %

Found: C, 79.47 ; H, 10.20 ; N, 1.66 % .

## Bis[N -(4″-n -dodecylbiphenyl)-4 -n -pentyloxysalicylaldiminato]palladium(II):

A mixture of N-(2 -hydroxy-4 -n-pentyloxybenzylidene)-4″- n-dodecylphenylaniline (0.316 g, 0.6 mmol), palladium chloride (0.058 g, 0.33 mol), anhydrous potassium carbonate (0.124 g, 0.9 mmol) and dry acetonitrile (25 ml) was stirred and heated for eighteen hours in an oil bath maintained at 80°C. Then it was cooled and filtered. The yellow precipitate was collected, dissolved in chloroform (100 ml), washed with water (3x60 ml) and dried ($Na_2SO_4$). Removal of solvent and crystallisation of the residue from a mixture of butan-2-one and chloroform gave bright yellow crystals of the required complex.

Yield, 0.18 g, (52%); m.p. 209.0°C; IR $\nu_{max}$: 2900, 2850, 1608, 1592, 1470, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 403 (17,200), 299 (57,400), 264 (73,000).

Anal. calcd. for $C_{72}H_{96}O_4N_2Pd$,

C, 74.58 ;    H, 8.28 ;    N, 2.41 %

Found:  C, 74.97 ;    H, 8.44 ;    N, 2.46 % .

The physical data of the other bis[N-(4″-n-dodecylbiphenyl)-4-n-alkyloxysalicylaldiminato]palladium(II) complexes are given below:

## Bis[N -(4″-n -dodecylbiphenyl)-4 -methyloxysalicylaldiminato]palladium(II):

Yield, 48%; m.p. 185.0°C; IR $\nu_{max}$: 2900, 2850, 1608, 1590, 1470, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 401 (17,100), 298 (56,900), 263 (72,300).

**Anal.** calcd. for $C_{64}H_{80}O_4N_2Pd$,

C, 73.39 ;    H, 7.64 ;    N, 2.67 %

Found:  C, 73.20 ;   H, 7.83 ;    N, 2.59 % .

## Bis[N-(4″-n-dodecylbiphenyl)-4-ethyloxysalicylaldiminato]palladium(II):

Yield, 52%; m.p.  197.5°C; IR $\nu_{max}$: 2900, 2850, 1608, 1590, 1470, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 402 (18,000), 299 (58,500), 264 (73,900).

Anal. calcd. for $C_{66}H_{84}O_4N_2Pd$,

C, 73.71 ;    H, 7.81 ;    N, 2.60 %

Found:  C, 73.40 ;    H, 7.91 ;    N, 2.34 % .

## Bis[N -(4″-n -dodecylbiphenyl)-4 -n- propyloxysalicylaldiminato]palladium(II):

Yield, 51%; m.p.  203.5°; IR $\nu_{max}$:  2900, 2850, 1610, 1590, 1470, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda^{CHCl_3}$ ($\epsilon$): 403 (18,100), 299 (58,500), 264 (72,700).

Anal. calcd. for $C_{68}H_{88}O_4N_2Pd$,

C, 74.02 ;    H, 7.98 ;    N, 2.54 %

Found:  C, 74.49 ;    H, 8.15 ;    N, 2.54 % .

## Bis[N -(4″-n -dodecylbiphenyl) -4 -n- butyloxysalicylaldiminato]palladium(II):

Yield, 55%; m.p.  207.5°C; IR $\nu_{max}$:  2900, 2850, 1610, 1590, 1470, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 403 (18,100), 300 (58,500), 264 (73,300).

Anal. calcd. for $C_{70}H_{92}O_4N_2Pd$,

<div align="center">

C, 74.30 ;    H, 8.13 ;    N, 2.47 %

Found: C, 74.14 ;   H, 8.26 ;    N, 2.19 % .

</div>

## Bis[N -(4″-n -dodecylbiphenyl)-4 -n- hexyloxysalicylaldiminato]palladium(II):

Yield, 58%; m.p. 207.5°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1480, 1430, 1380, 1320, 1220, 1140 and 830 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 403 (18,700)) 299 (58,900), 264 (74,100).

Anal. calcd. for $C_{74}H_{100}O_4N_2Pd$,

<div align="center">

C, 74.84 ;    H, 8.42 ;    N, 2.36 %

Found: C, 74.43 ;    H, 8.51 ;    N, 2.22 % .

</div>

## Bis[N -(4″-n -dodecylbiphenyl)-4 -n- heptyloxysalicylaldiminato]palladium(II):

Yield, 54%; m.p. 207.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1480, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 402 (18,600), 299 (59,700), 264 (75,100).

Anal. calcd. for $C_{76}H_{104}O_4N_2Pd$,

<div align="center">

'C, 75.09 ;    H, 8.56 ;    N, 2.30 %

Found: C, 74.75 ;    H, 8.80 ;    N, 2.09 % .

</div>

Bis[N -(4″-n -dodecylbiphenyl)-4 -n- octyloxysalicylaldiminato]palladium(II):

Yield, 61%; m.p. 206.5°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1480, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 403 (18,000), 300 (58,000), 264 (72,900).

Anal. calcd. for $C_{78}H_{108}O_4N_2Pd$,

C, 75.33 ;    H, 8.69 ;    N, 2.25 %

Found:  C, 75.13 ;    H, 8.79 ;    N, 2.27 % .

Bis[N -(4″-n -dodecylbiphenyl)-4 -n- nonyloxysalicylaldiminato]palladium(II):

Yield, 57%; m.p. 201.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1480, 1430, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 402 (19,100), 299 (58,500), 264 (73,300).

Anal. calcd. for $C_{80}H_{112}O_4N_2Pd$,

C, 75.56 ;    H, 8.81 ;    N, 2.20 %

Found:  C, 75.41 ;    119.01 ;    N, 2.16 % .

Bis[N -(4″-n -dodecylbiphenyl)-4 -n- decyloxysalicylaldiminato]palladium(II):

Yield, 51%; m.p. 197.0°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1480, 1430, 1380, 1320, 1220, 1140 and 820 cm``; UV-Vis: $\lambda_{max}^{CHCl_3}$ (c): 403 (20,200), 299 (57,500), 263 (71,800).

Anal. calcd. for $C_{82}H_{116}O_4N_2Pd$,

<div style="text-align:center">

C, 75.78 ;   H, 8.93 ;   N, 2.15 %

Found: C, 75.41 ;  H, 9.03 ;   N, 1.98 % .

</div>

**Bis[N -(4″-n -dodecylbiphenyl)-4 -n- undecyloxysalicylaldiminato]palladium(II):**

Yield, 55%; m.p. 194.0°C; IR $\nu_{max}$: 2900, 2850, 1608, 1590, 1480, 1420, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 403 (18,600), 299 (59,200), 264 (74,600).

Anal. calcd. for $C_{84}H_{120}O_4N_2Pd$,

<div style="text-align:center">

C, 75.99 ;   H, 9.04 ;   N, 2.11 %
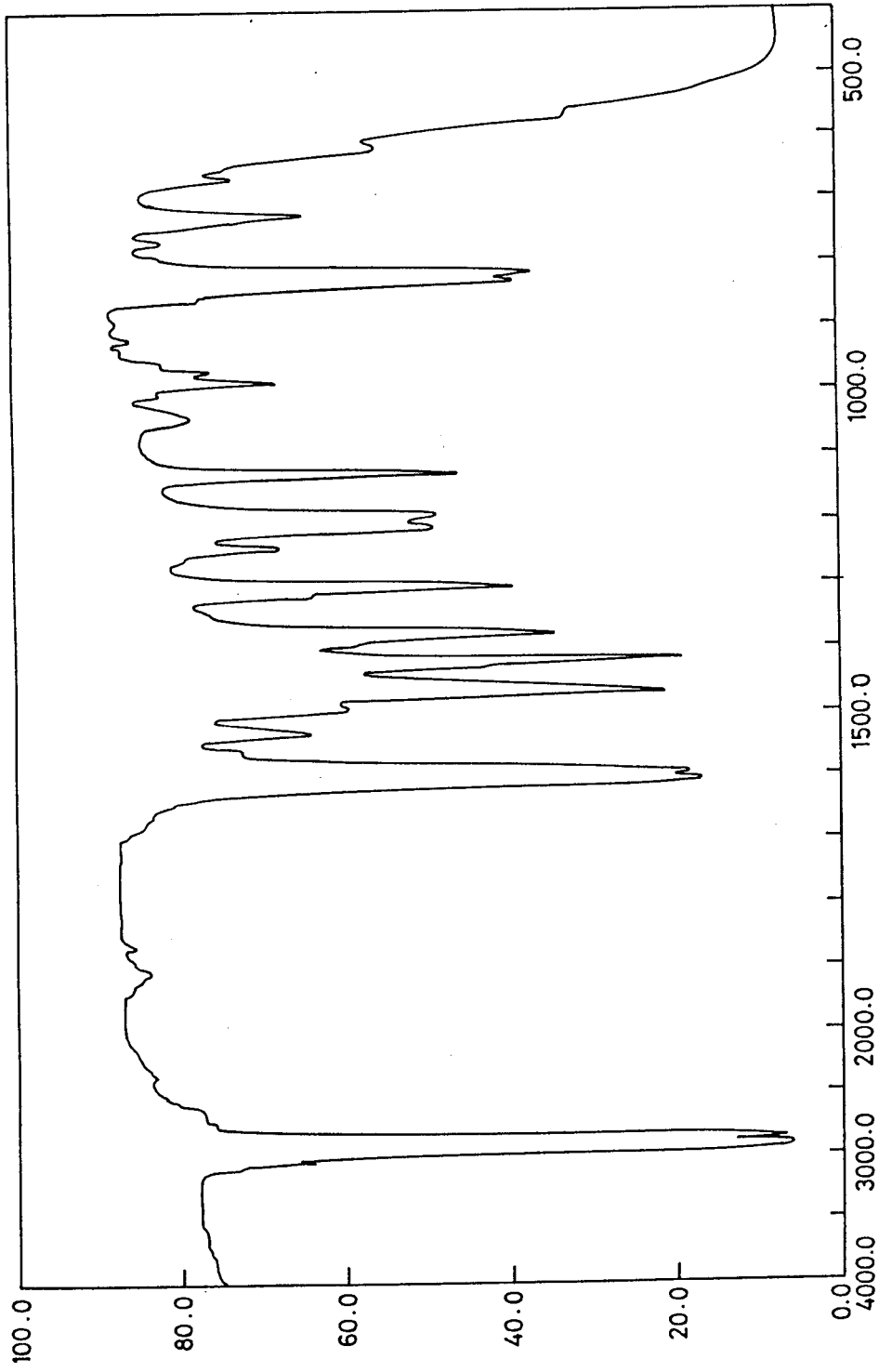
Found: C, 75.94 ;   H, 9.25 ;   N, 1.97 % .

</div>

**Bis[N -(4″-n -dodecylbiphenyl)-4 -n- dodecyloxysalicylaldiminato]palladium(II):**

Yield, 53%; m.p. 193.0°; IR $\nu_{max}$: 2900, 2850, 1608, 1590, 1480, 1420, 1380, 1320, 1220,'1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 402 (20,200), 299 (57,400), 264 (71,800).

Anal. calcd. for $C_{86}H_{124}O_4N_2Pd$,

<div style="text-align:center">

C, 76.19 ;   H, 9.15 ;   N, 2.06 %

Found: C, 75.78 ;   H, 9.22 ;   N, 1.92 % .

</div>

IR spectrum for compound 6.g.12.

**Bis[N -(4″-n -dodecylbiphenyl)-4 -n- octadecyloxysalicylaldiminato]palladium(II):**

Yield, 57%; m.p. 172.5°C; IR $\nu_{max}$: 2900, 2850, 1610, 1590, 1480, 1420, 1380, 1320, 1220, 1140 and 820 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (E): 400 (18,700), 300 (58,300), 264 (73,800).

Anal. calcd. for $C_{98}H_{148}O_4N_2Pd$,

<div align="center">

C, 77.24 ;    H, 9.72 ;    N, 1.83 %

Found:  C, 77.70 ;    H, 9.40 .;    N, 1.98 % .

</div>

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-pentyloxysalicylaldiminato]nickel(II):**

In a 100 ml round bottom flask fitted with a reflux condenser was placed a mixture of N-(2-hydroxy-4-n-pentyloxybenzylidene)-4″-n- dodecylphenylaniline (1.06 g, 2 mmol), nickel acetate tetrahydrate (0.25 g, 1 mmol), anhydrous potassium carbonate (0.414 g, **3** mmol) and dry acetonitrile (50 ml). This was stirred magnetically and heated in an oil bath maintained at 60°C for eighteen hours. Then it was cooled, filtered and the precipitate was dissolved in chloroform (100 ml), washed with water (5×50 ml) and dried ($Na_2SO_4$). Removal of solvent and crystallisation of the residue using butan-2-one, gave dark green crystals of the required complex.

Yield, 0.8 g, (72%); m.p. 152.0"; IR $\nu_{max}$: 2950, 2850, 1610, 1595, 1525, 1465, 1430, 1200 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (E): 352 (30,200), 277 (50,600), 258 (45,400), 226 (42,500).

Anal. calcd. for $C_{72}H_{96}O_4N_2Ni$,

<div align="center">

C, 77.78 ;    H, 8.64 ;    N, 2.52 %

Found:  C, 78.12 ;    H, 8.34 ;    N, 2.63 % .

</div>

The physical data of other bis[N-(4″-n-dodecylbiphenyl)-4-n-alkyloxysalicylaldi-minato]nickel(II) complexes are given below:

## Bis[N-(4″-n-dodecylbiphenyl)-4-methyloxysalicylaldiminato]nickel(II):

Yield, 58%; m.p. 158.5°C; IR $\nu_{max}$: 2950, 2860, 1610, 1595, 1525, 1465, 1440, 1420, 1318, 1220 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (r): 353(30,300), 274 (49,800), 257 (48,600), 226 (41,900).

Anal. calcd. for $C_{64}H_{80}O_4N_2Ni$,

C, 76.89 ;    H, 8.01 ;    N, 2.80 %

Found: C, 77.25 ;    H, 8.26 ;    N, 2.66 % .

## Bis[N-(4″-n-dodecylbiphenyl)-4-ethyloxysalicylaldiminato]nickel(II):

Yield, 49%; m.p. 144.5°C; IR $\nu_{max}$: 2950, 2850, 1610, 1595, 1525, 1470, 1430, 1308, 1205 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (r): 353 (29,600), 276 (52,900), 258 (48,700), 225 (42,500).

Anal. calcd. for $C_{66}H_{84}O_4N_2Ni$,

C, 77.14 ;    H, 8.16 ;    N, 2.72 %

Found: C, 77.68 ;    H, 8.29 ;    N, 2.58 % .

## Bis[N-(4″-n-dodecylbiphenyl)-4-n-propyloxysalicylaldiminato]nickel(II):

Yield, 38%; m.p. 161.5°C; IR $\nu_{max}$: 2950, 2860, 1610, 1595, 1525, 1465, 1430, 1310, 1205 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 353 (30,500), 279 (53,800); 259 (48,400), 226 (41,800).

Anal. calcd. for $C_{68}H_{88}O_4N_2Ni$,

C, 77.36 ;    H, 8.34 ;    N, 2.65 %

Found: C, 77.66 ;    H, 8.60 ;    N, 2.25 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-butyloxysalicylaldiminato]nickel(II):**

Yield, 64%; m.p. 157.5°C; IR $\nu_{max}$: 2900, 2850, 1610, 1595, 1525, 1465, 1430, 1310, 1205 and 808 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ε): 352 (31,000), 278 (52,800), 259 (48,300), 227 (42,500).

Anal. calcd. for $C_{70}H_{92}O_4N_2Ni$,

<div align="center">

C, 77.58 ;   H, 8.49 ;   N, 2.58 %

Found: C, 77.51 ;   H, 8.66 ;   N, 2.56 % .

</div>

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-hexyloxysalicylaldiminato]nickel(II):**

Yield, 40%; m.p. 160.0°C; IR $\nu_{max}$: 2900, 2860, 1608, 1595, 1525, 1465, 1430, 1310, 1200 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ε): 352 (30,600), 277 (50,000), 257 (45,200), 227 (38,800).

Anal. calcd. for $C_{74}H_{100}O_4N_2Ni$,

<div align="center">

C, 77.98 ;   H, 8.78 ;   N, 2.45 %

Found: C, 77.96 ;   H, 9.13 ;   N, 2.16 % .

</div>

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-heptyloxysalicylaldiminato]nickel(II):**

Yield, 44%; m.p. 176.5°C; IR $\nu_{max}$: 2900, 2860, 1608, 1595, 1520, 1465, 1430, 1315, 1205 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ε): 354 (32,700), 282 (49,000), 256 (45,200), 225 (44,200).

Anal. calcd. for $C_{76}H_{104}O_4N_2Ni$,

<div align="center">

C, 78.16 ;   H, 8.91 ;   N, 2.39 %

Found: C, 78.49 ;   H, 9.10 ;   N, 2.04 % .

</div>

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-octyloxysalicylaldiminato]nickel(II):**

Yield, 42%; m.p. 180.0°C; IR $\nu_{max}$: 2950, 2880, 1608, 1595, 1530, 1470, 1435, 1320, 1210 and 810 cm$^{-1}$; UV-Vis: $\lambda^{CHCl_3}$ (ε): 353 (30,000), 281 (48,000), 257 (44,100), 226 (39,800).

Anal. calcd. for $C_{78}H_{108}O_4N_2Ni$,

C, 78.34 ;    H, 9.03 ;    N, 2.34 %

Found:  C, 78.05 ;    H, 9.17 ;    N, 2.30 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-nonyloxysalicylaldiminato]nickel(II):**

Yield, 37%; m.p. 156.5°C; IR $\nu_{max}$: 2920, 2860, 1610, 1595, 1525, 1465, 1430, 1310, 1200 and 810 cm$^{-1}$: UV-Vis: $\lambda^{CHCl_3}_{max}$ (ε): 353 (29,400)) 277 (51,300)) 258 (46,500), 226 (41,300).

Anal. calcd. for $C_{80}H_{112}O_4N_2Ni$,

C, 78.51 ;    H, 9.16 ;    N, 2.29 %
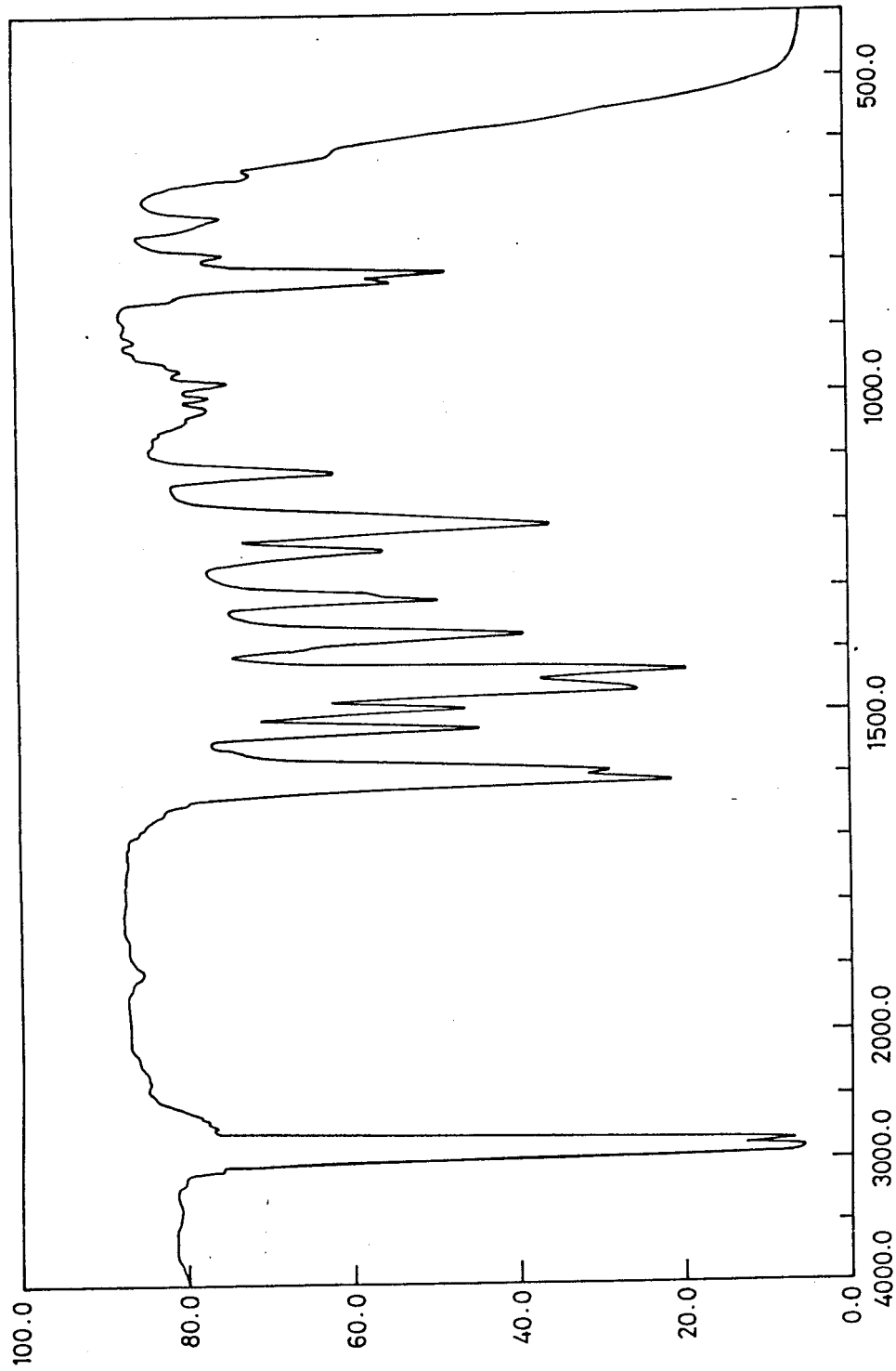
Found:  C, 78.70 ;    H, 8.96 ;    N, 2.16 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-decyloxysalicylaldiminato]nickel(II):**

Yield, 32%; m.p. 157.0°C; IR $\nu_{max}$: 2920, 2860, 1610, 1595, 1525, 1465, 1430, 1308, 1200 and 810 cm$^{-1}$; UV-Vis: $\lambda^{CHCl_3}_{max}$ (ε): 353 (29,500)) 277 (54,700)) 257 (48,200), 226 (40,400).

Anal. calcd. for $C_{82}H_{116}O_4N_2Ni$,

C, 78.67 ;    H, 9.27 ;    N, 2.23 %

Found:  C, 78.49 ;    H, 8.94 ;    N, 2.34 % .

IR spectrum for compound 6.h.8.

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-undecyloxysalicylaldiminato]nickel(II):**

Yield, 34%, m.p. 140.0°C; IR $\nu_{max}$: 2920, 2860, 1610, 1595, 1525, 1465, 1425, 1310, 1200 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ (c): 353 (34,700), 280 (51,700)) 257 (47,100), 226 (42,600).

Anal. calcd. for $C_{84}H_{120}O_4N_2Ni$,

$\quad\quad\quad\quad\quad$ C, 78.83 ;    H, 9.38 ;    N, 2.18 %

$\quad\quad\quad$ Found:  C, 78.45 ;    H, 9.59 ;    N, 2.08 % .

**Bis[N-(4″-n-dodecylbiphenyl)-4-n-dodecyloxysalicylaldiminato]nickel(II):**

Yield, 38%; m.p. 141.0°C; IR $\nu_{max}$: 2920, 2860, 1615, 1595, 1525, 1465, 1430, 1310, 1200 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (43,700)) 286 (39,400), 254 (39,400).

Anal. calcd. for $C_{86}H_{124}O_4N_2Ni$,

$\quad\quad\quad\quad\quad$ C, 78.97 ;    H, 9.48 ;    N, 2.10 %

$\quad\quad\quad$ Found:  C, 79.12 ;    H, 9.80 ;    N, 1.79 % .

**Bis[N -(4″-n -dodecylbiphenyl) -4- n-octadecyloxysalicylaldiminato]nickel(II):**

Yield, 49%; m.p. 122.5°C; IR $\nu_{max}$: 2920, 2860, 1610, 1595, 1465, 1420, 1380, 1125 and 810 cm$^{-1}$; UV-Vis: $\lambda_{max}^{CHCl_3}$ ($\epsilon$): 351 (51,300), 287 (36,400), 287 (39,000).

Anal. calcd. for $C_{98}H_{148}O_4N_2Ni$,

$\quad\quad\quad\quad\quad$ C, 79.74 ;    H, 10.03 ;    H, 1.89 %

$\quad\quad\quad$ Found:  C, 79.51 ;    H, 10.40 ;    H, 1.76 % .

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