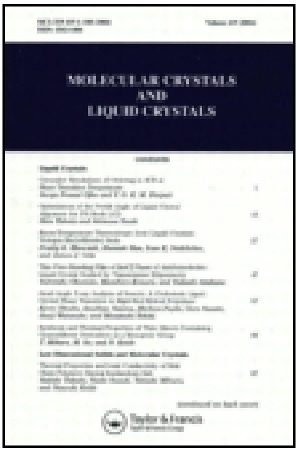

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# Liquid Crystalline Properties of o-Hydroxy Substituted Schiff's Bases and their Copper(II) and Palladium(II) Complexes

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# Liquid Crystalline Properties of *o*-Hydroxy Substituted Schiff's Bases and their Copper(II) and Palladium(II) Complexes

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The synthesis and liquid crystalline properties of thirty nine compounds are reported. These include a homologous series of N-(2-hydroxy-4-*n*-alkoxybenzylidene)-4″-*n*-dodecylphenylanilines and their corresponding copper(II) and palladium(II) complexes. Differential scanning calorimetry and optical microscopy were used to characterise the mesophases. The Schiff's bases exhibit polymesomorphism while their metal chelates basically show smectic A ($S_A$) and smectic C ($S_C$) phases except for a few derivatives. The transition temperatures of the metal chelates are considerably higher than the ligands from which they are derived. A comparison of the mesomorphic properties of the copper chelates with those of bis[4-(4-alkoxybenzoyloxy)-N-(4-ethoxyphenyl)salicylaldiminato]copper(II) complexes have also been made. Though the melting points of copper(II) and their corresponding palladium(II) chelates of many homologues are comparable, the clearing points of the latter are consistently higher.

*Keywords: Schiff's bases, chelates, smectic A, smectic C*

## INTRODUCTION

It is only in the last decade or so that metal containing liquid crystalline substances (metallomesogens) are being investigated in greater detail. This is in view of the fact that metallomesogens may offer useful magnetic, electrical and optical properties. Also, structure property relationships are not clearly understood and efforts are under way to investigate the same. Of the several different ligands that may be utilised to obtain metal complexes, the β-diketones and *ortho*-hydroxy substituted Schiff's bases (N-salicylideneaniline derivatives) have been employed widely.[1] The first mesogenic salicylaldimine copper(II) complexes were reported by Ovchinnikov et al.[2] These exhibited enantiotropic smectic mesophases. Since then a number of different series of N-salicylideneaniline derivatives have been reported.[3–9]

In this paper, we report the liquid crystalline properties of a homologous series of N-(2-hydroxy-4-*n*-alkoxybenzylidene)-4″-*n*-dodecylphenylanilines (ligands) and two homologous series of bis[N-(4″-*n*-dodecylbiphenyl)4-*n*-alkoxysalicylaldiminato]copper(II) and bis[N-(4″-*n*-dodecylbiphenyl)4-*n*-alkoxysalicylaldiminato]palladium(II) complexes.

## EXPERIMENTAL

4-*n*-Dodecyl-4′-aminobiphenyl was prepared from 4-*n*-dodecyl-4′-acetylbiphenyl following a procedure similar to that described by Van der Veen et al.[10] The precursor anilide exhibited a smectic phase from 149.5° to 155°C. This showed a natural Schlieren texture and is believed to be a smectic C phase. 2-Hydroxy-4-n-alkoxybenzaldehydes were prepared by mono alkylation of resorcylaldehyde using an appropriate n-alkyl bromide in the presence of sodium ethoxide in ethanol. The Schiff's bases and the corresponding copper(II) and palladium(II) complexes were synthesised according to the general scheme shown in Figure 1. A typical procedure for the preparation of these is given below.

### N-(2-Hydroxy-4-*n*-pentyloxybenzylidene)-4″-*n*-dodecylphenylaniline(I), (*n* = 5)

A mixture of 2-hydroxy-4-*n*-pentyloxybenzaldehyde (0.62 g, 0.003 mole), 4-*n*-dodecyl-4′-aminobiphenyl (1.01 g, 0.003 mole), ethanol (20 ml) and glacial acetic acid

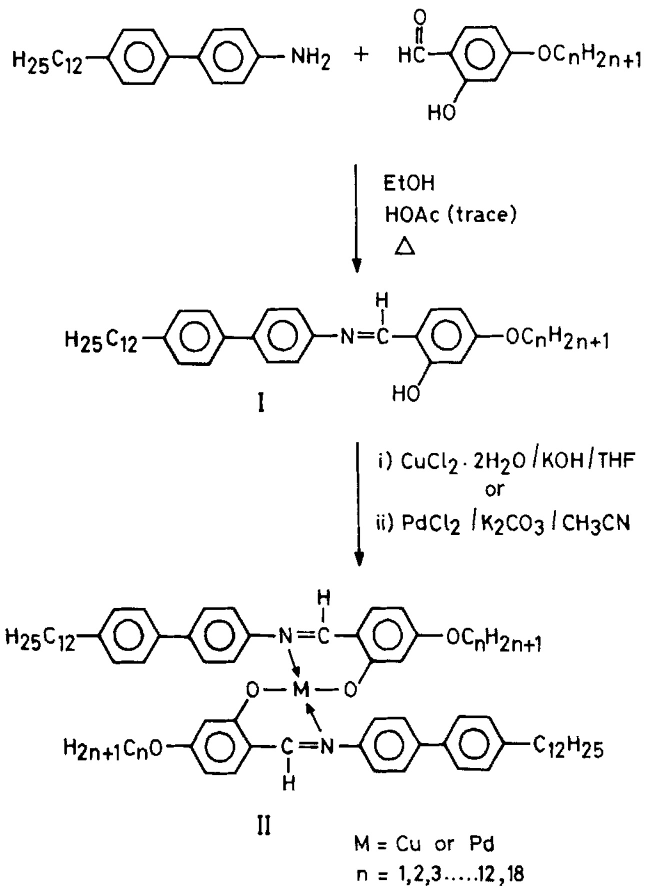

FIGURE 1 Synthetic route for the preparation of Schiff's bases and their copper(II) and palladium(II) chelates.

(a few drops) was refluxed for four hours and cooled. The pale yellow precipitate obtained was filtered off, washed with ethanol and dried. Recrystallisation of the precipitate from butan-2-one gave crystals of the Schiff's base. Yield 1.1 g (70%); m.p. 82.5°C; $\mathrm{IR}_{\max}^{\mathrm{nujol}}$ (cm$^{-1}$): 1592 and 1623; UV-VIS$_{\max}^{\mathrm{CHCl_3}}$ (ε): 352(31,150) 288(15,650) and 250(19,200); PMR($CDCl_3$) δ0.9(t,6H,2x—C$\underline{H}_3$) 1.2–2.0(m,6H,13x—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$\underline{H}$) and 13.75(s,1H,—O$\underline{H}$). 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%.

### Bis[N-(4″-*n*-dodecylbiphenyl)4-*n*-pentyloxysalicylaldiminato]copper(II), II, *M* = Cu, *n* = 5

To a stirred mixture N-(2-hydroxy-4-n-pentyloxybenzylidene)-4″-n-dodecylphenylaniline (0.53 g, 0.001 mole), tetrahydrofuran (5 ml), powdered potassium hydroxide (0.056 g, 0.001 mole) and ethyl alcohol (5 ml) was added a solution of cupric chloride dihydrate (0.085 g, 0.0005 mole) 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 and the solid filtered off. The green precipitate was dissolved in chloroform (75 ml), washed with water (3 × 50 ml) and dried ($Na_2SO_4$). Removal of solvent and crystallisation of the residue from butan-2-one afforded green crystals of the complex. Yield, 0.32 g (59%), m.p. 191.5°C, $\mathrm{IR}_{\max}^{\mathrm{nujol}}$ (cm$^{-1}$): 1588 and 1608; UV-VIS$_{\max}^{\mathrm{CHCl_3}}$ (ε)389(40,400)310(56,800) and 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%.

### Bis[N-(4″-*n*-dodecylbiphenyl)-4-*n*-pentyloxysalicylaldiminato]palladium(II), II, *M* = Pd, *n* = 5

A mixture of N-(2-hydroxy-4-*n*-pentyloxybenzylidene)-4″-*n*-dodecylphenylaniline (0.316 g, 0.0006 mole), palladium chloride (0.054 g, 0.0003 mole) and anhydrous potassium carbonate (0.318 g, 0.001 mole) dry acetonitrile (25 ml) was stirred and refluxed for 18 hours, cooled and filtered. The yellow precipitate was collected, dissolved in chloroform (100 ml), washed with water (3 × 60 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 complex. Yield, 0.18 g (52%); m.p. 209°C; $\mathrm{IR}_{\max}^{\mathrm{nujol}}$ (cm$^{-1}$): 1592 and 1608; UV-VIS$_{\max}^{\mathrm{CHCl_3}}$ (ε) 403(17,200)299(57,450) and 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 purity of the compounds synthesised was checked by spectral and microanalytical data. The infrared spectra in the range 4000 to 400 cm$^{-1}$ were recorded as Nujol mulls on a Shimadzu IR-435 spectrophotometer. The electronic absorption spectra were obtained using chloroform solutions on a Hitachi U-3200 spectrophotometer. The PMR spectra were taken on a Bruker WP80SY FT-NMR spectrometer using deuterochloroform with tetramethylsilane as an internal standard. Satisfactory elemental analyses were obtained for all the compounds on a Carlo-Erba 1106 elemental analyser. Textures of the mesophases and the transition tem-

TABLE I

Transition temperatures (°C) and enthalpies (kcals/mole) of Schiff's base I†

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

†See Table III for abbreviations.
*Compounds 2, 6 and 8 have crystal-crystal transitions at 74.5°, 74.5° and 71.5° respectively.
**Enthalpies of transitions could not be measured.

peratures were determined under a Leitz Laborlux 12 POL polarising microscope equipped with a Mettler FP52 heating stage and FP5 controller. The enthalpies of transitions were determined from thermograms obtained on a Perkin-Elmer, Model DSC-2 differential scanning calorimeter. The calorimeter was calibrated using pure indium as a standard. The heating and cooling rates were 5°C/min.

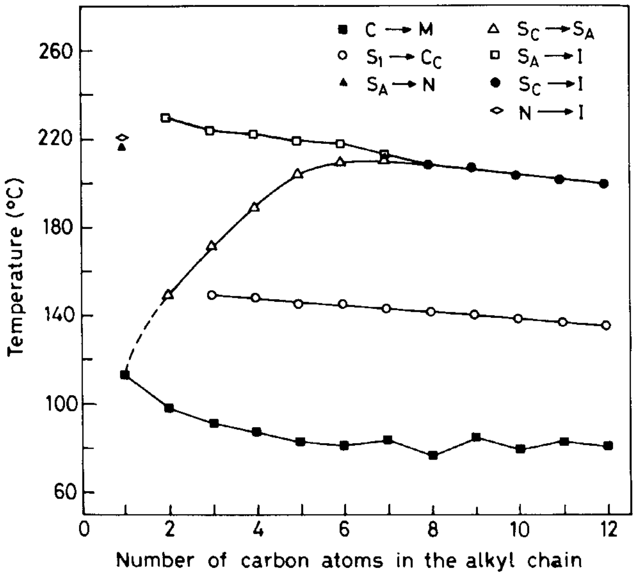

FIGURE 2 Plot of transition temperatures versus the number of carbon atoms in the alkyl chain for Schiff's bases, I.

## RESULTS AND DISCUSSION

The transition temperatures and the thermodynamic data for the Schiff's base ligands, N-(2-hydroxy-4-*n*-alkyloxybenzylidene)-4″-*n*-dodecylphenylanilines,I are given in Table I. All the compounds of this series are enantiotropic and have fairly wide mesophase ranges. Except for the first homologue which melts above 100°C and exhibits a nematic phase over a 4° range, the rest are all smectogenic and have melting points below 100°C. The higher temperature phases of the compounds up to $n = 7$ show a focal-conic texture and are characterised as smectic A. It is also observed from this table that the range of this mesophase decreases as the chain is lengthened. For $n = 2$ to $n = 7$, a broken focal-conic texture is observed below the smectic A phase. The enthalpy of this transition is quite low and could not be measured for two homologues. This has been characterised as smectic C. However, for $n = 8$ to $n = 18$, the enthalpy could be measured as this phase goes over directly to the isotropic liquid. It is seen that the $S_C$ mesophase range initially increases up to $n = 11$ and then tend to decrease. Most of the compounds have a fairly wide $S_C$ mesophase range. For compounds from $n \geq 3$ a higher order smectic phase is obtained directly on melting. This mesophase range is between 50° and 65° for most homologues. The texture of this phase obtained on cooling the smectic C phase shows a paramorphotic broken focal-conic fan texture. 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.

A comparison of the mesomorphic properties of the above ligands with those of a similar series of 3-hydroxy-4(((4-ethoxhyphenyl)imino)methyl)-phenyl 4-alkoxybenzoates[11] indicate that the latter ester Schiff's bases which have more

TABLE II

Transition temperatures (°C) and enthalpies (kcals/mole) of chelates, II, M = Cu

| Compound number | n | $C_1$ | | C | | $S_C$ | | $S_A$ | | I |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | - | | . | 182.0<br>13.86 | - | | . | 282.0$^{@}$ | . |
| 2 | 2* | . | 146.5<br>6.08 | . | 174.0<br>12.28 | - | | . | 290.0$^{@}$ | . |
| 3 | 3 | - | | . | 177.0<br>13.56 | - | | . | 295.0$^{@}$ | . |
| 4 | 4 | . | 88.5<br>0.78 | . | 168.0<br>12.35 | - | | . | 288.0$^{@}$ | . |
| 5 | 5* | . | 164.5<br>4.07 | . | 191.5<br>6.51 | - | | . | 278.0 | . |
| 6 | 6 | . | 147.5<br>1.25 | . | 200.5<br>9.53 | - | | . | 268.0<br>2.88 | . |
| 7 | 7 | . | 138.5<br>1.77 | . | 207.0<br>11.54 | . | 212.0** | . | 263.0<br>3.11 | . |
| 8 | 8 | - | | . | 206.0<br>11.44 | . | 224.0** | . | 255.5<br>2.68 | . |
| 9 | 9 | - | | . | 202.0<br>11.83 | . | 228.5<br>0.04 | . | 248.0<br>2.45 | . |
| 10 | 10 | - | | . | 201.0<br>13.39 | . | 229.0<br>0.21 | . | 243.5<br>2.33 | . |
| 11 | 11 | - | | . | 194.0<br>13.71 | . | 230.0<br>0.40 | . | 242.0<br>3.96 | . |
| 12 | 12 | - | | . | 191.5<br>13.26 | . | 223.0<br>0.55 | . | 232.0<br>2.13 | . |
| 13 | 18 | . | 69.0<br>2.53 | . | 181.5<br>16.92 | . | 207.5<br>0.38 | . | 212.5<br>1.80 | . |

*Compound 2 has C—C transitions at 36.0° and 87.0° while compound 5 has a C—C transition at 84.5°.

@These compounds decompose before going to isotropic phase.

**Enthalpies of transitions could not be measured.

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.

Figure 2 shows the plot of transition temperatures versus the number of carbon atoms in the alkyl chain for the Schiff's bases, I. The curves for the like mesophase transitions seem to follow the normal behaviour observed in a large number of 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 the bis[N-(4″-*n*-dodecyl biphenyl)4-*n*-alkyloxysalicylaldiminato]copper(II) chelates are summarised in Table II. These green complexes are obtained in crystalline form. It is seen from this table that on introduction of a metal atom into the Schiff's base, the transition temperatures are elevated. However, the higher order smectic phase $S_1$ is 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 complexes ($n$ = 1, 2, 3 and 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) complexes, $(CuL_2)^{11}$ 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 phase $S_1$ observed in the ligands is not seen in the chelates. While the smectic phase has been suppressed upon complexation in the present series of compounds, an opposite effect is observed in $CuL_2$ series.

Figure 3 shows a plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for the copper chelates. 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.

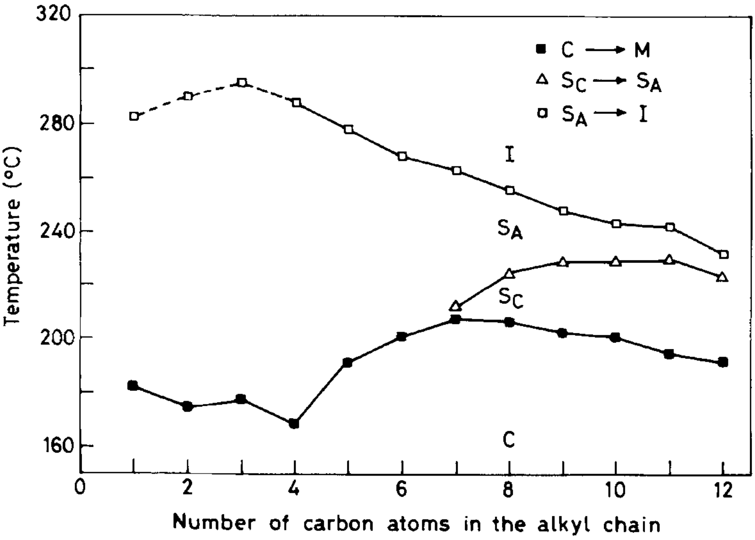

FIGURE 3 Plot of transition temperatures versus the number of carbon atoms in the alkyl chain for copper(II) chelates, II, M = Cu.

TABLE III

Transition temperatures (°C) and enthalpies (kcals/mole) of chelates II, M = Pd

| Compound number | n | $C_1$ | | C | | $S_C$ | | $S_A$ | | I |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | . | 132.0<br>4.70 | . | 185.0<br>13.0 | – | | . | 290.0$^{@}$ | . |
| 2 | 2 | . | 160.0<br>4.91 | . | 197.5<br>3.78 | – | | . | 290.0$^{@}$ | . |
| 3 | 3* | . | 158.5<br>2.51 | . | 203.5<br>3.90 | – | | . | 290.0$^{@}$ | . |
| 4 | 4* | . | 173.0<br>1.95 | . | 207.5<br>4.31 | – | | . | 290.0$^{@}$ | . |
| 5 | 5 | . | 115.0<br>8.78 | . | 209.0<br>8.74 | – | | .. | 290.0$^{@}$ | . |
| 6 | 6 | . | 106.5<br>6.77 | . | 207.5<br>8.60 | . | 228.5** | . | 290.0$^{@}$ | . |
| 7 | 7 | . | 96.5<br>3.82 | . | 207.0<br>8.70 | . | 250.0** | . | 290.0$^{@}$ | . |
| 8 | 8 | . | 94.0<br>3.90 | . | 206.5<br>9.59 | . | 259.0** | . | 282.0<br>2.06 | . |
| 9 | 9 | . | 80.5<br>2.17 | . | 201.0<br>10.33 | . | 260.0** | . | 278.0<br>1.76 | . |
| 10 | 10 | . | 65.0<br>0.93 | . | 197.0<br>10.57 | . | 257.0<br>0.30 | . | 268.0<br>1.63 | . |
| 11 | 11 | . | 164.0<br>0.47 | . | 194.0<br>10.66 | . | 254.5<br>0.33 | . | 262.0<br>1.47 | . |
| 12 | 12* | . | 165.0<br>1.58 | . | 193.0<br>12.96 | . | 253.0<br>0.40 | . | 262.5<br>1.65 | . |
| 13 | 18 | . | 150.5<br>2.72 | . | 172.5<br>12.05 | . | 223.0** | . | 226.5<br>2.17 | . |

*Compound 3 has C—C transitions at 94.0° and 112.0°, compound 4 has 78.0°, 103.7° and 143.0° and compound 12 at 54.5°.

**Enthalpies of transitions could not be measured.

@These compounds decompose before going to isotropic phase.

Key: $C_1$, C: crystalline phase; $S_1$: unidentified smectic phase; $S_C$: smectic C phase; $S_A$: smectic A phase; N: nematic phase; I: isotropic phase.

· The phase exists; - The phase does not exist. The enthalpies of transitions are recorded immediately below the transition temperatures.

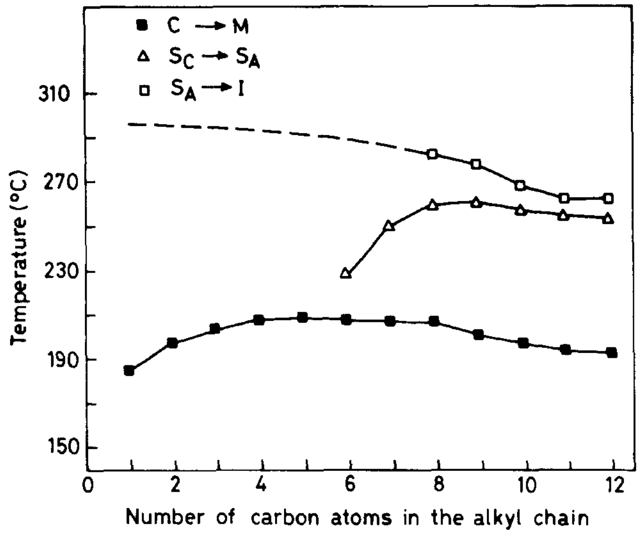

FIGURE 4 Plot of transition temperatures versus the number of carbon atoms in the alkyl chain for palladium(II) chelates, II, M = Pd. The dotted line indicates the temperature beyond which observations were not made as the complexes decompose.

The transition temperatures and enthalpies of bis[N-(4″-*n*-dodecyl biphenyl)4-*n*-alkyloxysalicylaldiminato]palladium(II) chelates are given in Table III. These orange-yellow complexes are obtained as fine microcrystals in fairly good yield. For complexes $n = 1$ to $n = 7$, the clearing temperatures are >290° and these start decomposing at this high temperature. All the homologues exhibit a focal-conic texture like their copper(II) congeners and the phase is believed to be smectic A. Similarly, for complexes $n \geqslant 6$ a broken focal-conic texture is observed and the phase is characterized as smectic C. All the complexes also show crystal-crystal transitions. All the transition temperatures have been raised as a result of replacing copper with palladium as has been observed in other series of compounds.[4] Also these two metal atoms do not seem to affect the nature of the mesophases for the ligands. The enthalpies for $S_C$—$S_A$ and $S_A$—I transitions of the palladium complexes are comparable to those of the corresponding copper chelates.

Figure 4 shows a graphic representation of the transition temperatures as a function of alkyl chain length for the palladium chelates. As observed for the copper chelates, the lower homologues of this series also thermally decompose and hence have not been plotted. The $S_C$—$S_A$ and $S_A$—I transition points follow a general trend that is seen for such transitions in many homologous series.

Further work is in progress to introduce other metal atoms to study the influence of these on the mesophases formed.

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## References

1. A. M. Giroud-Godquin and P. M. Maitlis, *Angew. Chem. Int. Ed. Engl.*, **30**, 375 (1991).
2. I. V. Ovchinnikov, Yu. G. Galyametdinov, G. I. Ivanova and L. M. Yagfarova, *Dokl. Akad. Nauk SSR*, **276**, 126 (1984); I. V. Ovchinnikov, Yu. G. Galyametdinov and I. G. Bikchantaev, *Izv. Akad. Nauk SSSR Ser. Fiz.*, **53**, 1870 (1989).
3. U. Caruso, A. Roviello, A. Sirigu and P. Iannelli, *Liq. Cryst.*, **3**, 1515 (1988); *ibid.*, **7**, 421 (1990); *ibid.*, **7**, 431 (1990).
4. A. Roviello, A. Sirigu, P. Iannelli and A. Immirzi, *Liq. Cryst.*, **3**, 115 (1988).
5. M. Marcos, P. Romero, J. L. Serrano, C. Bueno, J. A. Cabeza and L. A. Oro, *Mol. Cryst. Liq. Cryst.*, **167**, 123 (1989).
6. M. Ghedini, S. Armentano, R. Bartolino, G. Torquati and F. Rustichelli, *Solid State Commun.*, **64**, 1191 (1987); M. Ghedini, S. Armentano, R. Bartolino, N. Kirov, M. Petrov and S. Nenova, *J. Mol. Liq.*, **38**, 207 (1988).
7. M. Marcos, P. Romero and J. L. Serrano, *J. Chem. Soc. Chem. Commun.*, 1641 (1989).
8. N. Hoshino, H. Murakami, Y. Matsunaga, T. Inabe and Y. Maruyama, *Inorg. Chem.*, **29**, 1177 (1990).
9. R. Paschke, H. Zaschke, A. Madicke, J. R. Chipperfield, A. B. Blake, P. G. Nelson and G. W. Gray, *Mol. Cryst. Liq. Cryst. Lett.*, **6**, 81 (1988).
10. J. Van der Veen, W. H. de Jeu, A. H. Grobben and J. Boven, *Mol. Cryst. Liquid Cryst.*, **17**, 291 (1972).
11. N. Hoshino, H. Murakami, Y. Matsunaga, T. Inabe and Y. Maruyama, *Inorg. Chem.*, **29**, 1177 (1990).