CHAPTER VI

Synthesis and mesogenic properties of

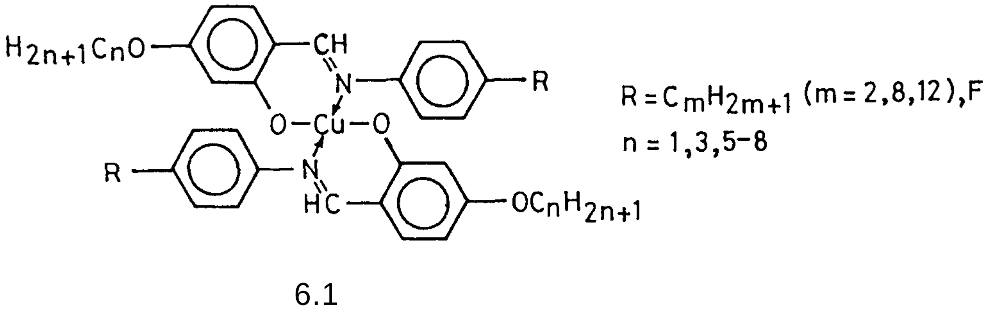
i) a homologous series of N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-decylphenylanilines, their platinum(II) and oxovanadium(IV) complexes, and

ii) a series of N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-alkylphenylanilines, their platinum(II) and oxovanadium(IV) complexes

6.1 A brief survey of the mesogenic properties of N-salicylaldiminato metal complexes

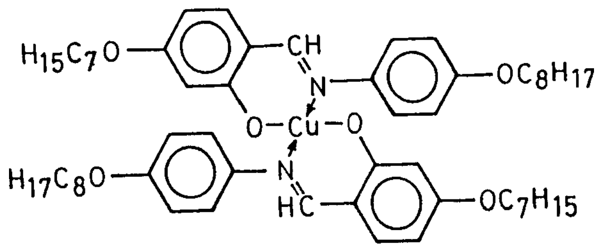
As mentioned in Chapter I, β-diketones and N-salicylideneamine derivatives are widely used as ligands for preparing the metal chelates. The N-salicylideneaniline derivatives are versatile ligands which form N-O chelates with many metals. There are several series of copper(II),[1] palladium(II)[2] and nickel(II)[3] complexes of N-salicylideneaniline derivatives known to show mesomorphism and a few series of mesogenic oxovanadium(IV)[4] and iron(III)[5] containing complexes are also known. In the present chapter the synthesis and mesomorphic behaviour of platinum(II) and oxovanadium(IV) complexes of N-salicylideneaniline derivatives have been discussed. The former represent the first examples of mesogenic platinum(II) containing salicyledeneamines reported to date.

The first report on mesogenic salicylaldiminato metal complexes was by Ovchinnikov et *al.*[1] They reported that complexes (6.1) exhibited enantiotropic smectic phases. Later on nematic phase was observed by Galyametdinov et *al.*[7] in some homologues of another series (n=7, R = $OOCPhOC_{12}H_{25}$) of complexes.



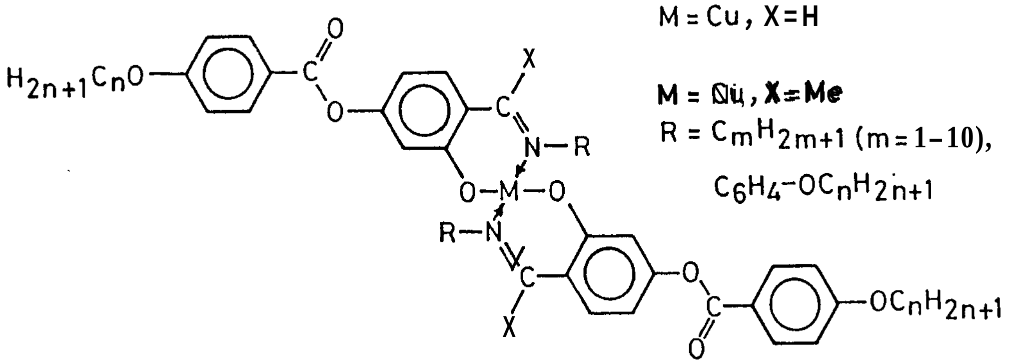
6.1

Bikchantaev et *al.*[8] obtained a smectic C and a smectic A phases in a copper complex of N-(2-hydroxy-4-n-heptyloxybenzylidene)-4''-octyloxyphenylaniline (6.2). They observed the coexistence of smectic A and isotropic liquid in the smectic A phase. The presence of this heterogeneous mesophase was explained on the basis that some of the planar molecules had undergone a tetrahedral distortion in the mesophase; thus, planar molecules formed the smectic phase while the tetrahedral ones formed isotropic droplets.



6.2

Marcos *et al.*[3,9,10] and Caruso *et al.*[11] synthesised several bis[N-[4-[4-(alkoxy)benzoyloxy]-2-hydroxyphenyl]methylene]-methanamino] copper(II) complexes and their corresponding nickel complexes, **(6.3)**. All these copper and nickel complexes derived from alkyl amines exhibited nematic or smectic C phase and when these complexes were derived from aryl amines exhibited mainly smectic phases. X-ray studies on a single crystal of the complex **6.3** (n=4, $R=C_6H_4$-C_6H_{13}) showed lath-like structure of the complex. This is due to a twist of N-phenyl and the benzoyl moieties relative to each other.

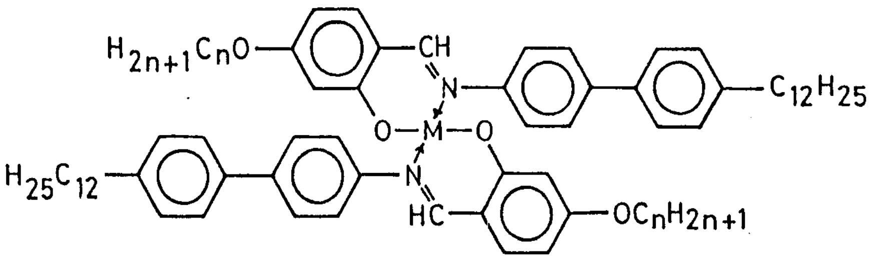


M = Cu, X = H

M = Ni, X = Me
R = C_mH_{2m+1} (m = 1–10),
C_6H_4-OC_nH_{2n+1}

6.3

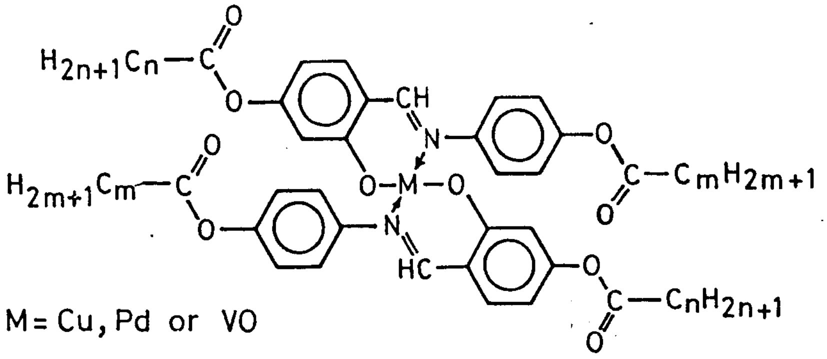
Ghedini *et al.*[12] have also synthesised a number of N-salicylaldiminato copper(II) complexes and examined the x-ray diffraction pattern of monodomain samples. The copper(II), palladium(II) and nickel(II) complexes of N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-n-dodecylphenylanilines, (6.4) have recently been reported by Veena Prasad and Sadashiva.[13,14] These complexes exhibited predominantly smectic A and smectic C phases. A comparison of the mesomorphic properties of these three metal complexes reveal that nickel complexes have lower melting as well as clearing points.



M = Cu, Pd or Ni
n = 1-12, 18

6.4

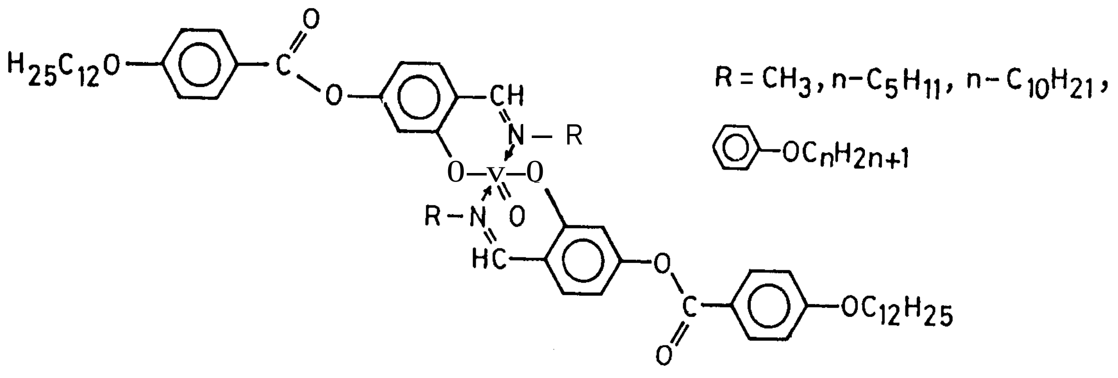
The copper(II) and palladium(II) complexes, (6.5) reported by Caruso et *al.*[2] exhibited smectic mesomorphism. The oxovanadium(IV) congener[1]=(m=8, n=7) showed smectic C and smectic **A** phases.



M = Cu, Pd or VO

6.5

Very few series of mesogenic salicylaldiminato oxovanadium(IV) complexes are known. The first Schiff's base vanadyl complex was reported in 1984 by Galyametdinov *et al.*.[4] Serrano *et al.*[16] synthesised *a* series of compounds (6.6) and found nematic as



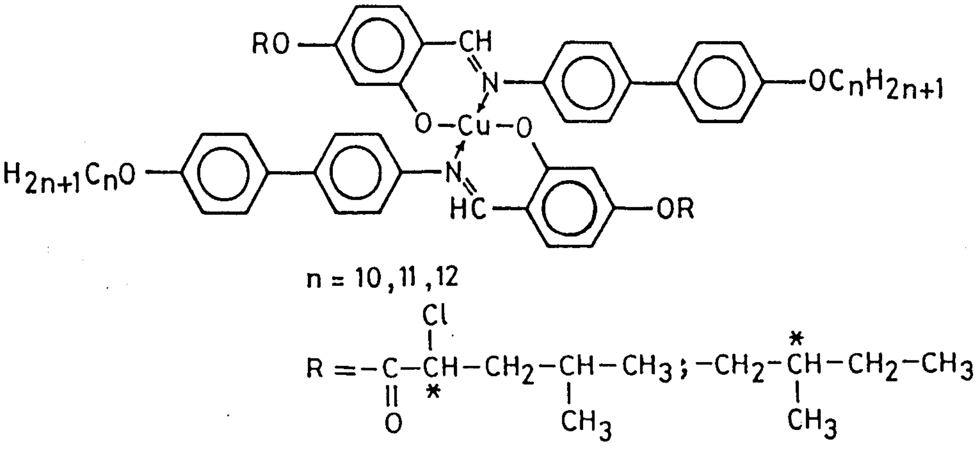
R = CH_3, n-C_5H_{11}, n-$C_{10}H_{21}$, $-OC_nH_{2n+1}$

6.6

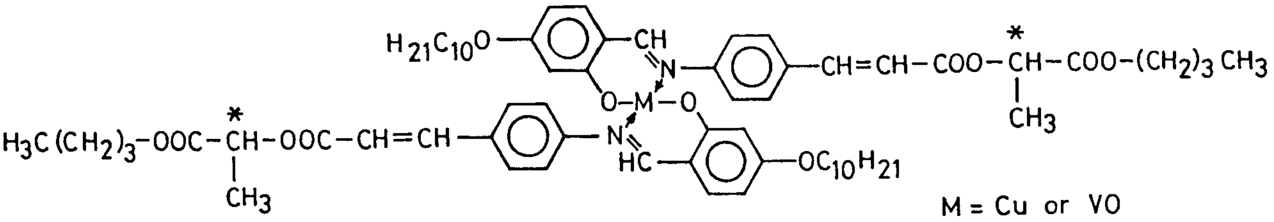
well as smectic phases in them. They observed low viscosity of the mesophases which resulted in the easy alignment of the molecules in a magnetic field. Hoshino *et al.*[17] synthesised bis[4-((4-alkoxybenzoyl)oxy)-N-n-propylsalicylaldiminato]oxovanadium(IV) and nickel(II) complexes. Both the complexes were nematogenic but the thermal stability of nematic phase in nickel complexes was found to be much higher than the corresponding oxovanadium(IV) complexes.

Barbera et *al.*[18] have carried out a comparative structural study of the mesophases of bis[4-((4-n-alkoxybenzoyl)oxy)-N-substitutedsalicylaldiminato]copper(II) and the corresponding nickel(II) and oxovanadium(IV) complexes using X-ray diffraction methods and found that for a given ligand, linked to different metal atoms, the nature of central metal atom influenced mainly the magnetic susceptibilities of the mesophases.

The first paramagnetic ferroelectric liquid crystal was reported by Sadashiva and Shivkumar[19] on a copper(II) complex, viz., [S]-bis-N-[4′-n-alkoxybiphenyl-4″-(2-chloro-4-methylpentanoyloxy)salicylaldiminato]copper(II) and [S]-bis-N-[4′-n-alkoxybiphenyl-4″-(2-methylbutoxy)salicylaldiminato]copper(II) complexes, (6.7). Some of these complexes exhibit the chiral smectic C phase (C* phase) in addition to other mesophases. All the ligands also show the S_{C^*} phase.



Recently Marcos *et al.*[20] have also reported paramagnetic chiral smectic C phase in complexes of type 6.8. Except for a very few mesogenic systems in which platinum has been incorporated[21–23] there is no report on platinum containing mesogenic salicylaldimines. It is believed that the platinum(II) complexes reported in the present chapter are the first examples of mesogenic platinum(II) containing salicylaldiminato derivatives.

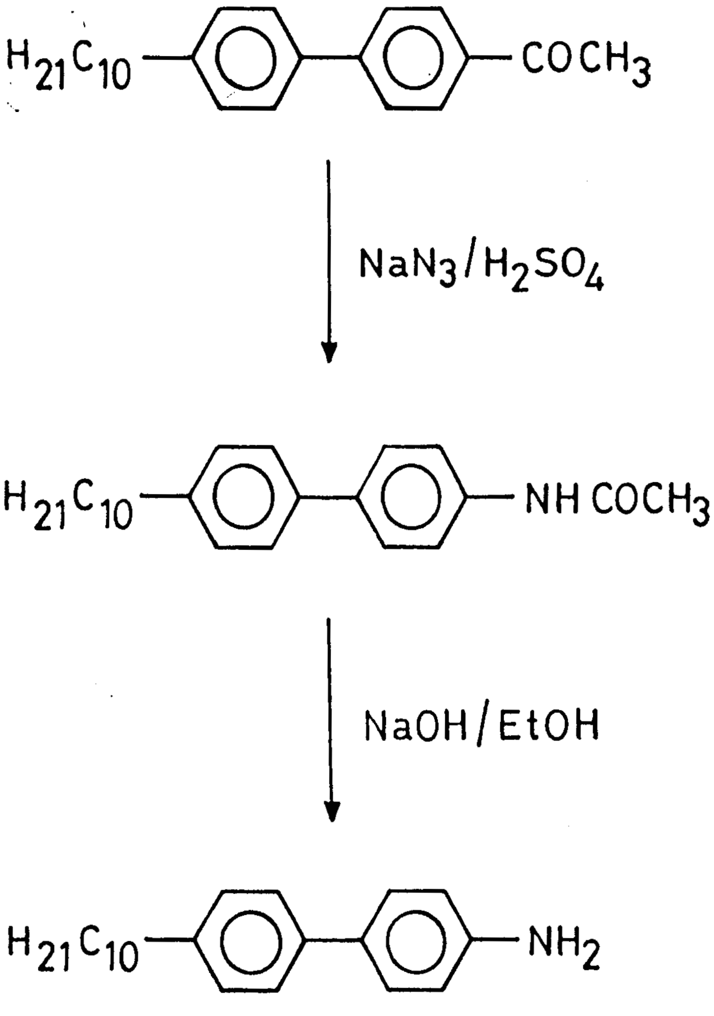

M = Cu or VO

6.8

5.2 Results and Discussion

The influence of metals on the mesophase and the structure property relationships of metallomesogens have not been studied thoroughly. In an effort to understand these aspects, oxovanadium(IV) and platinum(II) complexes of a homologous series of N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-n-decylphenylanilines have been synthesised. In addition to these, a few more similar salicylaldiminato platinum and oxovanadium complexes have also been synthesised to study the influence of the chain length on the mesophases. The synthesis of these compounds was carried out following the scheme outlined in figures 6.1, 6.2 and 6.3 respectively. 4-n-Decyl-4'-aminobiphenyl was synthesised from 4-n-decyl-4'-acetylbiphenyl following a procedure similar to that described by van der Veen et *al.*[24] Thus, sodium azide was added to a vigorously stirred solution of 4-n-decyl-4'-acetylbiphenyl in 80% sulphuric acid which afforded 4(4′-n-decylphenyl)aniline. The precursor anilide also shows a smectic phase from 153° to 163°*C*.

2-Hydroxy-4-n-alkoxybenzaldehydes were prepared by monoalkylation of



$H_{21}C_{10}$
$COCH_3$
NaN_3/H_2SO_4
$H_{21}C_{10}$
$NHCOCH_3$
$NaOH/EtOH$
$H_{21}C_{10}$
NH_2

Figure 6.1

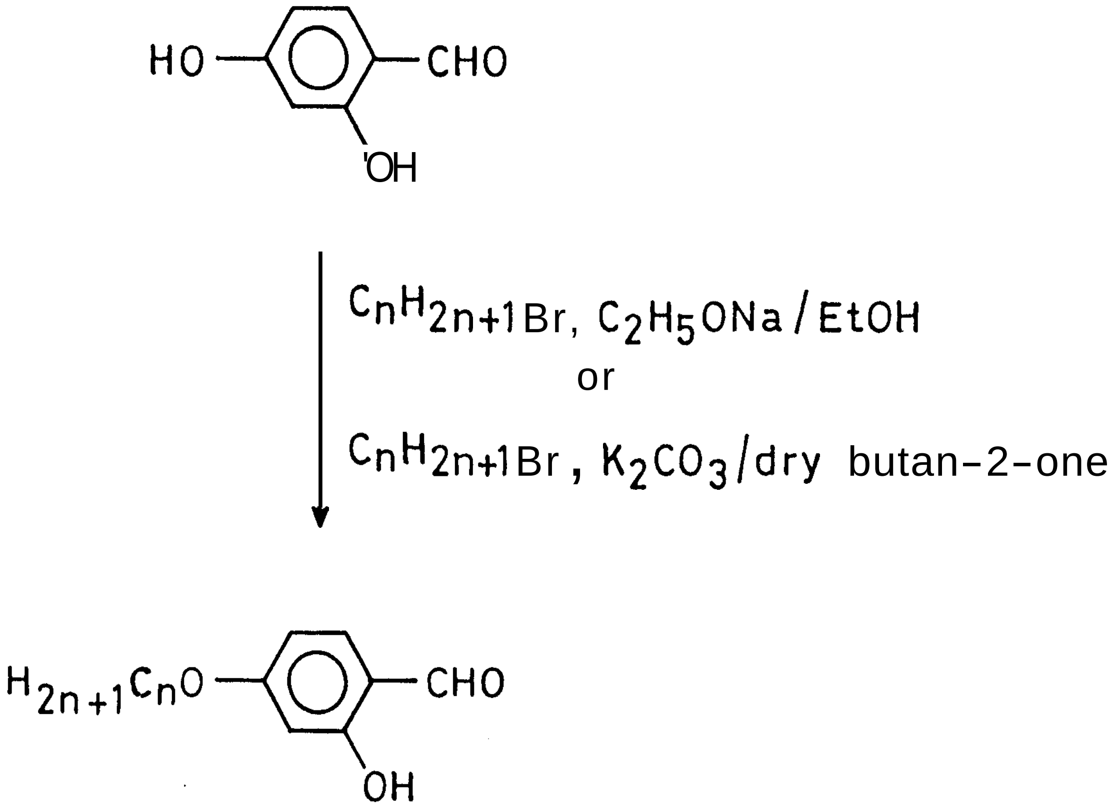
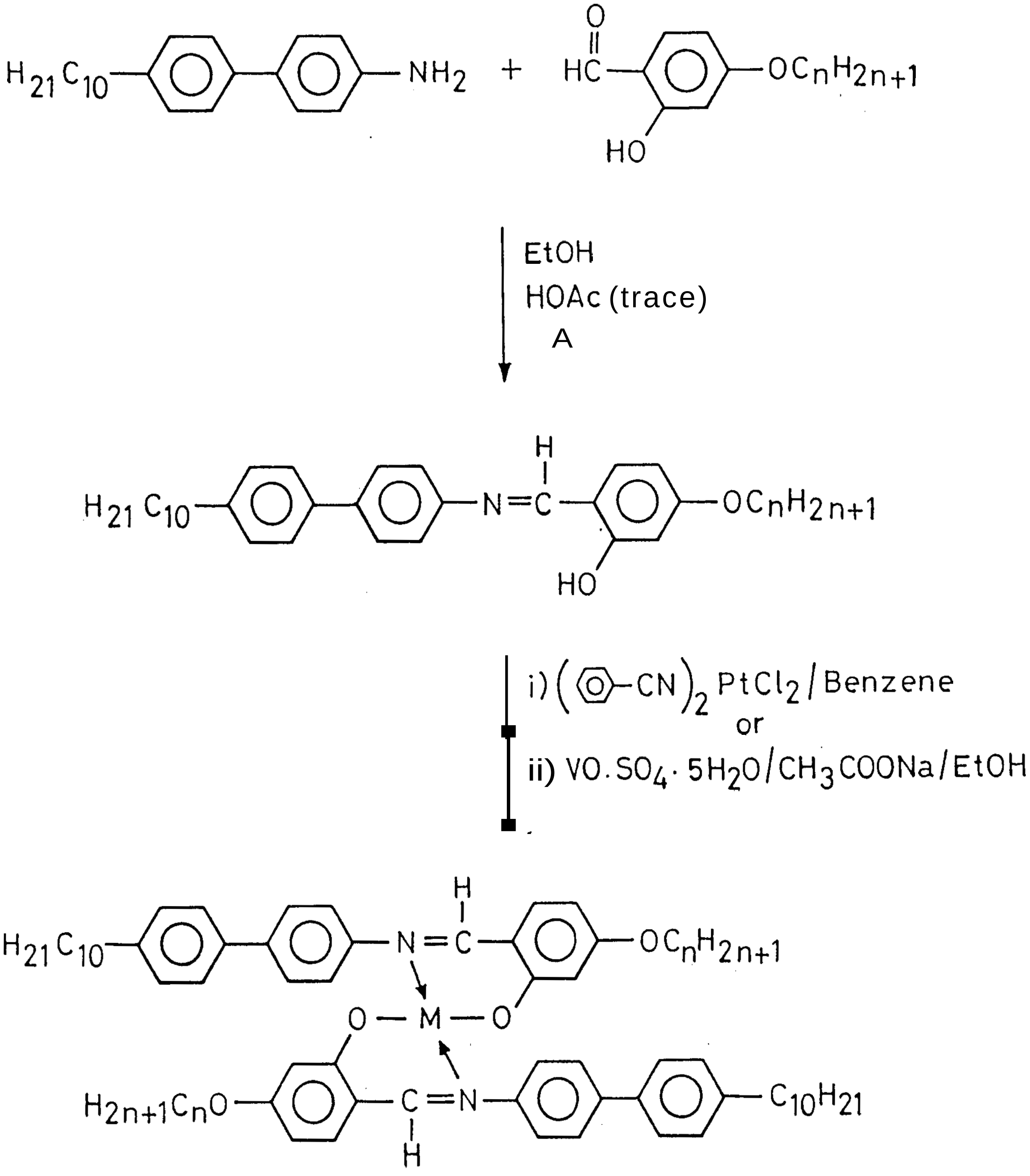

HO
CHO
OH
$C_nH_{2n+1}Br$, C_2H_5ONa/EtOH
or
$C_nH_{2n+1}Br$, K_2CO_3/dry butan-2-one
$H_{2n+1}C_nO$
CHO
OH

Figure 6.2



M = Pt or VO

n = 1,2,3.....12,18

Figure 6.3

2,4-dihydroxybenzaldehyde using an appropriate n-alkylbromide in the presence of sodium ethoxide in ethanol, or with n-alkylbromide and potassium carbonate in acetone. Schiff's bases were synthesised by refluxing 4-(4'-n-decylphenyl)aniline with appropriate aldehydes in the presence of a catalytic amount of acetic acid. *trans*-Bis(benzonitrile)dichloroplatinum(II) was prepared[25] by stirring a suspension of platinum chloride in benzonitrile at room temperature for seven hours. The solution so obtained was filtered and the required compound was precipitated out by the addition of petroleum ether to the filtrate. The precipitate was filtered and dried under vacuum. Platinum complexes were obtained by refluxing the Schiff's base with *trans*-bis(benzonitrile) dichloroplatinum(II) in dry benzene.

Oxovanadium(IV) complexes were obtained by treating a warm solution of a Schiff's base in ethyl alcohol with an aqueous solution of vanadyl sulphate and sodium acetate and refluxing the mixture for twenty minutes.

It is worth mentioning that all these oxovanadium(IV) complexes show a V=O stretching vibration frequency around 990 cm^{-1}. This has been observed in several oxovanadium(IV) complexes.[26] A typical IR spectrum for these complexes is shown in Figure **6.4.**

All the platinum(II) complexes are orange in colour while the oxovanadium(IV) complexes are greenish yellow in colour. The colour of these oxovanadium complexes suggests monomeric structure for the derivatives.[27,28].

The transition temperatures and the enthalpies for the homologous series of N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-n-decylphenylanilines are summarised in table **6.1.** All the homologues of this series are enantiotropic and have fairly wide mesophase ranges. The first two members of the series exhibit an enantiotropic nematic phase while the remaining predominantly show smectic A (S_A) and smectic C (S_C) phases, and have melting points below **100°C.** All the homologues show an enantiotropic smectic phase below the smectic C phase and this has been designated as **S** in table **6.1.** This exhibits a schlieren texture and the phase type has not

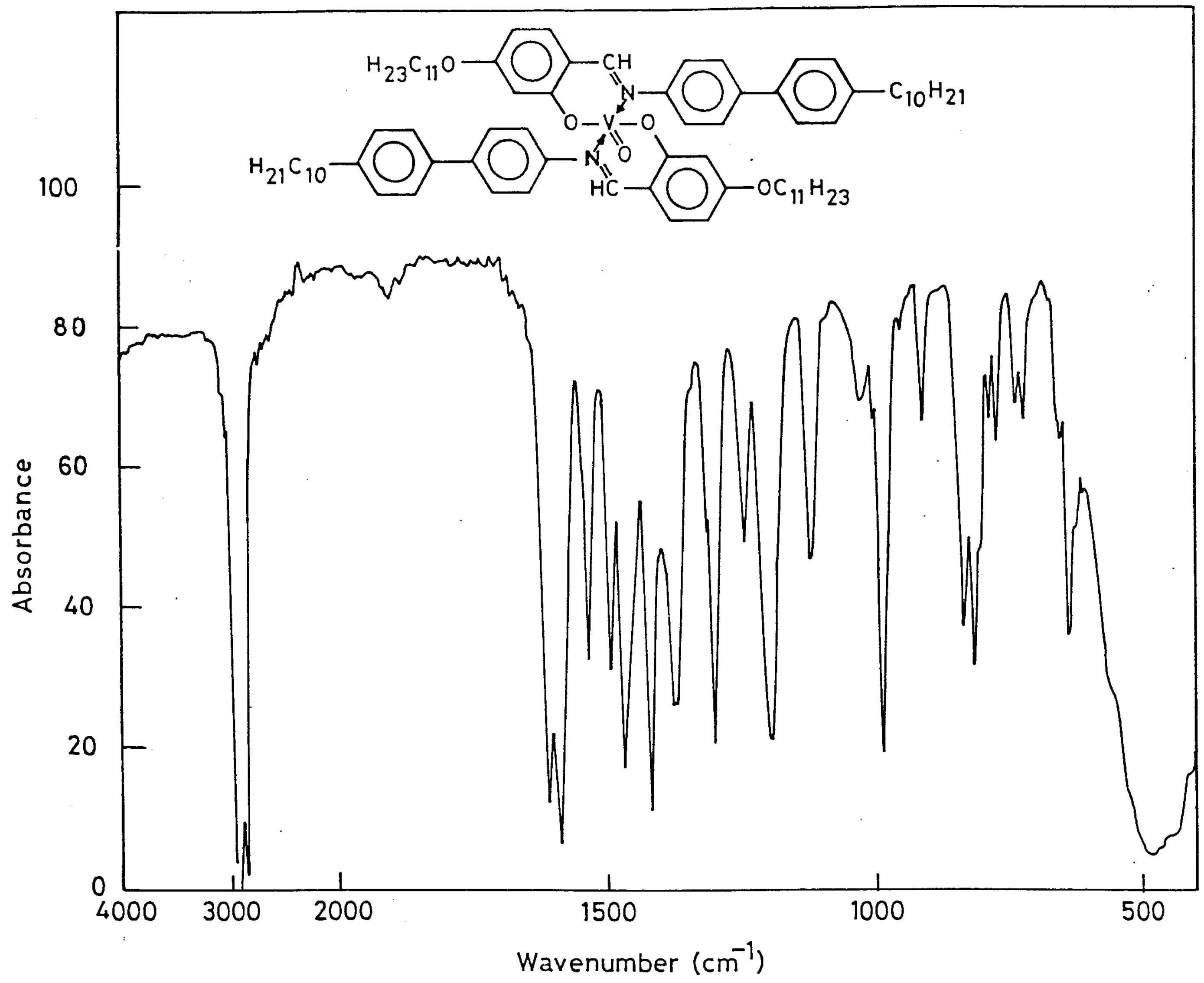
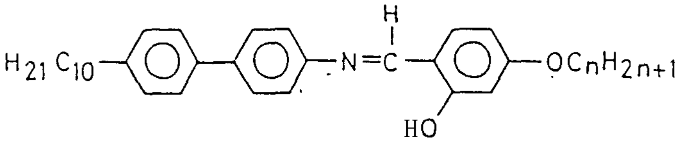


Fig.6.4. IR spectrum of compound 6.c.8.

Table 6.1

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) of



Series VI(1)

Compound number	n	C		S_I		S		S_C		S_A		N		I
6.a.1	1	.	115.0 7.38	.	(103.5) 0.42	.	144.5 0.32	-		.	218.5 0.28	.	231.0 0.21	.
6.a.2	2	.	104.5 4.12	.	(102.0) 0.45	.	150.5 0.40	-			235.5 0.66	.	238.0 0.24	
6.a.3	3	.	94.0 4.2		(91.5) 0.40	.	151.0 0.35	.	172.5*		228.5 1.69	-		
6.a.4	4	.	85.0 4.66	-		.	151.0 0.29	.	193.0*	.	233.0 1.84	-		.
6.a.5	5	.	78.0 6.36	-			147.0 0.20	.	204.5*		226.4 1.86	-		
6.a.6	6	.	83.0 3.87	-		.	146.5 0.24	.	212.0*	.	224.0 2.00	-		.
6.a.7	7	.	80.0 10.74	-		.	145.0 0.20	.	214.5 0.07	.	218.5 2.03	-		
6.a.8	8	.	80.0 8.36	-			144.0 0.21	.	214.5 0.08		216.5 2.03	-		
6.a.9	9	.	84.5 12.41	-			142.0 0.22	.	213.0 2.28	-				
6.a.10	10	.	78.0 7.65	-		.	141.0 0.16	.	210.0 1.74	-				
6.a.11	11	.	85.5 13.12	-		.	138.0 0.21	.	207.0 2.45	-				
6.a.12	12	.	80.0 13.20	-		.	137.0 0.28	.	204.0 2.47	-				
6.a.13	18	.	90.0 16.80	-			132.6 0.35	.	187.9 2.54	-				

*Enthalpies could not be determined.

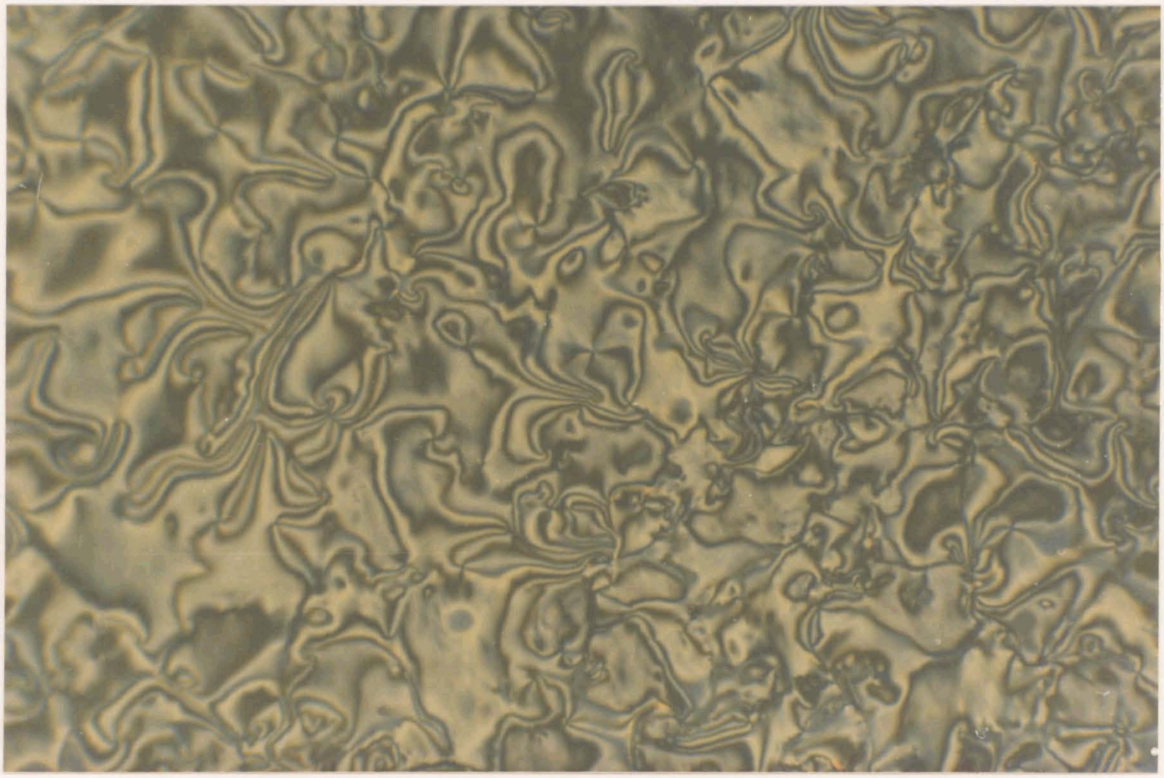


Plate 6.1. Schlieren texture exhibited by unidentified smectic phase (S) at 130°C of compound 6.a.l.

yet been determined. The photomicrograph of the schlieren texture exhibited by the unidentified mesophase is shown in plate 6.1. In addition to this, the first three homologues show a monotropic smectic phase S_1. This phase exhibited a mosaic texture, which has also not been identified. As can be seen in table 6.1 smectic **A** phase disappears for n=9 homologue and the remaining higher homologues show only a smectic C phase. The enthalpy of smectic C to smectic A transition is extremely low and hence could not be determined for four of the homologues.

A plot of the transition temperatures *versus* the number of carbon atoms in the alkoxy chain for this homologous series is given in figure 6.5. As can be seen the trend observed for like transition points is normal, viz., there is an alternation in the beginning followed by a gradual decrease in the S_A-I transition temperatures as the series is ascended. Similarly the curve joining the S_C-S_A transition points rise initially and merge with the falling of S_A-I curve at the octyloxy derivative. There is a gradual decrease in the clearing points and it is clear that there is a tendency to exhibit smectic property as the chain is lengthened.

In table 6.2, the transition temperatures and the associated enthalpeis of N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-alkylphenylanilines are summarised. An examination of this table indicates that with the exception of compounds 6.b.1 and 6.b.7, the other compounds exhibit an enantiotropic nematic phase in addition to S_A and S_C phases. Compounds derived from 4-(4′-ethylphenyl)aniline have a thermal range of nematic phase from 0.5 to $116°C$ and show higher clearing points than the compounds derived from 4-(4'-n-pentylphenyl)aniline. In this case only lower homologues (6.b.5 and 6.b.6) are found to exhibit the nematic phase. The enthalpies of S_C to S_A transitions are negligibly small and hence could not be determined. It is interesting to compare the mesogenic behaviour of N-(2-hydroxy-4-n-dodecyloxybenzylidene)-4″-n-pentylphenylaniline (6.b.7) with N-(2-hydroxy-4-n-heptyloxybenzylidene)-4″-n-decylphenylanilines because they are similar. Both of these compounds exhibit smectic A, smectic C and two higher ordered smectic phases. However, the mesomorphic properties of compounds N-(2-hydroxy-4-n-

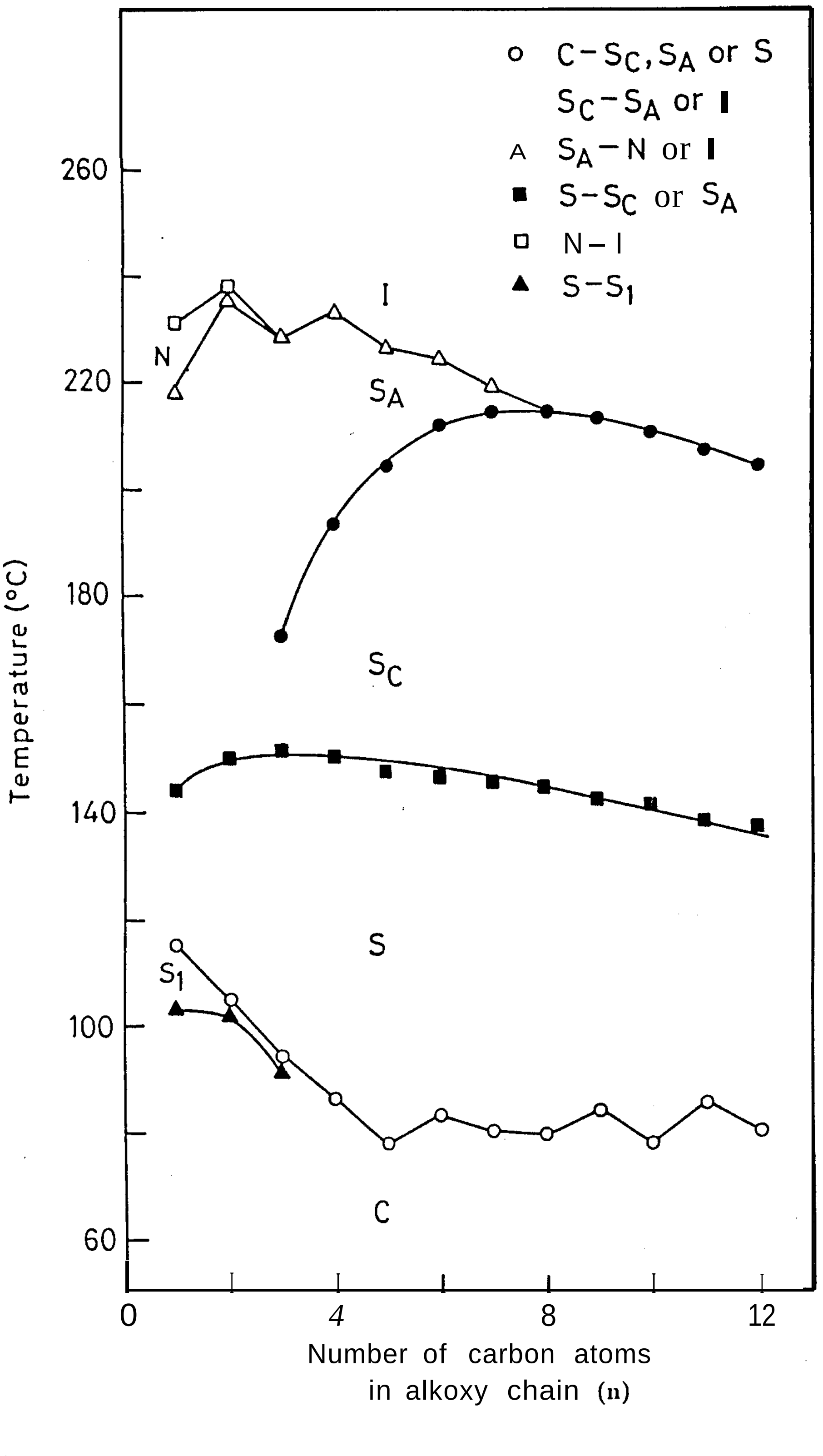
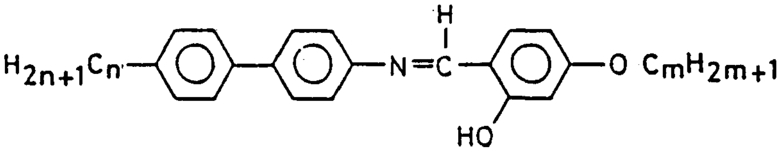


Figure 6.5. A plot of the transition temperatures versus the number of carbon atoms (n) in the alkoxy chain for a series of N-(2-hydroxy-4-n-allioxybenzylidene)-4″-n-decylbiphenylanilines.

Table 6.2

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) of



Series VI(2)

Compound number	m	n	C		S		S_C		S_A		N		I
6.b.1†	**0**	10	.	108.5 7.12	.	128.5 0.13	-		.	174.0 2.03	-		
6.b.2	1	2	.	144.0 5.57	-				.	161.0 0.05	.	277.5 0.15	.
6.b.3	6	2	.	113.5 4.67	-		.	172.0'	.	214.0 0.10	.	242.0 0.16	.
6.b.4	12	2	.	96.5 5.50	-		.	151.5'	.	213.5 0.10	.	214.0 0.16	.
6.b.5	1	5	.	119 2.61	.	139.0 0.23	-		.	204.5 0.18	.	262.5 0.20	.
6.b.6†	6	5	.	109.5 2.06	.	138.0 0.06	.	202.0*	.	238.0 0.53	.	241.5 0.30	.
6.b.7	12	5	.	80.5 10.74	.	131.0 0.06	.	183.0*	.	222.5 2.00	-		

†Compounds 6.b.1 and 6.b.6 have crystal-crystal transitions at 90.5 and 73.2°C respectively.
*Enthalpies could not be determined.

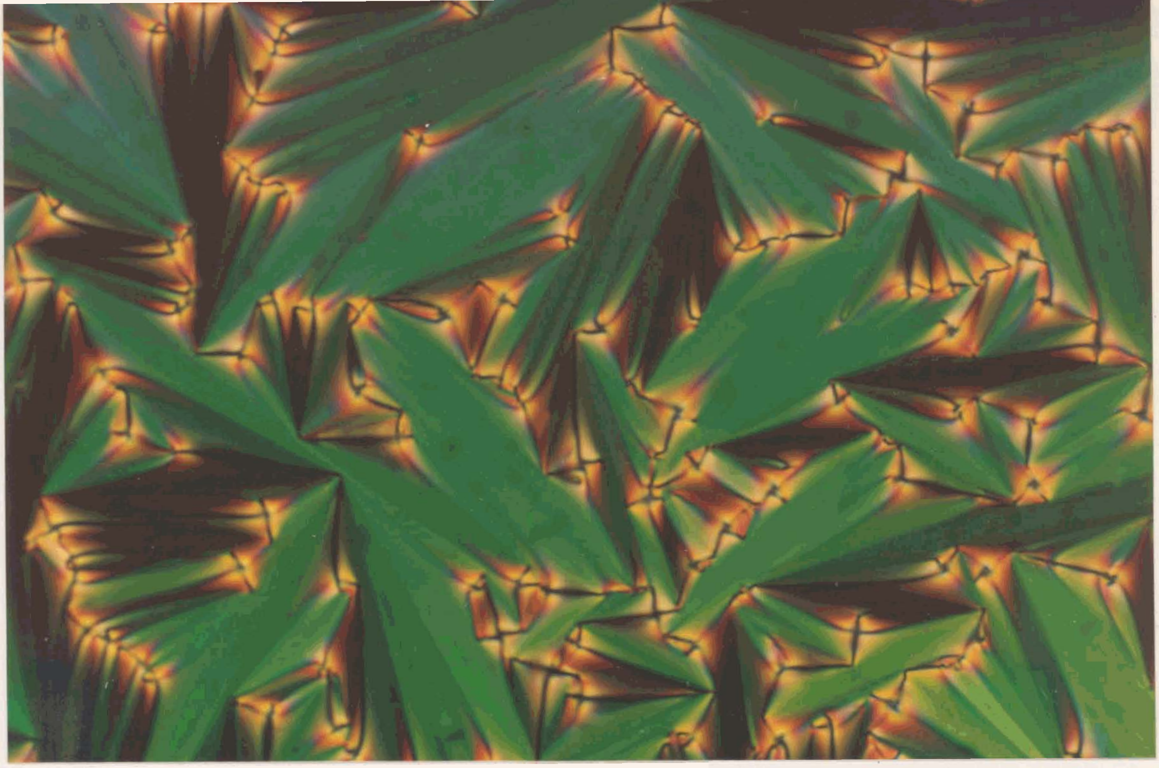


Plate 6.2. Focal-conic texture exhibited by the smectic A phase of compound 6.c.9 at 249.9°C.

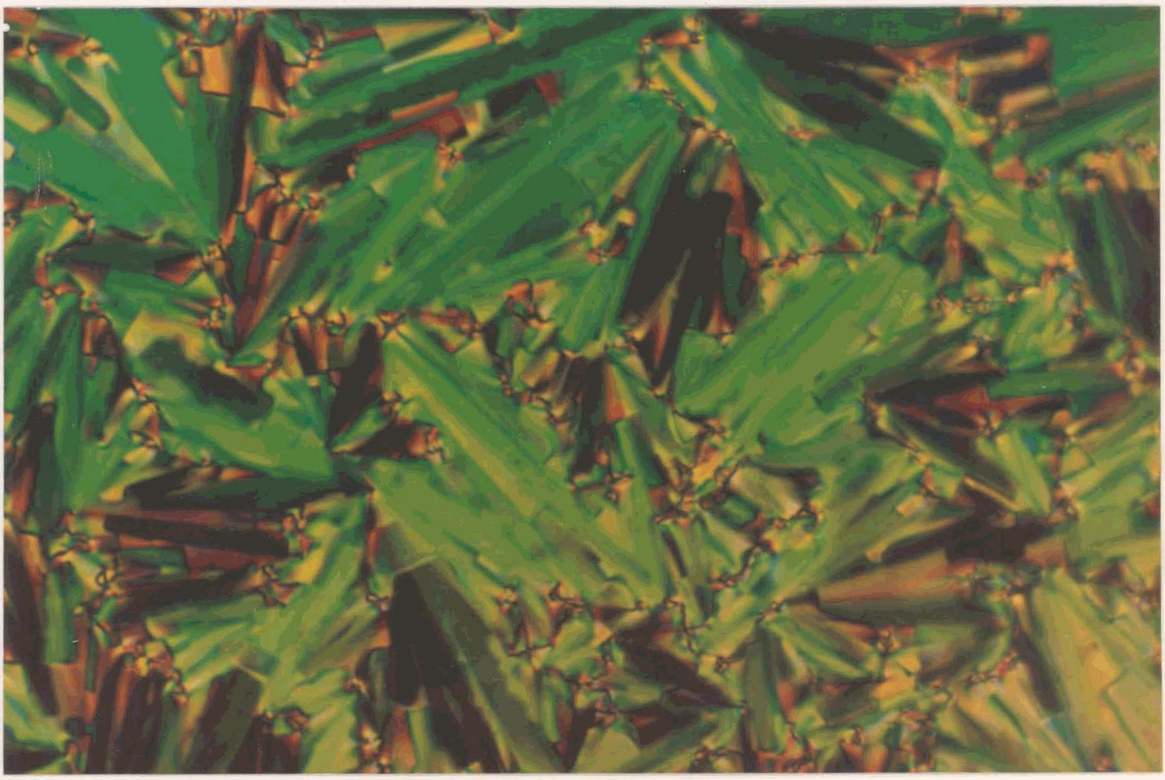
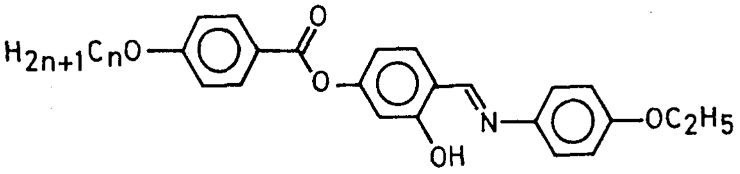


Plate 6.3. Broken focal-conic texture exhibited by the smectic C phase of compound 6.c.9 at 236°C. (same field of view as in plate 6.2).

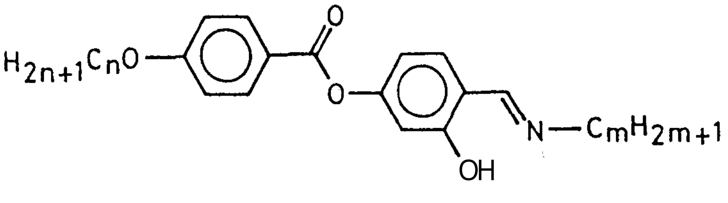
dodecyloxybenzylidene)-4″-ethylphenylaniline (6.b.4) and N-(2-hydroxy-4-n-butyloxy benzylidene)-4″-n-decylphenylaniline, are slightly different. Compound 6.b.4 exhibits a very small temperature range of nematic phase in addition to smectic A and smectic C phases while the latter compound exhibits only smectic phases, viz., smectic A, smectic C and the higher ordered smectic phases. Thus a small chain such as butoxy in the 4-position of the salicylaldehyde group destroys this nematic phase present in the ethyl susbstituted analogue.

A comparison of the mesomorphic behaviour of the above discussed ligands [series VI(1) and VI(2)] with those of a series of 2-hydroxy-4-(((4-ethoxyphenyl)imino) methyl)phenyl-4-alkoxybenzoates[29] (6.9) shows that the latter ester schiff's bases



6.9

which is a more flexible molecule, exhibits a nematic phase over a wide range of temperature. On replacing the N-phenyl moieties by N-propyl or N-hexyl groups, the resulting compound 2-hydroxy-4-((alkylimino)methyl)phenyl-4-alkoxybenzoates,[30] (6.10) also exhibits a nematic phase over a wide range of temperature.



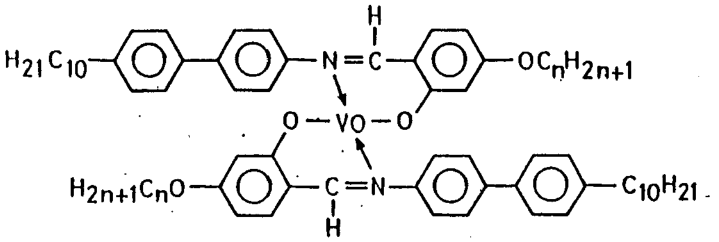
6.10

This indicates that probably the biphenyl moiety in the present series [VI(1), VI(2)] of compounds helps in promoting smectic phase through efficient molecular packing.

The transition temperatures and the accompanying enthalpies for bis[N-(4″-n-decylphenyl)-4-n-alkoxysalicylaldiminato]oxovanadium(IV) complexes are summarised in table 6.3. All the complexes exhibit fairly wide range of enantiotropic smectic

Table 6.3

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) of



Series VI(3)

Compound number	n	C		S_C		S_A		I
6.c.1	4	.	158.0 7.57	-		.	**>290.0***	.
6.c.2	5	.	169.0 9.95	-		.	**>290.0***	.
6.c.3†	6	.	175.0 9.69	-		.	**>290.0***	.
6.c.4	7	.	179.5 5.09	.	**193.5***	.	283.5 2.21	.
6.c.5	8	.	181.0 9.71	.	**226.5***	.	272.5 1.75	.
6.c.6†	9	.	179.5 8.95	.	**239.0***	.	266.0 2.19	.
6.c.7	10	.	182.5 11.92	.	241.0 0.09	.	262.5 2.24	.
6.c.8	11	,	181.5 12.39	.	243.5 0.06	.	258.0 2.26	.
6.c.9	12	.	178.0 13.19	.	244.5 0.09	.	255.5 2.26	.
6.c.10	18	.	167.0 13.09	.	226.0 0.10	.	233.5 2.09	.

†Compounds 6.c.3 and 6.c.6 have crystal-crystal transitions at 76°C and 76.5°C respectively.

*Enthalpies could not be determined.

phases. Lower homologues (n=4-6) exhibit only smectic A phase and the clearing temperatures are above 290°C. At this high temperature these complexes begin to decompose thermally. The smectic C phase appears in heptyloxy derivative (6.c.4) and these two phases (S_A, S_C) are retained in the remaining higher homologues. The smectic A and smectic C phases of these complexes exhibit focal-conic and broken focal-conic textures respectively. The photomicrograph of these textures for smectic A and smectic C phases exhibited by these complexes are shown in plates 6.2 and 6.3 respectively. As can be seen, introduction of an oxovanadium(IV) group into the Schiff's bases, the transition temperatures are elevated. However the higher order smectic phases present in the ligands are totally eliminated. A plot of the transition temperatures against the number of carbon atoms in the alkoxy chain for this series is shown in figure 6.6. As the chain length increases, the smectic C phase range increases while the smectic A phase and total mesophase ranges decrease. The dotted line in figure 6.6 indicates that the clearing temperature is above 290°C and could not be determined for the lower homologues due to thermal decomposition.

There are not many homologous series of oxovanadium(IV) complexes of Schiff's bases to understand the structure property relationship. In an effort to examine these a number of bis[N-(4″-n-alkylbiphenyl)-4-n-alkoxysalicylaldiminato]oxovanadium(IV) complexes have been synthesised. The transition temperatures and enthalpies of transitions of these complexes are summarised in table 6.4. All the complexes show fairly wide range of mesophases. Except complex 6.d.1, all have clearing points above 275°C. Complexes derived from N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-ethylphenylanilines have higher melting points than the complexes derived from N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-n-pentylphenylanilines. The introduction of the short terminal chains in the molecule is found to increase the thermal stability of mesophases, but at such high temperatures thermal decomposition (of the complexes) takes place. A comparison of the mesomorphic properties of the homologous series of bis[N-(4″-n-decylphenyl)-4-n-alkoxysalicylaldiminato]oxovanadium(IV) [series VI(3)] with bis[N-(4″-n-alkylphenyl)-4-n-alkoxysalicylaldiminato]oxovanadium(IV)

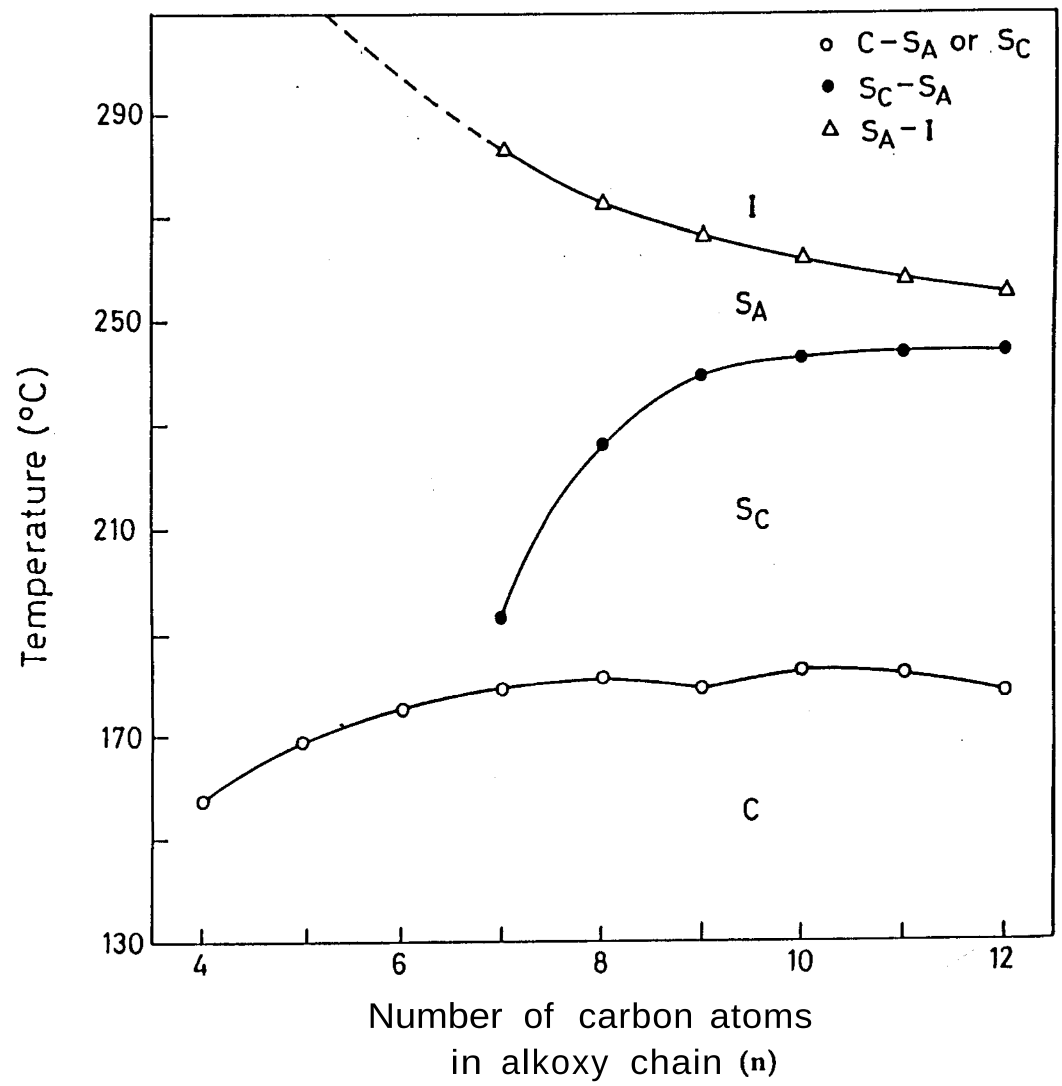
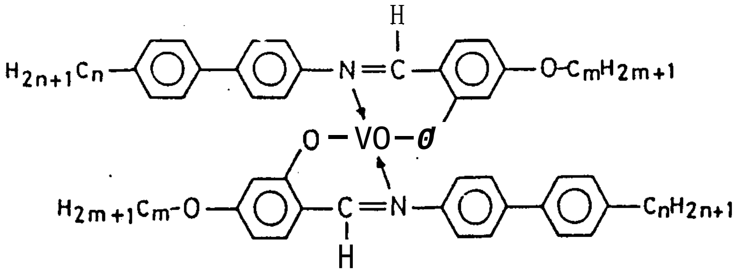


Figure 6.6. A plot of the transition temperatures versus the number of carbon atoms (n) in the alkoxy chain for bis[N-(4″-n-decylbiphenyl)-4-n-alkoxysalicylaldiminato]oxovanadium(IV) complexes.

Table 6.4

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) of



Series VI(4)

Compound number	m	n	C_1		C**		S_C		S_A		N		I
6.d.1†	0	10	.	97.5	.	155.5 5.56	.	184.0 0.04	-		.	196.8 0.12	.
6.d.2	1	2	-		.	277.5 10.66	-				.	>290.0	.
6.d.3	6	2	.	212.4	.	262.5 11.8	-		.	277.0 0.01	.	>290.0	.
6.d.4	12	2	.	173.0	.	193.0 9.20	.	274.5'	.	283.5 2.79	-		
6.d.5	1	5	-		.	239.5 11.10	-				.	>290.0	.
6.d.6	6	5	.	193.5	.	229.5 12.64	.	289.0*	.	294*.0	.	>300.0	.
6.d.7	12	5	-		.	185.0 11.03	.	246.5'	.	276.0 2.27	-		

†Compound 6.d.1 has additional crystal-crystal transitions at 84 and 90°C.

*Enthalpies could not be determined.

**The crystal to mesophase transition enthalpies include enthalpies of any previous crystal-crystal transitions.

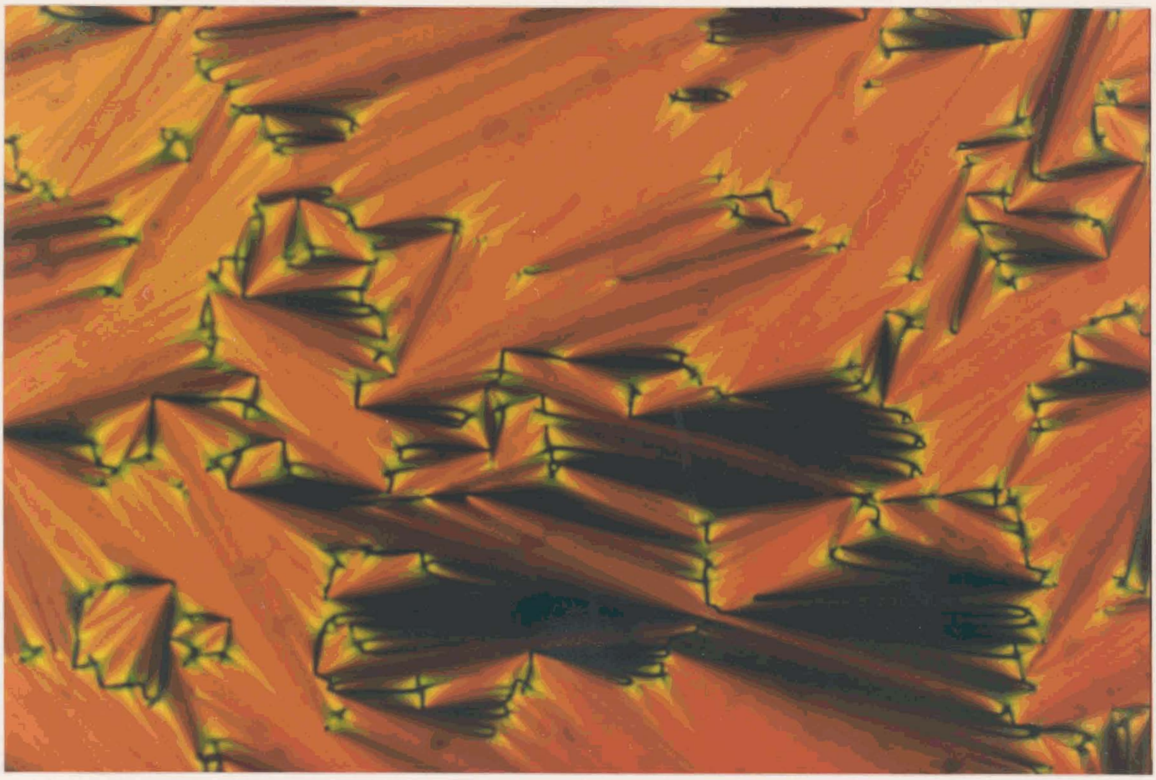


Plate 6.4. Photomicrograph of the focal-conic texture of the smectic A phase exhibited by compound 6.e.9 at 261.5°C.

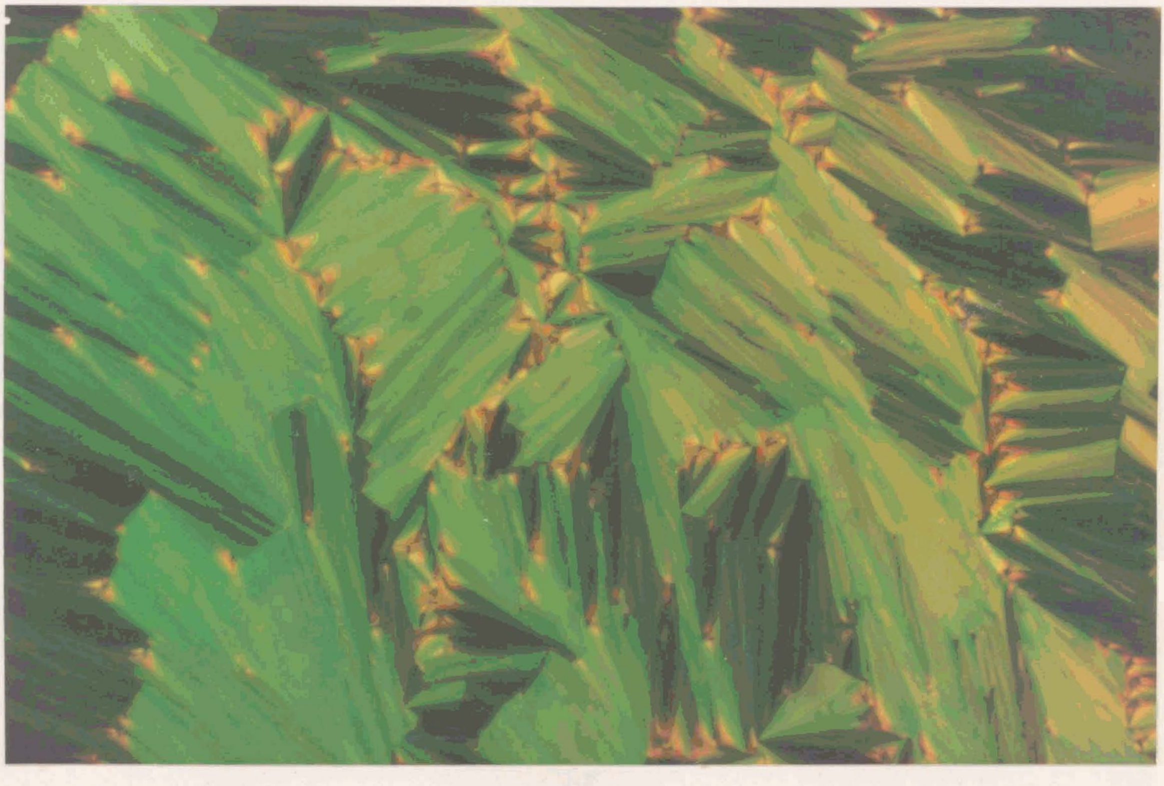
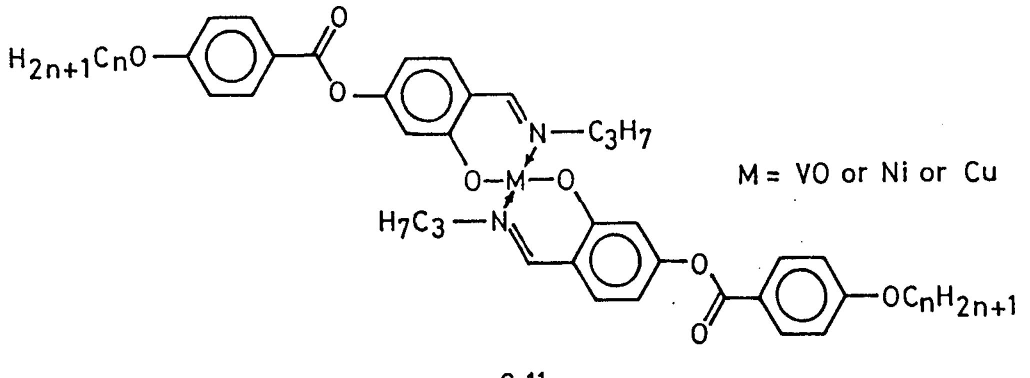


Plate 6.5. Photomicrograph of the broken focal-conic texture of the smectic C phase exhibited by compound 6.e.9 at 258°C.

[series VI(4)] indicates that the latter exhibit enantiotropic nematic phase in addition to smectic A and smectic C phases. It is observed that nematic phase is favoured in the complexes with short terminal chains.

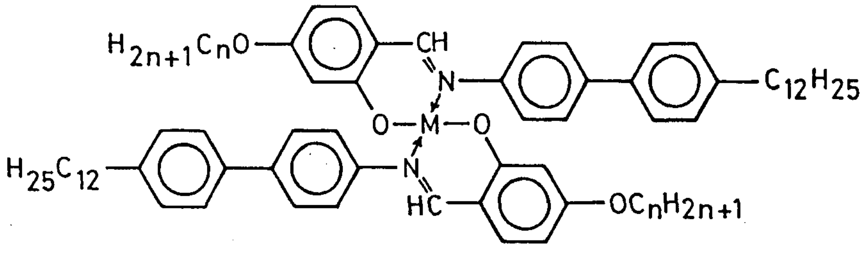
On comparing the mesogenic properties of series VI(3) with those of bis[N-(4-((4-n-alkoxybenzoyl)oxy)-N-n-propylsalicylaldiminato]oxovanadium(IV)[17] complexes (6.11), it is seen that the latter is completely nematogenic. Similar compounds



M = VO or Ni or Cu

6.11

with Ni and Cu atoms (6.10) also show only nematic phase.[30] A comparison of the mesomorphic properties of compounds of series VI(3) with those of bis[N-(4″-n-dodecylbiphenyl)-4-n-alkoxysalicylaldiminato] metal(II) (6.12) complexes,[13,14] reveals that the type of mesophases exhibited by these series of copper, palladium



M = Cu, Pd or Ni
n = 1–12, 18

6.12

nickel and oxovanadium complexes of N-salicylideneaniline derivatives predominantly show smectic phases. Lower homologues of all the four homologous series have relatively higher clearing temperature and the higher homologues exhibit smectic A and smectic C phases. The value of enthalpies for the S_C-S_A and S_A-I transitions are of the order of 0.06 to 0.5 kcal/mol and 1.4 to **3.9** kcal/mol respectively. The thermal behaviour and the calorimetric data for the bis[N-(4″-n-decylbiphenyl)-4-n-alkoxysalicylaldiminato]platinum(II) and bis[N-(4″-n-alkylbiphenyl)-4-n-alkoxysalicylaldimineto]platinum(II) complexes are shown in tables 6.5 and 6.6 respectively. These complexes also have fairly wide mesophase thermal range like their oxovanadium analogues, but the thermal stability of mesophases of all mesogenic platinum complexes are comparatively higher.

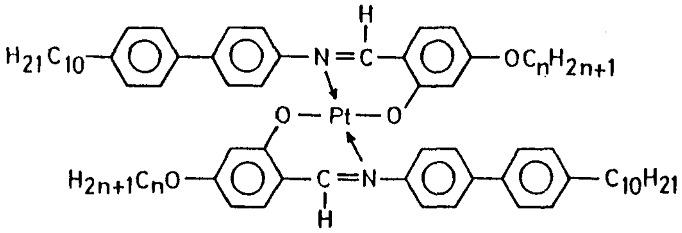
As can be seen in table 6.5, the first three homologues (n=4-6) exhibit only S_A phase. The smectic C phase appears with the S_A phase from heptyloxy derivative (n=7) and both these phases are retained in the higher homologues. The photomicrographs of the textures for S_A and S_C phases exhibited by compound 6.e.9 are shown in plates 6.4 and 6.5 respectively. As the series is ascended the S_C phase range increases while S_A phase range decreases. However the total mesophase range remains almost the same ($62\pm6°C$) irrespective of the chain length.

An examination of table 6.6 indicates that except compound 6.f.2 (which is non-mesogenic) all other platinum complexes are mesogenic. Compound 6.f.1, where (m=10, n=0) is the only complex which exhibits a $4°C$ range of nematic phase. All the complexes except 6.f.1 have clearing temperatures above $290°C$.

The melting and clearing temperatures for all the above discussed platinum complexes are higher than their corresponding oxovanadium(IV) complexes. The higher transition temperatures are due to square planar arrangement of the chelate rings as compared to the square pyramidal geometry at the centre of oxovanadium complex.[30] **A** comparison can be made about the thermal stability of mesophases of nickel,[13], copper,[12], palladium,[12] platinum and oxovanadium complexes of N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-n-alkylphenylanilines. Among these five series of metal complexes, nickel complexes have the lowest melting as well as clearing points and platinum complexes have the highest. Thus the sequence of mesophase thermal stability for these metal atoms is Ni < Cu < VO < Pd < Pt. The nature of metal atoms is thus important for determining the thermal stability of mesophase

Table 6.5

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) of



Series VI(5)

Compound number	n	C_1		C**		S_C		S_A		I
6.e.1 †	4	.	142.0	.	239.0 13.79	-		.	>290.0*	.
6.e.2†	5	.	153.5	.	234.5 12.75	-		.	>290.0*	.
6.e.3†	6		168.0	.	235.0 12.04	-		.	>290.0*	.
6.e.4†	7	.	170.0	.	227.5 9.90	.	257.0*	.	>290.0*	,
6.e.5†	8	.	167.0	.	224.0 8.09	,	272.5*	.	>290.0*	.
6.e.6	9	.	162.0	.	221.5 12.61	.	271.0*	.	>290.0*	.
6.e.7	10	.	168.5	.	218.0 12.97	.	272.5 0.15	.	284.5 1.69	.
6.e.8	11	.	165.5	.	211.0 10.52	.	267.5 0.15	.	278.0 2.12	.
6.e.9	12	.	170.1)	.	211.0 10.23	.	264.0 0.14	.	272.0 1.08	.
6.e.10	18	.	169.0	.	190.0 17.12	.	243.0 0.26	.	249.0 0.46	.

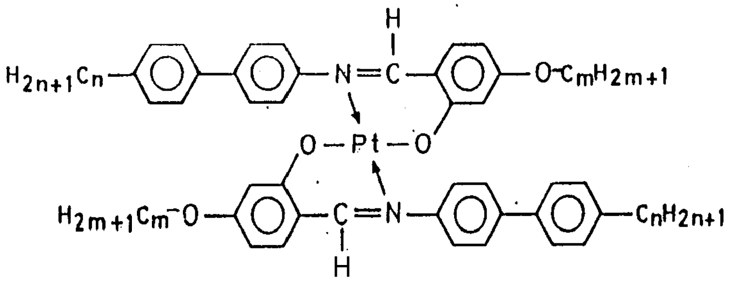
†Compounds 6.e.1, 6.e.2, 6.e.3, 6.3.4 and 6.e.5 have crystal-crystal transitions at 68.5°C, 113.8°C, 100.5°C 90.6°C and 80.5°C respectively.

*Enthalpies could not be determined.

**All the crystal to mesophase transition enthalpies include enthalpies of any previous crystal-crystal transitions.

Table 6.6

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) of



Series VI(6)

Compound number	m	n	C_1		C		S_C		S_A		N		I
6.f.1	0	10	.	229.0 15.35	-		.	240.5'	.	250.5 0.23	.	254.5 0.15	.
6.f.2	1	2	.	230.0 4.60	.	>290.0	-						
6.f.3	6	2	.	246.5 1.73	.	281.5	-		.	>290.0	-		
6.f.4	12	2	.	212.5 4.61	.	219.0 3.41	.	256.0*	.	>290.0	-		
6.f.5†	1	5	.	210.5 6.84	.	260.5 6.83	-		.	>290.0	-		
6.f.6†	6	5	.	195.4 2.91	.	275.0 9.05	-		.	>290.0	-		
6.f.7	12	5	.	196.0 8.18	.	237.5 5.18	.	285.5'	.	>290.0	-		

†Compounds 6.f.5 and 6.f.6 exhibit crystal-crystal transitions at 101.0 and 173.0°C respectively.

*Enthalpies could not be determined.

in metallomesogens.

In an effort to examine the influence of terminal chains on the mesomorphic properties of the platinum complexes, a few of the same have been synthesised and their mesomorphic transition temperatures are given in tables 6.5 and 6.6 respectively. These tables reveal that small chains at the 4 and $4''$ positions of the complex result in increase of melting point (the clearing temperatures for almost all the complexes are $>290^\circ C$). When there is no chain at the 4-position of the salicylaldehyde group, it is seen that the resulting complex exhibits a nematic phase with a decrease in clearing temperature as compared to all other platinum complexes. The PMR spectra of these platinum(II) complexes in $CDCl_3$ solution are consistent with their expected structures. Figure 6.7 shows the PMR spectrum of the complex 6.e.3.

In conclusion, it is seen that non-planarity of the chelate ring is responsible for lower transition temperatures as well as for longer range of mesophase. In addition, the nature of the metal atoms is important for the thermal stability of the mesophase. In all the above described complexes the order is platinum > oxovanadium.

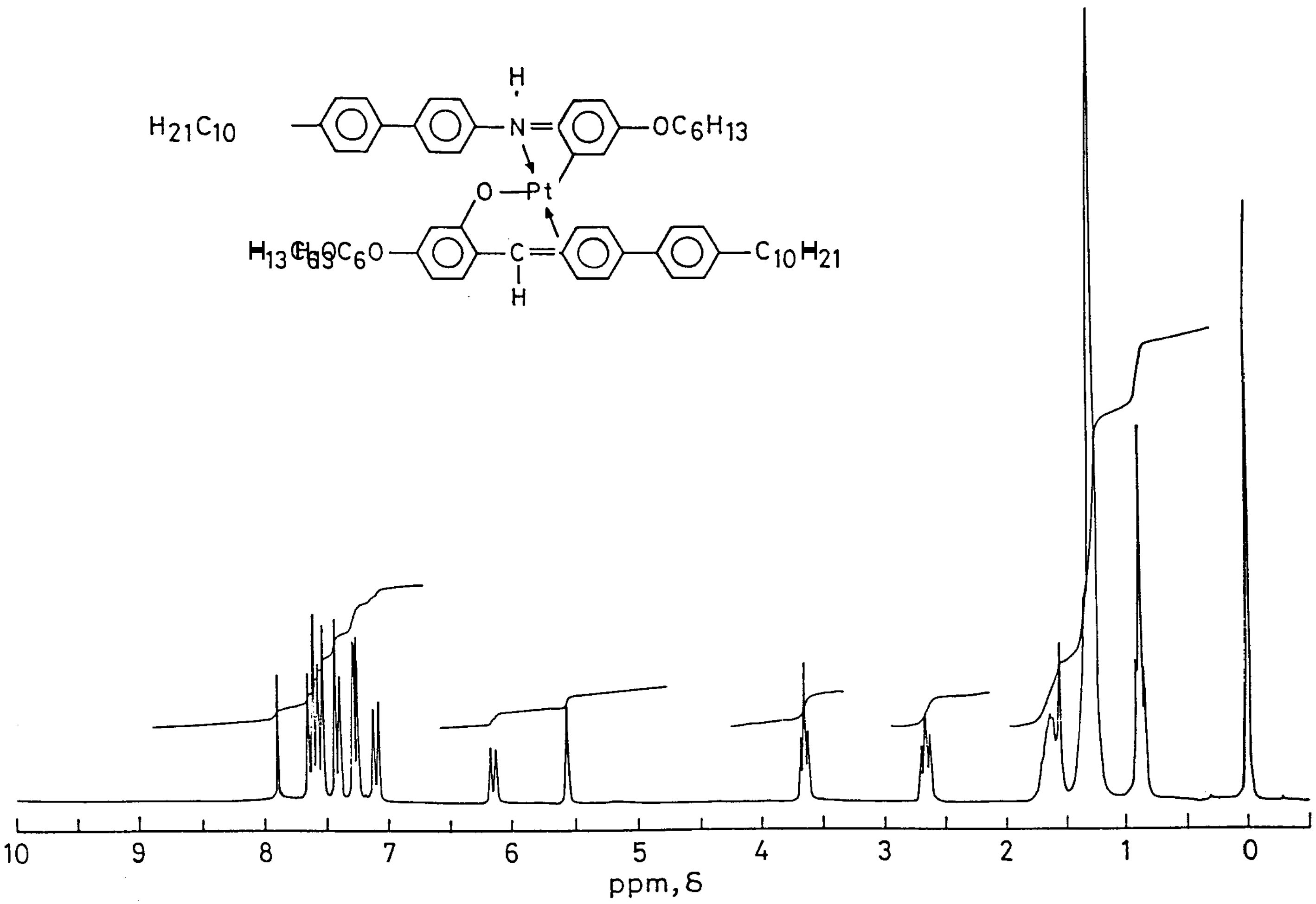


Fig.6.7. 200 MHz PMR spectrum of bis[N-(4″-n-decylbiphenyl)- 4′-n-hexyloxy salicylaldiminato]platinum(II) in $CDCl_3$ containing 1% TMS.

6.3 Experimental

4-(4′-*n*-Decylphenyl)acetanilide

This was prepared following the procedure of van der Veen *et al.*[24] Thus, sodium azide (5.3 g, 81.69 mmol) was added in small portions to a vigorously stirred mixture of 4-n-decyl-4′-acetylbiphenyl (25 g, 74.4 mmol) and 80% sulphuric acid (108 ml). After the completion of the addition, the reaction mixture was poured carefully to ice-cold water (500 ml) and extracted with chloroform (3x200 ml). The combined organic solution was washed with water (5x200 ml), dried (Na_2SO_4) and the solvent was removed. The crude product so obtained was crystallised from benzene.

Yield (22 g, 84%); transition temperature C153S163I; IR ν_{max}^{nujol} 3300, 2900, 2800, 1660, 1600, 1460, 1370, 810 cm^{-1}; NMR 6 0.93 (t, 3H, $C\underline{H}_3$), 1.2-1.4 (m, 16H, $8\times C\underline{H}_2$), 2.7-2.85 (m, 5H, $COC\underline{H}_3$ + $ArC\underline{H}_2$), 7.18-7.9 (m, 8H, $Ar\underline{H}$).

Elemental analysis: Found, C,81.96; H,9.53; N,3.75% $C_{24}H_{33}ON$ requires C,82.05; H,9.40; N,3.90%.

The physical data of the cognate preparations of other 4-(4′-*n*-alkylphenyl)acetanilides are as follows. NMR data of the following anilides could not be obtained due to their insolubility in $CDCl_3$, CD_3COCD_3, DMSO-d_6 and C_6D_6.

4-(4′-Ethylphenyl)acetanilide

Yield 78%; m.p. 189-191°C; IR ν_{max}^{nujol} 3300,2900, 2800, 1660, 1600, 1460, 1370, 810 cm^{-1}.

Elemental analysis: Found, C,79.85; H,7.00; N,5.53% $C_{16}H_{17}ON$ requires C,80.33; H,7.11; N,5.85%.

4-(4′-*n*-Pentylphenyl)acetanilide

Yield 58.5%; m.p.159.0°C; IR ν_{max}^{nujol} 3310, 2900, 2800, 1605, 1600, 1465, 1370, 805 cm^{-1}.

Elemental analysis: Found, C,80.95; H,7.68; N,4.47% $C_{19}H_{23}ON$ requires
C,81.13; H,8.18; N,4.98%.

4-(4′-*n*-Decylphenyl)aniline

This was prepared following the procedure of van der Veen et *al.*[24] Thus a mixture of 4-(4′-*n*-decylphenyl) acetanilide (22 g, 62.67 mmol), sodium hydroxide (50 g, 1250 mmol), ethyl alcohol (104.5 ml) and water (32.5 ml) was refluxed for six hours. Ethyl alcohol was removed under reduced pressure and the residue was poured into ice-water and extracted with diethyl ether (5×150 ml). The combined ethereal extracts was washed with water (5x100 ml) and dried (Na_2SO_4). Removal of the solvent afforded a pale yellow residue which was crystallised from petroleum ether.

Yield (13.6 g, 70%); m.p. 76.5°*C*; IR ν_{max}^{nujol} 3400, 2900, 2850, 1620, 1500, 1460, 1380, 1260, 810 cm^{-1}; NMR 6 0.88 (t, 3H, $C\underline{H}_3$), 1.12-1.7 (m, 16H, $8\times C\underline{H}_2$), 2.36 (q, 211, $ArC\underline{H}_2$), 2.6 (s, 2H, $N\underline{H}_2$), 5.56-5.64 (m, 8H, $Ar\underline{H}$).

4-(4′-Ethylphenyl)aniline

Yield 50%; m.p. 79.0°C; IR ν_{max}^{nujol} 3400, 2910, 2850, 1615, 1500, 1460, 1380, 1260, 805 cm^{-1}; NMR 6 1.3(t,3H,$C\underline{H}_3$), 2.5-2.9 (q, 2H, $ArC\underline{H}_2$), 3.6 (s, 2H, $N\underline{H}_2$), 6.7-7.5 (m, 8H, ArH).

Elemental analysis: Found, C, 85.19; H,7.68; N,6.96% $C_{14}H_{15}N$ requires
C,85.27; H,7.61; N,7.10%.

4-(4′-*n*-Pentylphenyl)aniline

Yield 50%; m.p. 81.0°C; IR ν_{max}^{nujol} 3400, 2900, 2850, 1615, 1500, 1465, 1380, 1260, 810 cm^{-1}; NMR δ 0.9 (t,3H,$C\underline{H}_3$), 1.16-1.83 (m, 6H, $3\times C\underline{H}_2$), 2.6 (t, 2H, $ArC\underline{H}_2$), 3.6 (s, 1H, $N\underline{H}_2$), 6.56-7.56 (m, 8H, ArH).

Elemental analysis: Found, C, 84.98; H,8.88; N,5.64% $C_{17}H_{21}N$ requires
C,85.35; H,8.70; N,5.80%.

2,4-Dihydroxybenzaldehyde

This was prepared following the standard procedure.[32] Thus, a mixture of resorcinol (20 g, 181.8 mmol), anhydrous zinc cyanide (40 g, 437.67 mmol) and sodium dried ether (200 ml) was placed in a 500 ml. three-necked flask fitted with a reflux condenser carrying a calcium chloride guard tube and a wide inlet tube extending nearly to the bottom of the flask. This was stirred magnetically and hydrogen chloride gas was passed into the flask through the inlet tube. The zinc cyanide gradually disappeared with the formation of a cloudy solution. Further passage of hydrogen chloride resulted in the separation of imine hydrochloride. The flow of hydrogen chloride gas was reduced and the stirring was continued for a period of thirty minutes. The ether was decanted and the solid material was crystallised from water (100 ml).

Yield 23.5 g, 94%; m.p. 135.0°*C* (Reported[32] m.p. 135-136°C).

2-Hydroxy-4-n-decyloxybenzaldehyde

A solution of sodium ethoxide was prepared by dissolving sodium (1 g, 43.4 mmol) in absolute ethyl alcohol and 2,4-dihydroxybenzaldehyde (5.5 g, 40 mmol) was added to it. This mixture was stirred and refluxed for thirty minutes. 1-Bromodecane (8.84 g, 39.28 mmol) was then added to it. The reaction mixture was stirred and refluxed for a period of twentyfour hours. Ethyl alcohol was removed by distillation under reduced pressure and the residue was poured into ice cold water. This was extracted with ether (3×200 ml). The combined ethereal solution was washed with 10% aqueous sodium hydroxide (3×150 ml), water (3x200 ml), and dried (Na_2SO_4). Removal of the solvent afforded a liquid which was distilled under reduced pressure to give pure 2-hydroxy-4-n-decyloxybenzaldehyde (3.8 g, 35%); b.p. 194-197° C/0.8 mm (Reported[33] b.p. 190°C/0.5mm)

2-Hydroxy-4-n-undecyloxybenzaldehyde

Yield 34%; b.p. 195-196°C/0.9 mm; IR ν_{max}^{nujol} 2900, 2850, 1670, 1630, 1600, 1580, 1460, 1430, 1295, 1260, 1185, 1120 cm^{-1}; NMR 6 0.8 (t, 3H, -C$\underline{H}_3$), 1-1.7 (m, 18H, 9×C$\underline{H}_2$), 3.8 (t, 2H, -OC$\underline{H}_2$), 6.2-7.5 (m, 3H, Ar$\underline{H}$), 9.7 (s, 1H, C$\underline{H}$O), 11.5 (s, 1H, O$\underline{H}$).

The physical constants of the cognate preparations of other 2-hydroxy-4-n-alkoxybenzaldehydes are given in table 6.7.

N-(2-Hydroxy-4-n-decyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.10)

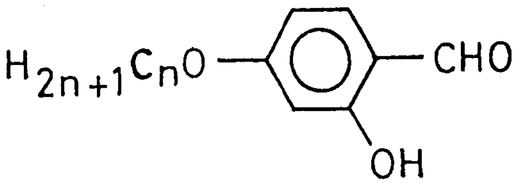
A mixture of 4-(4'-n-decylphenyl) aniline (1.26 g, 4.07 mmol), 2-hydroxy-4-n-decyloxybenzaldehyde (1.13 g, 4.06 mmol) and a few drops of acetic acid was refluxed in ethyl alcohol (35 ml) for a period of four hours. It was then cooled and the solid was filtered off, washed with cold ethyl alcohol, dried and crystallised repeatedly from butan-2-one.

Yield (1.9 g, 83.5%); m.p. 78.0" C; IR ν_{max}^{nujol} 2920, 2850, 1630, 1460, 1410, 1280, 810 cm^{-1}; NMR 6 0.87 (t, 6H, 2× -C$\underline{H}_3$), 1.04-1.8 (m, 32H, 16×C$\underline{H}_2$), 2.6 (t, 2H, C$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.4-7.8 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.7 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (t) 352 (37,000), 287 (16,700), 251.5 (20,000).

Elemental analysis: Found, C,82.50; H,9.92; N,2.40% $C_{39}H_{55}O_2N$ requires
C,82.24; H,9.66; N,2.46%.

Table 6.7

Physical data of



S.No.	n	m.p°C, b.p.°C/mm	Yield %	Reference
1	1	38.5	30.7	1,6
2	2	108-110/1	30.0	34
3	3	100-104/0.5	27.5	1,6
4	4	110-112/0.5	30	35
5	5	125-128/0.5	25	1,6
6	6	160-163/1.5	28	1,6
7	7	146-149/0.5	30	1,6
8	8	157-160/0.3	30	1,6
9	9	170-173/0.3	32	36
10	10	194-197/0.8	35	33
11	11	195-196/0.9	34	
12	12	195-197/1	25	37
13	18	59-61	37	38

The physical data of the cognate preparations of other N-(2-hydroxy-4-n-alkoxybenzylidene)-4''-*n*-decylphenylanilines are given below.

N-(2-Hydroxy-4-methoxybenzylidene)-4''-*n*-decylphenylaniline, (6.a.1)

Yield 70%; m.p. 115.0° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1470, 1400, 1285, 810 cm^{-1}; NMR δ 0.88 (t, 3H, -C$\underline{H}_3$), 1.12-1.84 (m, 16H, 8×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 3.8 (s, 3H, -OC$\underline{H}_3$), 6.5-7.8 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.84 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 351 (36,000), 288 (16,400), 248 (20,000).

Elemental analysis: Found, C,81.59; H,8.49; N,2.68% $C_{30}H_{37}O_2N$ requires
C,81.26; H,8.35; N,3.16%.

N-(2-Hydroxy-4-ethoxybenzylidene)-4''-*n*-decylphenylaniline, (6.a.2)

Yield 55%; m.p. 140.5° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1470, 1400, 1290, 810 cm^{-1}; NMR δ 0.84 (t, 6H, 2×-C$\underline{H}_3$), 1.08-1.96 (m, 16H, 8×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 3.88-4.32 (q, 2H, -OC$\underline{H}_2$), 6.28-7.8 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.84 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 352 (36,000), 288.5 (16,700), 249 (19,700).

Elemental analysis: Found, C,81.27; H,8.88; N,2.89% $C_{31}H_{39}O_2N$ requires
C,81.40; H,8.53; N,3.06%.

N-(2-Hydroxy-4-n-propyloxybenzylidene)-4''-*n*-decylphenylaniline, (6.a.3)

Yield 71%; m.p. 94.0" C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1465, 1410, 1280, 810 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1-2 (m, 18H, 9×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4 (s, 2H, -OC$\underline{H}_2$), 6.28-7.8 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.76 (s, 1H, O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 352 (36,400), 287.5 (15,700), 250 (20,000).

Elemental analysis: Found, C,81.27; H,8.88; N,2.95% $C_{32}H_{41}O_2N$ requires
C,81.52; H,8.70; N,2.97%.

N-(2-Hydroxy-4-n-butyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.4)

Yield 67%; m.p. 85.0° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1465, 1405, 1285, 815 cm^{-1}; NMR δ 0.96 (t, 6H, 2×-C$\underline{H}_3$), 1.12-1.92 (m, 20H, 10×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4.0 (s, 2H, -OC$\underline{H}_2$), 6.3-7.8 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 352 (37,000), 288 (16,000), 250 (20,200).

Elemental analysis: Found, C,81.85; H,9.04; N,2.48% $C_{33}H_{43}O_2N$ requires C,81.64; H,9.01; N,2.88%.

N-(2-Hydroxy-4-n-pentyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.5)

Yield 70%; m.p. 78.0° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1470, 1405, 1285, 810 cm^{-1}; NMR δ 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.07-1.92 (m, 22H, 11×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.4-7.8 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 352 (36,900), 288 (16,000), 251 (19,500).

Elemental analysis: Found, C,82.30; H,9.15; N,2.55% $C_{34}H_{45}O_2N$ requires C,81.76; H,9.01; N,2.80%.

N-(2-Hydroxy-4-n-hexyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.6)

Yield 65%; m.p. 83.0° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1465, 1410, 1280, 810 cm^{-1}; NMR δ 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1-1.88 (m, 24H, 12×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4.08 (t, 2H, -OC$\underline{H}_2$), 6.5-7.78 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.72 (s, 1H, O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 351.5 (37,000), 287.5 (16,500), 251.6 (19,900).

Elemental analysis: Found, C,81.54; H,9.35; N,2.51% $C_{35}H_{47}O_2N$ requires C,81.87; H,9.16; N,2.72%.

N-(2-Hydroxy-4-n-heptyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.7)

Yield 57%; m.p. 80.0" C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1465, 1410, 1280, 810 cm^{-1}; NMR δ 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.0-1.8 (m, 26H, 13×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4.0 (t, 2H, -OC$\underline{H}_2$), 6.4-7.7 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CIICl_3}$ (ϵ) 351.5 (37,000), 251 (19,900), 287.5(16,500).

Elemental analysis: Found, C,81.88; H,9.67; N,2.42% $C_{36}H_{49}O_2N$ requires C,81.97; H,9.29; N,2.65%.

N-(2-Hydroxy-4-n-octyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.8)

Yield 57%; m.p. 79.5° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1460, 1410, 1280, 810 cm^{-1}; NMR 6 0.8 (t, 6H, 2×-C$\underline{H}_3$), 1.2-2 (m, 28H, 14×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.2-7.85 (m, 11H, Ar$\underline{H}$), 8.7 (s, 1H, -N=C$\underline{H}$), 13.7 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 352 (37,500), 288 (16,500), 250.5 (17,000).

Elemental analysis: Found, C,81.88; H,9.67; N,2.42% $C_{37}H_{51}O_2N$ requires C,82.07; H,9.42; N,2.58%.

N-(2-Hydroxy-4-n-nonyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.9)

Yield 60%; m.p. 84.5" C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1465, 1410, 1285, 810 cm^{-1}; NMR δ 0.83 (1, 6II, 2×-C$\underline{II}_3$), 1.0-1.9 (m, 3011, 15×C$\underline{II}_2$), 2G (t, 211, ArC$\underline{II}_2$), 4 (1, 2H, -OC$\underline{H}_2$), 6.29-8 (m, 11H, Ar$\underline{H}$), 8.8 (s, 1H, -N=C$\underline{H}$), 13.7 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 352 (37,000), 287 (16,000), 251.5 (19,000).

Elemental analysis: Found, C,81.75; H,9.70; N,2.39% $C_{38}H_{53}O_2N$ requires C,82.16; H,9.56; N,2.72%.

N-(2-Hydroxy-4-n-undecyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.11)

Yield 54.5%; m.p. 85.5° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1465, 1410, 1285, 810 cm^{-1}; NMR δ 0.83 (t, 6H, 2×-C$\underline{H}_3$), 1.08-2 (m, 34H, 17×C$\underline{H}_2$), 2.62 (t, 2H, ArC$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.3-7.7 (m, 11H, Ar$\underline{H}$), 8.66 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 351.5 (36,900), 287 (16,500), 250 (19,500).

Elemental analysis: Found, C,82.48; H,10.04; N,2.31% $C_{40}H_{57}O_2N$ requires C,82.33; H, 9.77; N,2.40%.

N-(2-Hydroxy-4-n-dodecyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.12)

Yield 61.5%; m.p. 80.0° C; IR ν_{max}^{nujol} 2914, 2854, 1632, 1464, 1410, 1287, 813 cm^{-1}; NMR δ 0.87 (t, 6H, 2×-C$\underline{H}_3$), 1.08-1.6 (m, 36H, 18×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4.0 (t, 2H, -OC$\underline{H}_2$), 6.4-7.7 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 352 (36,000), 287.5 (17,000), 251.5 (20,000).

Elemental analysis: Found, C,82.14; H,10.11; N,2.08% $C_{41}H_{59}O_2N$ requires C,82.41; H, 9.88; N,2.34%.

N-(2-Hydroxy-4-n-octadecyloxybenzylidene)-4″-*n*-decylphenylaniline, (6.a.13)

Yield 56.5%; m.p. 90.0° C; IR ν_{max}^{nujol} 2900, 2850, 1630, 1470, 1405, 1290, 810 cm^{-1}; NMR δ 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.08-2 (m, 48H, 24×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.4-7.8 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 351.6 (38,200), 252 (19,300), 288 (17,000).

Elemental analysis: Found, C,83.0; H,10.62; N,1.98% $C_{47}H_{71}O_2N$ requires C,82.8; H,10.42; N,2.05%.

N-(2-Hydroxybenzylidene)-4-*n*-decylphenylaniline, (6.b.1)

Yield 80%; m.p.90.5° C; IR ν_{max}^{nujol} 2920, 2850, 1620, 1460, 1280, 840, 810 cm^{-1}; NMR δ 0.88 (t, 3H, 2×-C$\underline{H}_3$), 1.1-1.8 (m, 20H, 10×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 7-7.6 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.3 (s, 1H, OH); UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 273.5 (49,500), 330 (22,500), 351 (25,500).

Elemental analysis: Found, C,84.24; H,8.66; N,3.24% $C_{29}H_{35}ON$ requires C,84.26; H,8.47; N,3.38%.

N-(2-Hydroxy-4-methoxybenzylidene)4″-ethylphenylaniline, (6.b.2)

This was preapred from 2-hydroxy-4-methoxybenzaldehyde (1 g, 6.57 mmol), 4-(4′-n-decylphenyl)aniline (1.4 g, 7.1 mmol) and a few drops of acetic acid, by following a procedure similar to the one described for the synthesis of compound 6.a.10.
Yield 0.87 g, 40%; m.p.144.0° C; IR ν_{max}^{nujol} 2945, 2850, 1630, 1575, 1470, 1380, 1290, 830 cm^{-1}; NMR δ 1.2 (m, 3H, C$\underline{H}_3$), 2.4-2.8 (q, 2H, C$\underline{H}_2$), 3.8 (s, 3H, -OC$\underline{H}_3$), 6.4-7.7 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ) 248.5 (19,500), 286 (15,300), 350.5 (34,300).

Elemental analysis: Found, C,79.55; H,6.36; N,4.23% $C_{22}H_{21}O_2N$ requires C,80.00; H,6.60; N,4.05%.

The physical data of the cognate preparations of other N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-n-decylphenylanilines are given below.

N-(2-Hydroxy-4-n-hexyloxybenzylidene) 4"-ethylphenylaniline, (6.b.3)

Yield 42%; m.p.113.5° C; IR ν_{max}^{nujol} 2950, 2850, 1630, 1595, 1465, 1380, 1300, 830 cm^{-1}; NMR δ 0.88 (t, 3H, -C$\underline{H}_3$), 1.1-1.9(m, 8H, 4×C$\underline{H}_2$), 2.5-2.9 (q, 2H, ArC$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.4-7.7 (m, 11H, Ar$\underline{H}$), 8.5 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 250 (19,400), 286.5 (16,400), 352.5 (35,000).

Elemental analysis: Found, C,80.95; H,7.88; N,3.49% $C_{27}H_{31}O_2N$ requires C,80.79; H,7.73; N,3.49%.

N-(2-Hydroxy-4-n-dodecyloxybenzylidene)4″-ethylphenylaniline, (6.b.4)

Yield 42%; m.p.96.0° C; IR ν_{max}^{nujol} 2950, 2850, 1630, 1570, 1460, 1400, 1290, 820 cm^{-1}; NMR δ 0.8 (t, 6H, 2×$C\underline{H}_3$), 1.2-2 (m, 20H, 10×$C\underline{H}_2$), 2.4-2.7 (q, 2H, $ArC\underline{H}_2$), 4 (t, 2H, $-OC\underline{H}_2$), 6.2-7.8 (m, 11H, $Ar\underline{H}$), 8.4 (s, 1H, $-N{=}C\underline{H}$), 13.6 (s, 1H, $O\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 250 (19,200)) 287 (15,900)) 351.5 (34,700).

Elemental analysis: Found, C,81.30; H,9.08; N,2.74% $C_{33}H_{43}O_2N$ requires C,81.64; H,8.86; N,2.88%.

N-(2-Hydroxy-4-methoxybenzylidene)4″-pentylphenylaniline, (6.b.5)

This was prepared from 4-(4′-n-pentylphenyl)aniline (1.5 g, 6.65 mmol), 2-hydroxy-4-methoxybenzaldehyde (1.01 g, 6.64 mmol) and a few drops of acetic acid, by following a procedure similar to the one described for the synthesis of compound 6.a.10. The yellow product thus obtained was crystallised from but an-2-one several times until the melting point was constant. Yield (1.19 g, 48%); m.p.119.5° C; IR ν_{max}^{nujol} 2920, 2850, 1630, 1570, 1465, 1400, 1290, 885 cm^{-1}; NMR 6 0.9 (t, 3H, $C\underline{H}_3$), 1.2-1.8 (m, 6H, 3×$C\underline{H}_2$), 2.6 (t, 2H, $ArC\underline{H}_2$), 3.8 (s, 3H, $-OC\underline{H}_3$), 6.4-7.7 (m, 11H, $Ar\underline{H}$), 8.5 (s, 1H, $-N{=}C\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ) 249.5 (18,900), 285.5 (15,900)) 350.5 (33,400).

Elemental analysis: Found, C,80.01; H,7.38; N,3.86% $C_{25}H_{27}O_2N$ requires C,80.42; H,7.30; N,3.75%.

The physical data of the cognate preparations of other N-(2-hydroxy-4-n-alkoxybenzylidene)-4″-n-pentylphenylanilines are given below.

N-(2-Hydroxy-4-n-hexyloxybenzylidene)4″-*n*-pentylphenylaniline, (6.b.6)

Yield 41%; m.p.73.0° C; IR ν_{max}^{nujol} 2920, 2850, 1625, 1565, 1465, 1400, 1285, 810 cm^{-1}; NMR δ 0.9 (t, 6H, 2×C$\underline{H}_3$), 1.2-2 (m, 14H, 7×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.4-7.8 (m, 11H, Ar$\underline{H}$), 8.5 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, O$\underline{H}$); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ) 250 (18,600))287 (15,800), 351 (33,200).

Elemental analysis: Found, C,79.90; H,9.50; N,3.12% $C_{30}H_{42}O_2N$ requires C,80.35; H,9.37; N,3.12%.

N-(2-Hydroxy-4-n-dodecyloxybenzylidene)4″-*n*-pentylphenylaniline, (6.b.7)

Yield 65.5%; m.p.80.8° C; IR ν_{max}^{nujol} 2920, 2850, 1625, 1570, 1465, 1400, 1290, 885 cm^{-1}; NMR 6 0.9 (t, 6H, 2×C$\underline{H}_3$), 1.1-1.8 (m, 26H, 13×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 4 (t, 2H, -OC$\underline{H}_2$), 6.5-7.7 (m, 11H, Ar$\underline{H}$), 8.6 (s, 1H, -N=C$\underline{H}$), 13.8 (s, 1H, OH); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ) 252 (19,900), 286 (16,000), 351.5 (34,000).

Elemental analysis: Found, C,82.19; H,9.57; N,2.54% $C_{36}H_{49}O_2N$ requires C,81.97; H,9.29; N,2.65%.

Bis[N-(4″-n-decylbiphenyl)-4-n-decyloxysalicylaldiminato] oxovanadium(IV), (6.c.7)

To a warm stirred solution of N-(2-hydroxy-4-n-decyloxybenzylidene)-4″-n-decylphenylaniline (0.113 g, 0.2 mmol) in ethyl alcohol (25 ml) was added a solution of vanadyl sulphate pentahydrate (0.025 g, 0.096 mmol) in water (5 ml). The mixture turned dark green in colour. An aqueous solution (7 ml) of sodium acetate (0.034 g, 0.41 mmol) was added to it and precipitation occurred immediately. The suspension was boiled with stirring for 20 minutes and was allowed to stand for 2 hours at room temperature. The green solid was filtered off and washed with water (50 ml), ethyl alcohol (25 ml) and diethylether (50 ml) respectively. This was crystallised from a mixture of chloroform and ethyl alcohol, till the transition temperatures were constant.

Yield (0.114 g, 47.5%); m.p.182.8° C; IR ν_{max}^{nujol} 2900, 2850, 1610, 1590, 1470, 1380, 1190, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 359.5 (61,400), 259.6 (62,900).

Elemental analysis: Found, C,77.74; H,9.20; N,2.22% $C_{78}H_{108}O_5N_2V$ requires C,77.80; H,8.97; N,2.32%.

The physical data of the cognate preparations of other bis[N-(4″-n-decylbiphenyl) -4-n-alkoxysalicylaldiminato] oxovanadium(IV) complexes are given below.

Bis[N-(4″-n-decylbiphenyl)-4-n-butyloxysalicylaldiminato]-oxovanadium(IV), (6.c.1)

Yield 45%; m.p.158.0° C; IR ν_{max}^{nujol} 2900, 2850, 1620, 1580, 1460, 1380, 1190, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 360.5 (61,300), 260 (62,100).

Elemental analysis: Found, C,75.97; H,8.26; N,3.28% $C_{64}H_{80}O_5N_2V$ requires C,76.27; H,7.94; N,2.78%.

Bis[N-(4″-n-decylbiphenyl)-4-n-pentyloxysalicylaldiminato] oxovanadium(IV), (6.c.2)

Yield 45%; m.p.169.0° C; IR ν_{max}^{nujol} 2900, 2850, 1615, 1580, 1460, 1380, 1190, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (e) 361 (61,000), 261 (61,500).

Elemental analysis: Found, C,77.19; H,8.48; N,2.39% $C_{66}H_{84}O_5N_2V$ requires C,76.76; H,8.27; N,2.63%.

Bis[N-(4″-n-decylbiphenyl)-4-n-hexyloxysalicylaldiminato] oxovanadium(IV), (6.c.3)

Yield 56.5%; m.p.175.0° C; IR ν_{max}^{nujol} 2900, 2850, 1620, 1585, 1460, 1380, 1190, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 361.5 (61,500), 260.5 (62,000).

Elemental analysis: Found, C,76.64; H,8.64; N,2.38% $C_{68}H_{88}O_5N_2V$ requires C,76.99; H,8.43; N,2.56%.

Bis[N-(4″-n-decylbiphenyl)-4-n-heptyloxysalicylaldiminato] oxovanadium(IV), (6.c.4)

Yield 54%; m.p.179.5° C; IR ν_{max}^{nujol} 2900, 2850, 1615, 1585, 1460, 1375, 1190, 985 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 361.5 (61,000), 261 (62,500).

Elemental analysis: Found, C,77.78; H,8.83; N,2.34% $C_{72}H_{96}O_5N_2V$ requires C,77.31; H,8.57; N,2.50%.

Bis[N-(4″-n-decylbiphenyl)-4-n-octyloxysalicylaldiminato] oxovanadium(IV), (6.c.5)

Yield 61.5%; m.p.181.0° C; IR ν_{max}^{nujol} 2900, 2850, 1615, 1580, 1460, 1380, 1195, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 361 (60,600), 262 (63,600).

Elemental analysis: Found, C,76.98; H,8.92; N,2.01% $C_{74}H_{100}O_5N_2V$ requires C,77.42; H,8.71; N,2.40%.

Bis[N-(4″-n-decylbiphenyl)-4-n-nonyloxysalicylaldiminato] oxovanadium(IV), (6.c.6)

Yield 50.5%; m.p.179.5° C; IR ν_{max}^{nujol} 2900, 2850, 1610, 1585, 1465, 1380, 1190, 985 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 360.5 (61,800))260.5 (62,600).

Elemental analysis: Found, C,77.93; H,9.14; N,2.86% $C_{76}H_{104}O_5N_2V$ requires C,77.62; H,8.85; N,2.38%.

Bis[N-(4″-n-decylbiphenyl)-4-n-undecyloxysalicylaldiminato] oxovanadium(IV), (6.c.8)

Yield 45%; m.p.180.0° C; IR ν_{max}^{nujol} 2900, 2850, 1610, 1585, 1470, 1370, 1190, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 359.5 (59,800), 259.6 (62,000).

Elemental analysis: Found, C,78.24; H,9.19; N,1.79% $C_{80}H_{112}O_5N_2V$ requires C,77.98; H,9.09; N,2.27%.

Bis[N-(4″-n-decylbiphenyl)-4-n-dodecyloxysalicylaldiminato] oxovanadium(IV), (6.c.9)

Yield 47.5%; m.p.177.5° C; IR ν_{max}^{nujol} 2914, 2854, 1611, 1585, 1464, 1380, 1194, 987 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 359.5 (59,800), 259.5 (60,300).

Elemental analysis: Found, C,77.83; H,9.41; N,1.79% $C_{82}H_{116}O_5N_2V$ requires C,78.16; H,9.21; N,2.22%.

Bis[N-(4″-n-decylbiphenyl)-4-n-octadecyloxysalicylaldiminato] oxovanadium(IV), (6.c.10)

Yield 38.0%; m.p.167.0° C; IR ν_{max}^{nujol} 2900, 2850, 1620, 1575, 1460, 1395, 1190, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 361.5 (67,700), 259 (60,000).

Elemental analysis: Found, C,79.09; H,10.30; N,2.13% $C_{94}H_{140}O_5N_2V$ requires C,79.05; H,9.81; N,1.96%.

Bis[N-(4″-n-decylbiphenyl)-4-n-salicylaldiminato]oxovanadium(IV), (6.d.1)

Yield 38.5%; m.p.155.5° C; IR ν_{max}^{nujol} 2950,2850, 1600, 1575, 1550, 1470, 1380, 1300, 980 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 322.5 (34,100))260 (76,100) 371.5 (26,100).

Elemental analysis: Found, C,78.60; H,7.77; N,3.33% $C_{58}H_{68}O_3N_2V$ requires C,78.11; H,7.63; N,3.14%.

Bis[N-(4″-ethylbiphenyl)-4-methoxysalicylaldiminato] oxovanadium(IV), (6.d.2)

This complex was prepared from N(2-hydroxy-4-methoxybenzylidene)-4″-ethylphenylaniline (0.22 g, 0.66 mmol), vanadyl sulphate pentahydrate (0.085 g, 0.33 mmol), sodium acetate (0.114 g, 1.39 mmol), water (10 ml) and ethyl alcohol (200 ml) by following a procedure similar to the one described for the synthesis of compound 6.c.7.

Yield (0.1 g, 41.5%); m.p.277.0° C; IR ν_{max}^{nujol} 2950, 2850, 1620, 1585, 1550, 1460, 1380, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 361 (60,300), 320.5 (35,400) 260 (40,700).

Elemental analysis: Found, C,72.94; H,5.44; N,3.49% $C_{44}H_{40}O_5N_2V$ requires C,72.63; H,5.50; N,3.85%.

The physical data of the cognate preparations of other bis[N-(4″-ethylbiphenyl)-4-n-alkoxysalicylaldiminato]oxovanadium(IV) complexes are given below.

Bis[N-(4″-ethylbiphenyl)4-n-hexyloxysalicylaldiminato] oxovanadium(IV), (6.d.3)

Yield 41%; m.p.262.5° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1460, 1380, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 362 (62,300), 318 (35,900) 262 (44,200).

Elemental analysis: Found, C,74.92; H,6.98; N,3.22% $C_{54}H_{60}O_5N_2V$ requires . C, 74.74; H,6.92; N,3.22%.

Bis[N-(4″-ethylbiphenyl)4-n-dodecyloxysalicylaldiminato] oxovanadium(IV), (6.d.4)

Yield 46.5%; m.p.192.5° C; IR ν_{max}^{nujol} 2950, 2850, 1620, 1570, 1460, 1380, 985 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 360 (63,600), 322 (45,700) 260 (40,900).

Elemental analysis: Found, C,76.11; H,8.17; N,2.49% $C_{66}H_{84}O_5N_2V$ requires C, 76.52; H,8.11; N,2.70%.

Bis[N-(4″-n-pentylbiphenyl)4-methoxysalicylaldiminato] oxovanadium(IV), (6.d.5)

This complex was prepared from N(2-hydroxy-4-methoxybenzylidene)-4″-pentylphenylaniline (0.4 g, 1.07 mmol), vanadyl sulphate pentahydrate (0.138 g, 0.53 mmol), sodium acetate (0.184 g, 2.24 mmol), water (5 ml) and ethyl alcohol (25 ml) by following a procedure similar to the one described for the synthesis of compound 6.c.7.

Yield 0.2 g, 46%; m.p.239.5° C; IR ν_{max}^{nujol} 2920, 2850, 1620, 1590, 1460, 1380, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 259.5 (65,400), 318 (40,000) 360.5 (45,000).

Elemental analysis: Found, C,74.31; H,6.35; N,3.19% $C_{50}H_{52}O_5N_2V$ requires C,73.98; H,6.41; N, 3.45%.

The physical data of the cognate preparations of other bis[N-(4″-n-pentylbiphenyl)-4-n-alkoxysalicylaldiminato]oxovanadium(IV) complexes are given below.

Bis[N-(4″-n-pentylbiphenyl)4-n-hexyloxysalicylaldiminato] oxovanadium(IV), (6.d.6)

Yield 46%; m.p.229.5° C; IR ν_{max}^{nujol} 2950, 2850, 1620, 1590, 1460, 1380, 985 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 260 (65,000), 317 (39,000) 361.5 (44,700).

Elemental analysis: Found, C,76.57; H,7.67; N,2.50% $C_{60}H_{68}O_5N_2V$ requires C,76.03; H,7.18; N,2.95%.

Bis[N-(4″-n-pentylbiphenyl)4-n-dodecyloxysalicylaldiminato]-oxovanadium(IV), (6.d.7)

Yield 43%; m.p.184.5° C; IR ν_{max}^{nujol} 2930, 2850, 1620, 1590, 1460, 1380, 990 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 261.5 (65,100), 318 (39,900) 362 (45,500).

Elemental analysis: Found, C,76.68; H,8.20; N,2.67% $C_{72}H_{96}O_5N_2V$ requires C,77.21; H,8.57; N,2.50%.

Bis[N-(4″-n-decylbiphenyl)4-n-decyloxysalicylaldiminato] platinum(II), (6.e.7)

A mixture of N-(2-hydroxy-4-n-decyloxybenzylidene)-4″-n-decylphenylaniline (0.114 g, 0.2 mmol), *trans*-bis(benzonitrile) dichloroplatinum(II) (0.0427 g, 0.099 mmol) was refluxed in dry benzene (25 ml) for 20 hours. The reaction mixture was cooled and the orange coloured precipitate was filtered and washed with cold benzene (2.0 ml) and crystallised several times from benzene.

Yield (0.079 g, 30.5%); m.p.218.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1470, 1370, 1208, 815 cm^{-1}; NMR δ 0.83 (t, 6H, 2×-C$\underline{H}_3$), 1.1-1.9 (m, 64H, 32×C$\underline{H}_2$), 2.7[t, 4H, (ArC$\underline{H}_2$)$_2$], 7.76 (m, 18H, ArH), 7.9 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (37,500), 265 (75,000).

Elemental analysis: Found, C,70.04; H,8.22; N, 1.77% $C_{78}H_{108}O_4N_2Pt$ requires C,70.31; H,8.11; N,2.10%.

The physical data of the cognate preparations of other bis[N-(4″-n-decylphenyl)-4-n-alkoxysalicylaldiminato]platinum(II) complexes are given below.

Bis[N-(4″-n-decylbiphenyl)4-n-butyloxysalicylaldiminato] platinum(II), (6.e.1)

Yield 30%; m.p.239.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1470, 1380, 1210, 810 cm^{-1}; NMR 6 0.8 (t, 6H, 2×-$\mathrm{C\underline{H}_3}$), 1-1.7 (m, 40H, 20×$\mathrm{C\underline{H}_2}$), 2.6 [t, 4H, $(\mathrm{ArC\underline{H}_2})_2$], 3.6 [t, 4H, $(\mathrm{OC\underline{H}_2})_2$], 5.6 (s, 2H, Ar$\underline{\mathrm{H}}$), 6.08-6.2 (d, 2H, Ar$\underline{\mathrm{H}}$), 6.8-7.7 (m, 18H, Ar$\underline{\mathrm{H}}$), 7.8 (s, 2H, 2×-N=C$\underline{\mathrm{H}}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (39,000), 266.5 (77,100).

Elemental analysis: Found, C,68.07; H,7.31; N, 2.50% $\mathrm{C_{66}H_{84}O_4N_2Pt}$ requires C,68.09; H,7.22; N,2.40%.

Bis[N-(4″-n-decylbiphenyl)4-n-pentyloxysalicylaldiminato] platinum(II), (6.e.2)

Yield 30%; m.p.234.5° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1470, 1380, 1210, 810 cm^{-1}; NMR 6 0.9 (t, 6H, 2×-$\mathrm{C\underline{H}_3}$), 1.02-1.68 (m, 44H, 22×$\mathrm{C\underline{H}_2}$), 2.6 [t, 4H, $(\mathrm{ArC\underline{H}_2})_2$], 3.7 [t, 4H, $(\mathrm{OC\underline{H}_2})_2$], 5.6 (s, 2H, Ar$\underline{\mathrm{H}}$), 6.12-6.24 (d, 2H, Ar$\underline{\mathrm{H}}$), 7-7.7 (m, 18H, Ar$\underline{\mathrm{H}}$), 7.8 (s, 2H, 2×N=C$\underline{\mathrm{H}}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (39,000), 266 (76,500).

Elemental analysis: Found, C,68.98; H,7.56; N, 2.64% $\mathrm{C_{68}H_{88}O_4N_2Pt}$ requires C,68.50; H,7.30; N,2.35%.

Bis[N-(4″-n-decylbiphenyl)4-n-hexyloxysalicylaldiminato] platinum(II), (6.e.3)

Yield 41%; m.p.235.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1470, 1380, 1210, 810 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-$\mathrm{C\underline{H}_3}$), 1.2-1.6 (m, 48H, 24×$\mathrm{C\underline{H}_2}$), 2.6 [t, 4H, $(\mathrm{ArC\underline{H}_2})_2$], 3.6 [t, 4H, $(\mathrm{OC\underline{H}_2})_2$], 5.5 (s, 2H, Ar$\underline{\mathrm{H}}$), 6.12-6.17 (d, 2H, Ar$\underline{\mathrm{H}}$), 7-7.7

(m, 18H, Ar$\underline{H}$), 7.8 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344.5 (41,000), 266.5 (77,000).

Elemental analysis: Found,. C,69.25; H,7.75; N, 2.07% $C_{70}H_{92}O_4N_2Pt$ requires C,68.90; H,7.54; N,2.29%.

Bis[N-(4″-n-decylbiphenyl)4-n-heptyloxysalicylaldiminato] platinum(II), (6.e.4)

Yield 34%; m.p.227.5° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1595, 1460, 1380, 1210, 810 cm^{-1}; NMR 6 0.9 (t, 6H, 2×-C$\underline{H}_3$), 1-1.6 (m, 52H, 26×C$\underline{H}_2$), 2.7 [t, 4H, (ArC$\underline{H}_2$)$_2$], 3.6 [t, 4H, (ArC$\underline{H}_2$)$_2$], 5.5 (s, 2H, Ar$\underline{H}$), 6.02-6.2 (d, 2H, Ar$\underline{H}$), 7-7.7 (m, 18H, Ar$\underline{H}$), 7.8 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (39,000), 265.5 (75,000).

Elemental analysis: Found, C,69.37; H,7.78; N,2.04% $C_{72}H_{96}O_4N_2Pt$ requires C,69.28; H,7.69; N,2.24%.

Bis[N-(4″-n-decylbiphenyl)4-n-octyloxysalicylaldiminato] platinum(II), (6.e.5)

Yield 34%; m.p.224.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1585, 1460, 1410, 1380, 815 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.1-2 (m, 56H, 28×C$\underline{H}_2$), 2.6 [t, 4H, (ArC$\underline{H}_2$)$_2$], 3.6 [t, 4H, (OC$\underline{H}_2$)$_2$], 5.5 (s, 2H, Ar$\underline{H}$), 6.12-6.17 (d, 2H, Ar$\underline{H}$), 7-7.6 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (38,500), 265.5 (76,200).

Elemental analysis: Found, C,69.26; H,7.94; N,2.04% $C_{74}H_{100}O_4N_2Pt$ requires C,69.64; H,7.84; N,2.19%.

Bis[N-(4″-n-decylbiphenyl)4-n-nonyloxysalicylaldiminato] platinum(II), (6.e.6)

Yield 31%; m.p.221.5° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1470, 1410, 1380, 820 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.1-1.6 (m, 60H, 30×C$\underline{H}_2$), 2.6 [t, 4H, (ArC$\underline{H}_2$)$_2$], 3.6 [t, 4H, (OC$\underline{H}_2$)$_2$], 5.5 (s, 2H, Ar$\underline{H}$), 6.12-6.17 (d, 2H, Ar$\underline{H}$), 7-7.65 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344.5 (37,500), 266.5 (77,000).

Elemental analysis: Found, C,69.50; H,8.09; N,1.71% $C_{76}H_{104}O_4N_2Pt$ requires C,69.64; H,7.9; N,2.14%.

Bis[N-(4″-n-decylbiphenyl)4-n-undecyloxysalicylaldiminato] platinum(II), (6.e.8)

Yield 31.5%; m.p.211.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1470, 1380, 1210, 810 cm^{-1}; NMR 6 0.86 (t, 6H, 2×-C$\underline{H}_3$), 1-1.6 (m, 68H, 34×C$\underline{H}_2$), 2.6 [t, 4H, (ArC$\underline{H}_2$)$_2$], 3.6 [t, 4H, (OC$\underline{H}_2$)$_2$], 5.5 (s, 2H, Ar$\underline{H}$), 6.1-6.2 (d, 2H, Ar$\underline{H}$), 7-7.7 (m, 18H, Ar$\underline{H}$), 7.86 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (36,500), 266 (74,700).

Elemental analysis: Found, C,70.07; H,8.40; N,1.88% $C_{80}H_{112}O_4N_2Pt$ requires C,70.63; H,8.24; N,2.06%.

Bis[N-(4″-n-decylbiphenyl)4-n-dodecyloxysalicylaldiminato] platinum(II), (6.e.9)

Yield 31.5%; m.p.211.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1470, 1380, 1210, 815 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1-1.6 (m, 72H, 36×C$\underline{H}_2$), 2.6 [t, 4H, (ArC$\underline{H}_2$)$_2$], 3.6 [t, 4H, (OC$\underline{H}_2$)$_2$], 5.5 (s, 2H, Ar$\underline{H}$), 6.1-6.2 (d, 2H, Ar$\underline{H}$), 7.1-7.65 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (40,780), 266.5 (74,680).

Elemental analysis: Found, C,70.53; H,8.44; N,2.00% $C_{82}H_{116}O_4N_2Pt$ requires C,70.94; H,8.36; N,2.01%.

Bis[N-(4″-n-decylbiphenyl)4-n-octadecyloxysalicylaldiminato] platinum(II), (6.e.10)

Yield 31%; m.p.190.0° C; IR ν_{max}^{nujol} 2900, 2850, 1610, 1590, 1470, 1370, 1300, 810 cm^{-1}; NMR δ 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1-1.7 (m, 64H, 32×C$\underline{H}_2$), 2.6 [t, 4H, (ArC$\underline{H}_2$)$_2$], 3.6 [t, 4H, (OC$\underline{H}_2$)$_2$], 5.5 (s, 2H, Ar$\underline{H}$), 6.1-6.2 (d, 2H, Ar$\underline{H}$), 7.1-7.65 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 344 (37,000)) 265.5 (77,000).

Elemental analysis: Found, C,72.58; H,9.25; N,1.60% $C_{94}H_{140}O_4N_2Pt$ requires C,72.53; H,9.00; N,1.80%.

Bis[N-(4″-n-decylbiphenyl)salicylaldiminato]platinum(II), (6.f.1)

Yield 30%; m.p.212.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1470, 1380, 1280 cm^{-1}; NMR 6 0.89 (t, 6H, 2×-C$\underline{H}_3$), 1.1-1.7 (m, 32H, 16×C$\underline{H}_2$), 2.6 (t, 4H, 2×ArC$\underline{H}_2$), 6.1-6.2 (d, 2H, Ar$\underline{H}$), 7.15-7.7 (m, 18H, Ar$\underline{H}$), 8.07 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 470 (89,300), 341.5 (21,400)) 324 (26,300)) 261 (66,700).

Elemental analysis: Found, C,68.51; H,6.81; N,2.49% $C_{58}H_{68}N_2O_2Pt$ requires C,68.30; H,6.67; N,2.74%.

Bis[N-(4″-ethylbiphenyl)-4-methoxysalicylaldiminato] platinum(II), (6.f.2)

This complex was synthesised from N-(2-hydroxy-4-methoxybenzylidene)-4″-ethylphenylaniline (0.1 g, 0.3 mmol), *trans*-bis(benzonitrile) dichloroplatinum(II) (0.071 g, 0.15 mmol) and dry benzene (15 ml) by following a procedure similar to the one described for the synthesis of compound 6.e.7.

Yield (0.04 g, 31.2%); m.p.>290.0° C; IR ν_{max}^{nujol} 2920, 2850, 1615, 1470, 1380, 1210 cm^{-1}; NMR δ 1.25 (t, 6H, 2×-C$\underline{H}_3$), 2.7-2.8 (q, 4H, 2×ArC$\underline{H}_2$), 3.55 (s, 6H, 2×OC$\underline{H}_3$), 5.6 (s, 2H, Ar$\underline{H}$), 6.1-6.2 (d, 2H, Ar$\underline{H}$), 7.1-7.6 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 446.5 (12,500), 343 (11,500), 327.5 (35,000), 265.5

(74,000).

Elemental analysis: Found, C,61.99; H,4.55; N,2.85% $C_{44}H_{34}0_4N_2Pt$ requires C,62.18; H,4.00; N,3.20%.

The physical data of the cognate preparations of other bis[N-(4″-ethylbiphenyl)-4-n-alkoxysalicylaldiminato]platinum(II) complexes are given below.

Bis[N-(4″-ethylbiphenyl)-4-n-hexyloxysalicylaldiminato] platinum(II), (6.f.3)

Yield 32%; m.p.281.5° C; IR ν_{max}^{nujol} 2320, 2850, 1615, 1470, 1380, 1210 cm^{-1}; NMR δ 0.88 (t, 12H, 4×-$C\underline{H}_3$), 1.2-1.8 (m, 16H, 8×-$C\underline{H}_2$), 2.4-2.9 (q, 4H, 2×$ArC\underline{H}_2$), 3.6 (t, 4H, 2×$OC\underline{H}_2$), 5.5 (s, 2H, $Ar\underline{H}$), 6.14-6.2 (d, 2H, $Ar\underline{H}$), 7.1-7.6 (m, 18H, $Ar\underline{H}$), 7.9 (s, 2H, 2×-N=$C\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 448 (13,150), 344 (34,500), 328 (34,900), 266 (74,200).

Elemental analysis: Found, C,65.52; H,6.21; N,2.51% $C_{54}H_{60}0_4N_2Pt$ requires C,65.12; H,6.02; N,2.81%.

Bis[N-(4″-ethylbiphenyl)-4-n-dodecyloxysalicylaldiminato] platinum(II), (6.f.4)

Yield 31%; m.p.219.0° C; IR ν_{max}^{nujol} 2920, 2850, 1615, 1470, 1380, 1210 cm^{-1}; NMR 6 0.91 (t, 12H, 4×-$C\underline{H}_3$), 1.3-1.6 (m, 40H, 20×-$C\underline{H}_2$), 2.6-2.7 (q, 4H, $ArC\underline{H}_2$), 3.65 (t, 4H, 2×$OC\underline{H}_2$), 5.5 (s, 2H, $Ar\underline{H}$), 6.14-6.2 (d, 2H, $Ar\underline{H}$), 7-7.8 (m, 18H, $Ar\underline{H}$), 7.9 (s, 2H, 2×-N=$C\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 449 (13,800), 344.5 (35,000))327.5 (35,300), 265.5 (74,600).

Elemental analysis: Found, C,67.60; H,7.29; N,1.99% $C_{66}H_{84}0_4N_2Pt$ requires C,68.09; H,7.22; N,2.40%.

Bis[N-(4″-n-pentylbiphenyl)-4-methoxysalicylaldiminato]platinum(II), (6.f.5)

This complex was synthesised from N-(2-hydroxy-4-methoxybenzylidene)-4″-n-pentylphenylaniline (0.1 g, 0.26 mmol), *trans*-bis(benzonitrile)dichloroplatinum(II) (0.063 g, 0.133 mmol) and dry benzene (25 ml) following a procedure similar to the one described for the synthesis of compound 6.e.7.
Yield (0.05 g, 39.5%); m.p.260.5°C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1520, 1460, 1380, 1220 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.1-1.8 (m, 12H, 6×-C$\underline{H}_2$), 2.66 (t, 4H, 2×ArC$\underline{H}_2$), 3.5 (s, 6H, 2×OC$\underline{H}_3$), 5.6 (s, 2H, Ar$\underline{H}$), 6.13-6.14 (d, 2H, Ar$\underline{H}$), 7.0-7.7 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×-N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 447.5 (14,200), 343 (33,900), 313 (36,500), 265.5 (71,300).

Elemental analysis: Found, C,64.04; H,5.44; N,2.64% $C_{50}H_{52}O_4N_2Pt$ requires C,63.89; H,5.53; N,2.98%.

The physical data of the cognate preparations of the other bis[N-(4″-n-pentylbiphenyl)-4-n-alkoxysalicylaldiminato]platinum(II) complexes are given below.

Bis[N-(4″-n-pentylbiphenyl)-4-n-hexyloxysalicylaldiminato]platinum(II), (6.f.6)

Yield 30%; m.p.277.0° C; IR ν_{max}^{nujol} 2950, 2850, 1610, 1520, 1460, 1380, 1220 cm^{-1}; NMR 6 0.88 (t, 12H, 4×-C$\underline{H}_3$), 1.1-1.7 (m, 28H, 14×-C$\underline{H}_2$), 2.6 (t, 4H, 2×ArC$\underline{H}_2$), 3.6 (t, 4H, 2×OC$\underline{H}_2$), 5.5 (s, 2H, Ar$\underline{H}$), 6.1-6.2 (d, 2H, Ar$\underline{H}$), 7-7.6 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 448.5 (15,000), 344 (34,500), 314.5 (37,000), 266 (70,500).

Elemental analysis: Found, C,66.25; H,6.89; N,2.19% $C_{60}H_{72}O_4N_2Pt$ requires C,66.72; H,6.67; N,2.59%.

Bis[N-(4″-n-pentylbiphenyl)-4-n-dodecyloxysalicylaldiminato] platinum(II), (6.f.7)

Yield 30%; m.p. 231.5' C; IR ν_{max}^{nujol} 2950,2850, 1615, 1520, 1465, 1380, 1220 cm^{-1}; NMR 6 0.88 (t, 12H, 4×-C$\underline{H}_3$), 1.1-1.7 (m, 42H, 26×-C$\underline{H}_2$), 2.65 (t, 4H, ArC$\underline{H}_2$), 3.65 (t, 4H, 2×OC$\underline{H}_2$), 5.5 (s, 2H, Ar$\underline{H}$), 6.1-6.2 (d, 2H, Ar$\underline{H}$), 7-7.7 (m, 18H, Ar$\underline{H}$), 7.9 (s, 2H, 2×N=C$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (r) 447 (14,500))343 (34,000), 313.5 (36,500), 267 (71,000).

Elemental analysis: Found, C,69.02; H,7.81; N,1.87% $C_{72}H_{96}O_4N_2Pt$ requires C,69.28; H,7.69; N,2.24%.

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