

Chapter 3

Synthesis and mesomorphic properties of

**(i) Bis[1-(4''-n-alkylbiphenyl)-3-(phenyl)-
propane-1,3-dionato]palladium(II)**

complexes

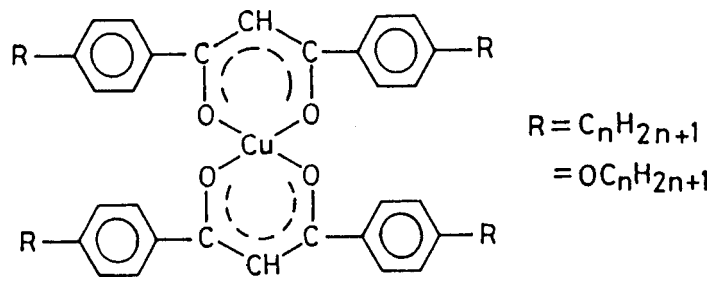
**(ii) 1-(4''-n- Alkyloxybiphenyl)-3-(phenyl)-
propane-1,3-diones and their**

copper(II) complexes

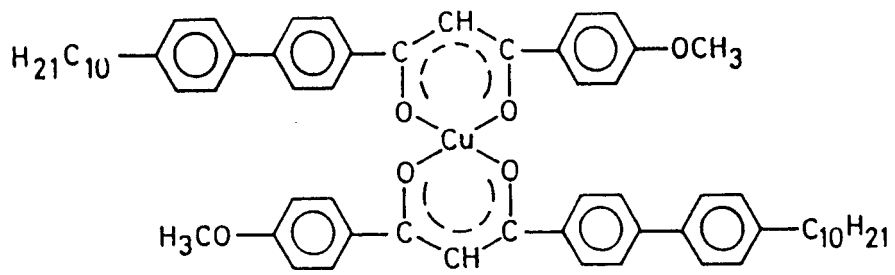
3.1 A brief account of the mesomorphic properties of metallo β -diketonates containing a biphenyl moiety

β -Diketones form flat bis-ligand complexes with a variety of metals *viz.*, Ni, Pd, Cu etc., which can take up square planar geometries. Giroud and Billard¹ and Ohta *et al.*^{2,3} have reported a number of copper β -diketonates derived from ligands containing phenyl units, *viz.*, bis[1,3-di(p-n-alkylphenyl)propane-1,3-dionato]copper(II) (3.a). These molecules have somewhat disc-like or plate-like shape rather than rod-like shape. They exhibited either columnar or discotic lamellar phases depending on the number of chains attached to the central core. Many such examples are in the literature and these as well as a series of mesomorphic bis[1-(4'-n-alkylphenyl)-3-(4'-n-alkoxyphenyl)propane-1,3-dionato]copper(II) complexes synthesised by the author,⁴ have already been discussed in the previous chapter.

When a phenyl ring was replaced by a biphenyl moiety in the ligand, the nature of the mesophase exhibited by the complexes was completely different. This is due to the change in the molecular shape from disc-like to rod-like structure. The first β -diketonato metal complex containing a biphenyl moiety was reported by Chandrasekhar *et al.*⁵ The compounds investigated were bis[1-(p-n-decylbiphenyl)-3-(p-methoxyphenyl)propane-1,3-dionato]copper(II) (3.b), and the corresponding ethoxy derivative. They exhibited a monotropic nematic phase and these were the first examples of paramagnetic nematic liquid crystals. They have also synthesised⁶ and studied the effect of different substituents on the phenyl ring for the mesophase formed without altering the chain length on biphenyl moiety in 3.b. All these complexes exhibited a monotropic nematic mesophase. They have also reported magnetic, dielectric and electron paramagnetic resonance measurements of these complexes.



3.a



3.b

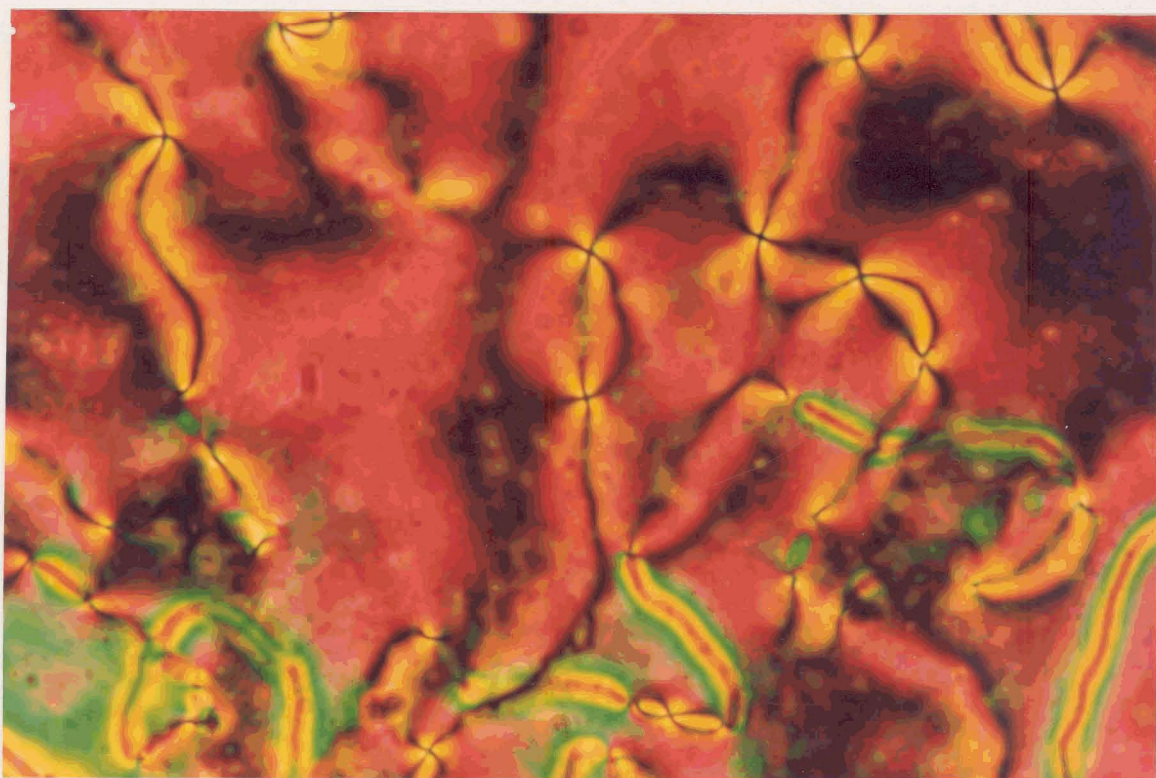


Plate 3.1: The schleiren texture of the nematic phase of complex 3.h.5 at 200°C.

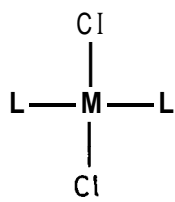
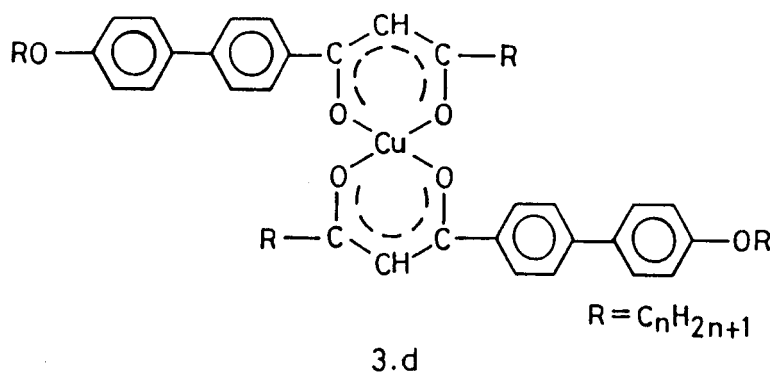
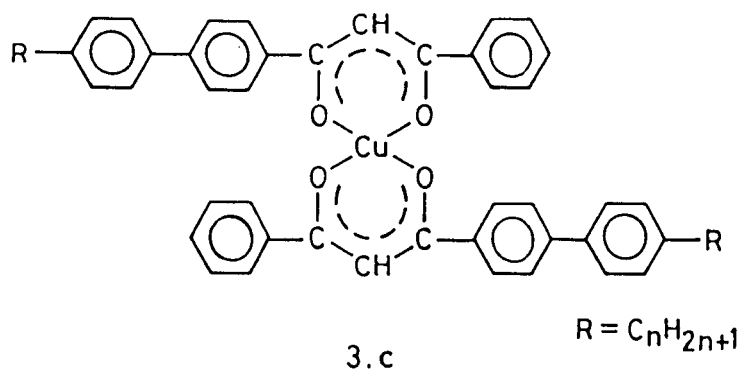
Sadashiva et al.⁷ have investigated a series of bis[1-(p-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) (3.c), and some related compounds. They have also reported some palladium(II) complexes with certain p-substituents on the phenyl ring. Once again all these complexes exhibited a metastable nematic phase. Some of the ligands used to prepare these complexes were also found to be mesogenic. Ohta et al.⁸ have reported a series of bis[1-(p-n-alkyloxybiphenyl)-3-(n-alkyl)propane-1,3-dionato]copper(II) complexes (3.d). Here, it can be seen that one of the phenyl rings has been replaced by a simple alkyl chain. All these complexes were found to be nematogenic. The ligands exhibited smectic A phase. The complexes substituted with shorter chains showed enantiotropic nematic whereas the complexes with longer chains exhibited monotropic nematic mesophase. They have stated "this monotropic nematic mesophase exhibits helical formation which can be thought to be extremely close to discotic columnar mesophase." These results were in contrast to those observed for bis[(p-n-alkyloxybiphenyl)-butane-1,3-dionato]copper(II) complexes.⁹ These complexes exhibited rectangular ordered columnar (D_{ro}) mesomorphism. In order to explain such a behaviour they argued that, in the case of 3.d, the steric hindrance on both sides of the molecule towards the neighbouring molecules may cause disturbance in the arrangement of molecules to change the mesophase from D_{ro} to nematic.

Sadashiva et al.¹⁰ have reported a series of bis[1-(p-n-dodecylbiphenyl)-3-(p-substituted biphenyl)propane-1,3-dionato]copper(II) complexes. Some of them exhibited an enantiotropic nematic mesophase; a few of the intermediate 1,3-diketones were also mesomorphic. Muhlberger and Haase¹¹ have investigated a series of bis(1-[4-(traits -4- alkylcyclohexyl)phenyl]-3-alkylpropane-1,3-dionato)copper(II) complexes. Again most of them exhibited a monotropic nematic mesophase. Thus, it

is clear that even the reduction of one of the phenyl rings to a cyclohexyl ring in biphenyl moiety did not affect the nature of the mesophase of the complexes.

Thompson *et al.*¹² have reported a number of copper(II) complexes of β -diketones containing a biphenyl moiety, which are similar to the complexes reported previously by Chandrasekhar *et al.*⁶ The former studied the effect of molecular shape on the mesophase types and transition temperatures. Most of the complexes exhibited a nematic phase. Some of the ligands used were also found to be mesogenic. Later, Thompson *et al.*¹³ studied the effect of position of a polar substituent on mesomorphic behaviour of some copper(II) complexes of β -diketones. Thompson *et al.*¹⁴ have investigated bis[1-(4'-decylbiphenyl-4-yl)-3-(4'-fluorobiphenyl-4-yl)propane-1,3-dionato]copper(II) and a series of copper(II) complexes of 1-biphenyl-3-phenylpropane-1,3-dione and 1,3-di(biphenyl)propane-1,3-dione, incorporated with polar terminal substituents *viz.*, Br, CF₃ and CN on the phenyl and biphenyl units respectively. Here, the ligands used themselves were mesogenic. They observed that many of the complexes containing polar substituents show enhanced smectic character when compared with their non-polar analogues. They have attributed the enhancement of smectic character in such compounds to the polarity of the substituents which increases the lateral interactions between the molecules leading to a layered arrangement.

Apart from metallo β -diketonates, there are some other examples of mesogenic metal complexes which also contain a biphenyl moiety. Bruce *et al.*¹⁵ have reported a number of such metal complexes (3.e), containing different metal atoms *viz.*, Pd, Pt, Rh and Au. These complexes were derived from different mesogenic organic ligands containing of a biphenyl moiety. The complexes exhibited nematic and a variety of smectic phases in the temperature range 60-200°C.



$M = Pd, Pt$

$L = H_{2n+1}C_n$ ---CN,

$H_{2n+1}C_n$ ---CN

3.2 Results and discussion

As already mentioned, a series of bis[1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) complexes (3.c), were reported exhibiting a monotropic nematic phase.⁷ In order to study the effect of different metal atoms on the nature of mesophase formed, a series of bis[1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II) complexes (3.f), were prepared. All these complexes also showed a monotropic nematic phase though the melting points were higher.

It is a usual practice to compare the effect of alkyl, alkyloxy and alkanoyloxy substituents on the nature of the mesophase. In all the above compounds [3.c and 3.f], the substitution on biphenyl ring was alkyl chain. Hence the corresponding alkyloxy derivatives, namely 1-(4''-n-alkyloxybiphenyl)-3-(phenyl)propane-1,3-diones (3.g), and their copper(II) complexes, (3.h) were prepared.

When an attempt was made to synthesise the corresponding alkanoyloxy derivatives i.e., 1-(4''-n-alkanoyloxybiphenyl)-3-(phenyl)propane-1,3-diones, from 1-(4''-hydroxybiphenyl)-3-(phenyl)propane-1,3-dione, in addition to phenolic -OH the enolic -OH group also got acylated. So the products were 1-(4''-n-alkanoyloxybiphenyl)-3-(di-alkanoyloxy)-3-(phenyl)-2-propene-1-ones, and all these diacylated compounds themselves were mesomorphic and these have been discussed in chapter 5.

4-n-Alkyl-4'-acetylbiphenyls and methyl benzoate were prepared following the standard procedures¹⁶ and these are schematically shown in figure 3.1. 4-n-Alkyl-4'-acetylbiphenyls were condensed with methyl benzoate, in the presence of sodium hydride using 1, 2-dimethoxyethane as a solvent, to get the ligand 1-(4''-n-alkylbiphenyl)-3-(phenyl)-propane-1,3-diones. Palladium complexes of these ligands were synthesised by refluxing them with palladium chloride in dry acetonitrile using potas-

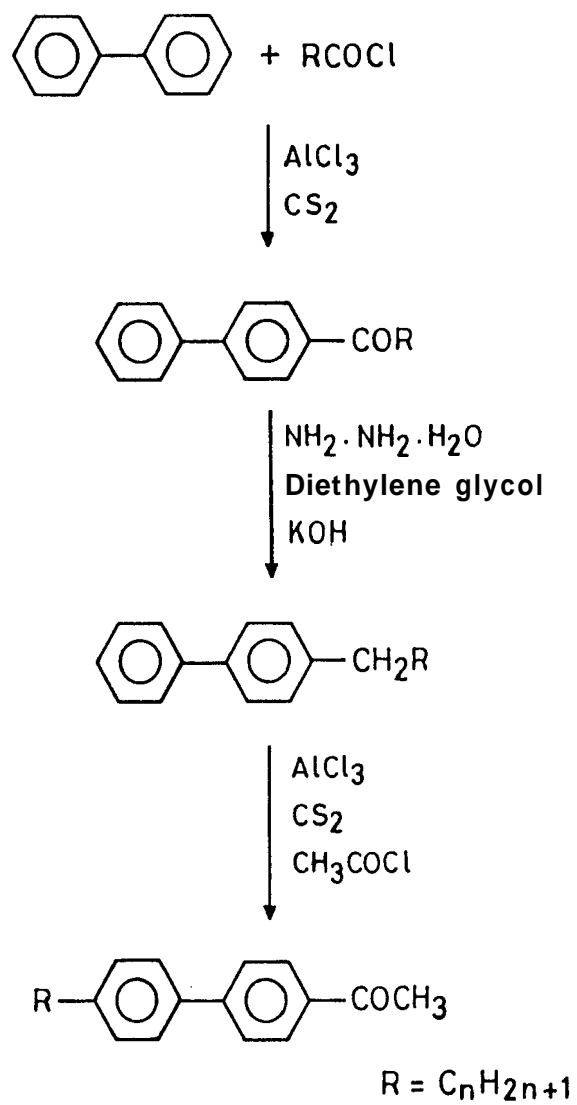


Figure 3.1

sium carbonate as a base. Schematic representation of the reactions sequence is shown in figure 3.2.

The transition temperatures for the above palladium complexes 3.f, are given in table 3.1. Compound 3.f.1 was found to be non-mesomorphic whereas the rest were all mesogenic. They exhibited a monotropic nematic mesophase. Because of their high melting points, all these complexes start decomposing as they reach their melting temperature. As can be seen from table 3.1, all the homologues supercooled to exhibit a mesophase. The nematic phase exhibited by these complexes showed a schlieren texture. Because of the thermal instability, the enthalpies of transitions could not be measured for these compounds.

Synthetic route for 4-n-alkoxy-4'-acetylbiphenyls starting from 4 - hydroxybiphenyl is shown in figure 3.3. The required β -diketones, 1-(4''-n-alkoxybiphenyl)-3-(phenyl)propane-1,3-diones and the copper(II) complexes of these β -diketones were prepared following the scheme shown in figure 3.4. Most of these ligands as well as their copper complexes were found to be mesogenic.

The transition temperatures and enthalpies of transitions for 1-(4''-n-alkoxybiphenyl)-3-(phenyl)propane-1,3-diones are given in table 3.2. As can be seen from the table, all these β -diketones except the compound 3.g.1, are found to be mesogenic. Compounds 3.g.2 and 3.g.3 are monotropic while the remaining are enantiotropic. They exhibit a focal-conic texture characteristic of smectic **A** phase with a range of about 20° for higher homologues. Some of the homologues show a crystal \rightarrow crystal transition as well. The dsc thermogram for compound 3.g.7 is shown in figure 3.5.

A similar series of β -diketones were reported by Sadashiva et al.¹⁷, where the substitution on biphenyl moiety being n-alkyl instead of n-alkoxy chain. They belong to a series of 1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-diones. Here, the

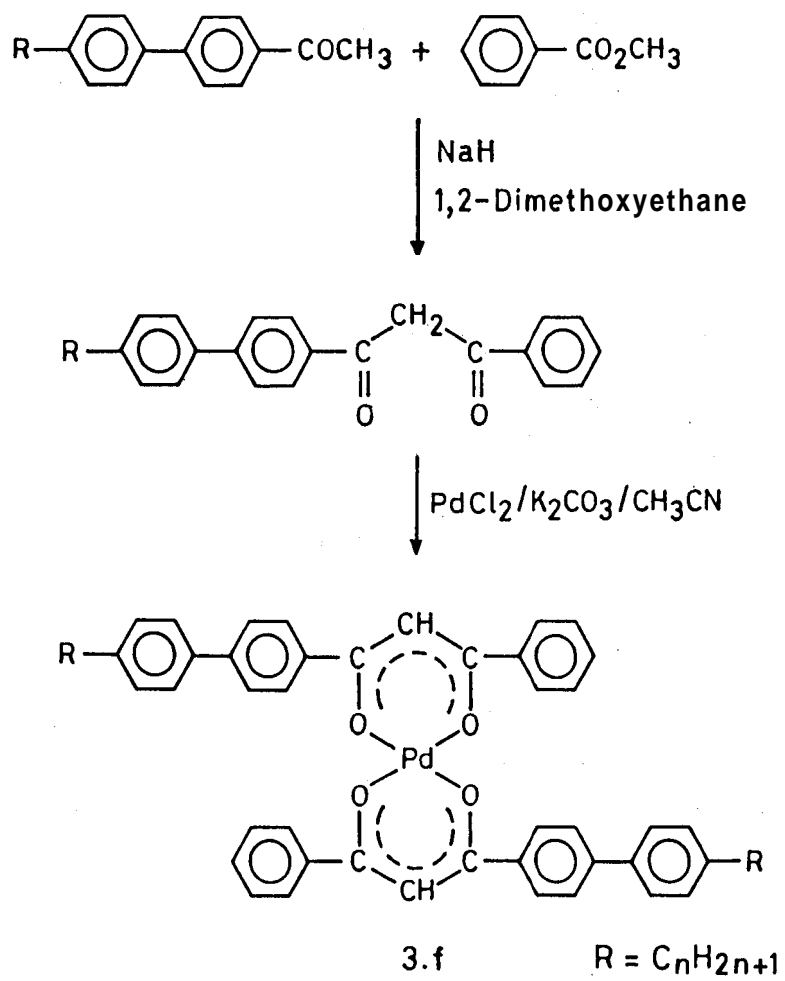


Figure 3.2

Table 3.1
Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for
bis[1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II),
3.f

Compound number	n	C	N	I
3.f.1	4	. 244.0	-	
3.f.2	5	. 254.0	(. 147.0)	.
3.f.3	6	. 230.0	(. 157.5)	.
3.f.4	7	. 230.5	(. 172.0)	.
3.f.5	8	. 214.0	(. 167.0)	.
3.f.6	9	. 209.0	(. 167.5)	.
3.f.7	10	. 203.5	(. 156.5)	.
3.f.8	11	. 194.0	(. 159.5)	.
3.f.9	12	. 194.5	(. 153.0)	.

Since the compounds begin to decompose at melting points, it was not possible to calculate enthalpies.

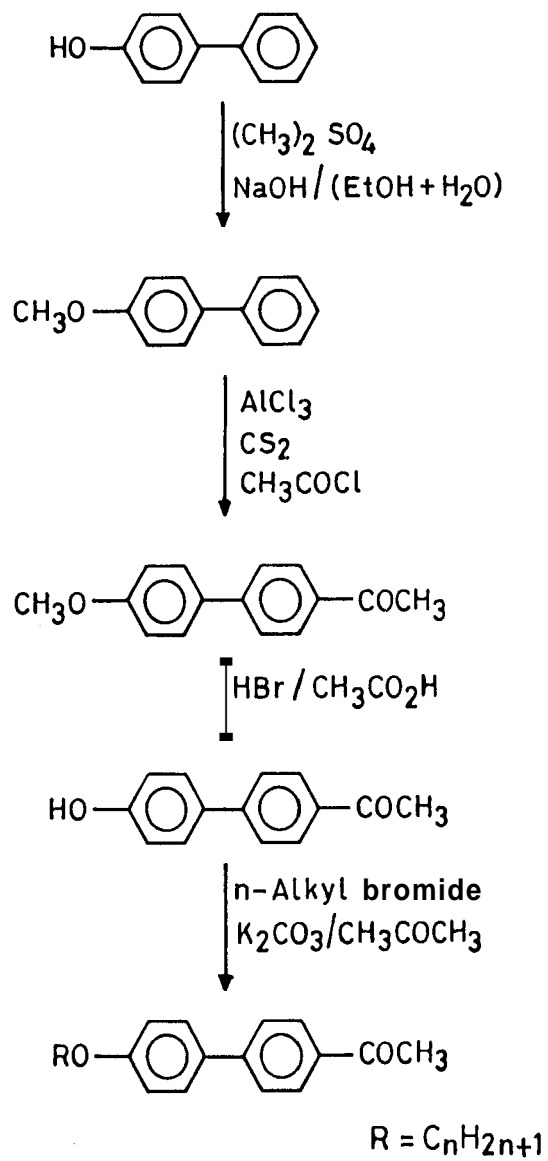


Figure 3.3

Table 3.2
 Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for
 1-(4''-n-alkyloxybiphenyl)-3-(phenyl)propane-1,3-dione,
 3.g

Compound number	n	C	S _A	Δ
3.g.1	2	125.5 7.99	-	-
3.g.2	3	139.0 8.94	(124.5)*	-
3.g.3	4	135.5 8.91	(135.0) 1.03	-
3.g.4	5	128.0 7.74	133.5 1.04	-
3.g.5	6	124.0 8.05	135.0 1.10	-
3.g.6	7 ⁺	121.5 7.93	134.5 1.13	-
3.g.7	8 ⁺	120.0 8.05	136.0 1.21	-
3.g.8	9	115.5 10.98	135.5 1.30	-
3.g.9	10 ⁺	116.5 8.25	136.5 1.30	-
3.g.10	11	118.5 12.61	136.5 1.40	-
3.g.11	12	116.5 13.05	136.0 1.33	-

⁺Compounds 3.g.6, 3.g.7 and 3.g.9 have crystal → crystal transitions at 90.0°C (1.61 kcal/mol), 87.0°C (1.31 kcal/mol) and 107.0°C (2.53 kcal/mol) respectively.

*Enthalpy could not be measured due to onset of crystallisation.

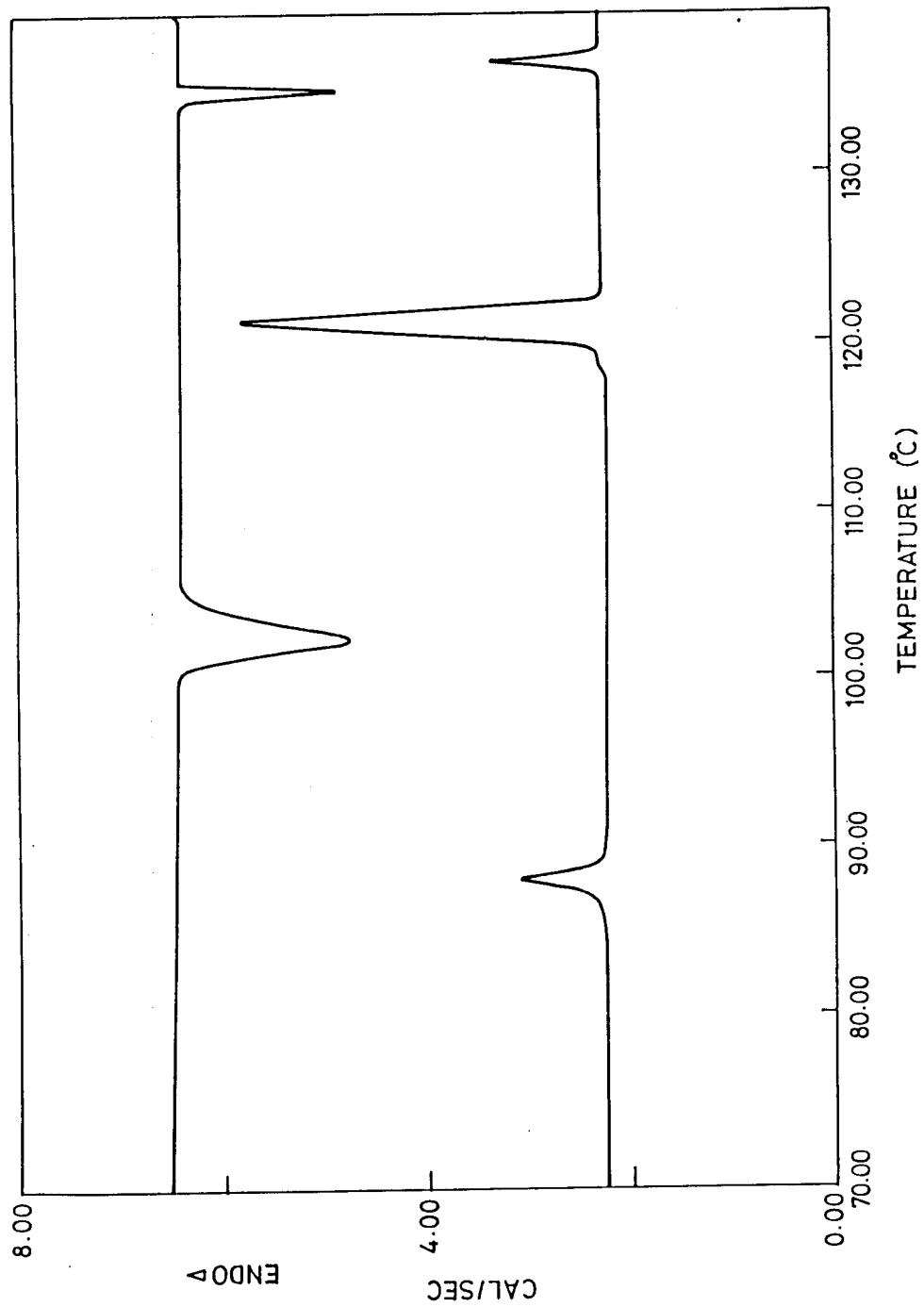


Figure 3.5: The dsc thermogram for compound 3.g.7.

lower homologues exhibited a nematic in addition to smectic A phase and from n-octyl homologue onwards the nematic phase disappeared completely. The melting points as well as clearing points of these compounds are considerably lower when compared with the corresponding alkyloxy derivatives, 3.g .

The graphic representation of the transition temperatures as a function of alkyl chain length for the β -diketones 3.g, is shown in figure 3.6. It can be seen from the plot that the $S_A \rightarrow I$ transition points follow a smooth curve.

The transition temperatures and enthalpies of transitions for bis[1-(4''-n-alkyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) chelates are given in table 3.3. All these copper complexes, except the compound 3.h.1, are mesogenic and exhibit a monotropic nematic phase. A typical texture of this phase shown by these compounds is given in plate 4.1. As can be seen from the table, the thermal stability of the mesophase goes on decreasing along the homologous series. Since the enthalpy associated with the change $N \rightarrow I$ is very small, the same could not be determined. Apart from mesomorphism, most of them exhibit polymorphism as well. Here, the transition temperatures are comparatively higher than those reported for bis[1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) complexes⁷, which exhibit a monotropic nematic mesophase.

A plot of transition temperatures versus the number of carbon atoms for the series 3.h, is shown in figure 3.7. It is seen that there is a decrease of $N \rightarrow I$ transition temperature as the chain is lengthened and these points lie on a smooth curve.

In conclusion, the following points can be noted. All the palladium(II) complexes of series 3.f, are mesogenic. They exhibit a monotropic nematic phase. All these complexes decompose as they reach their melting points. But, the corre-

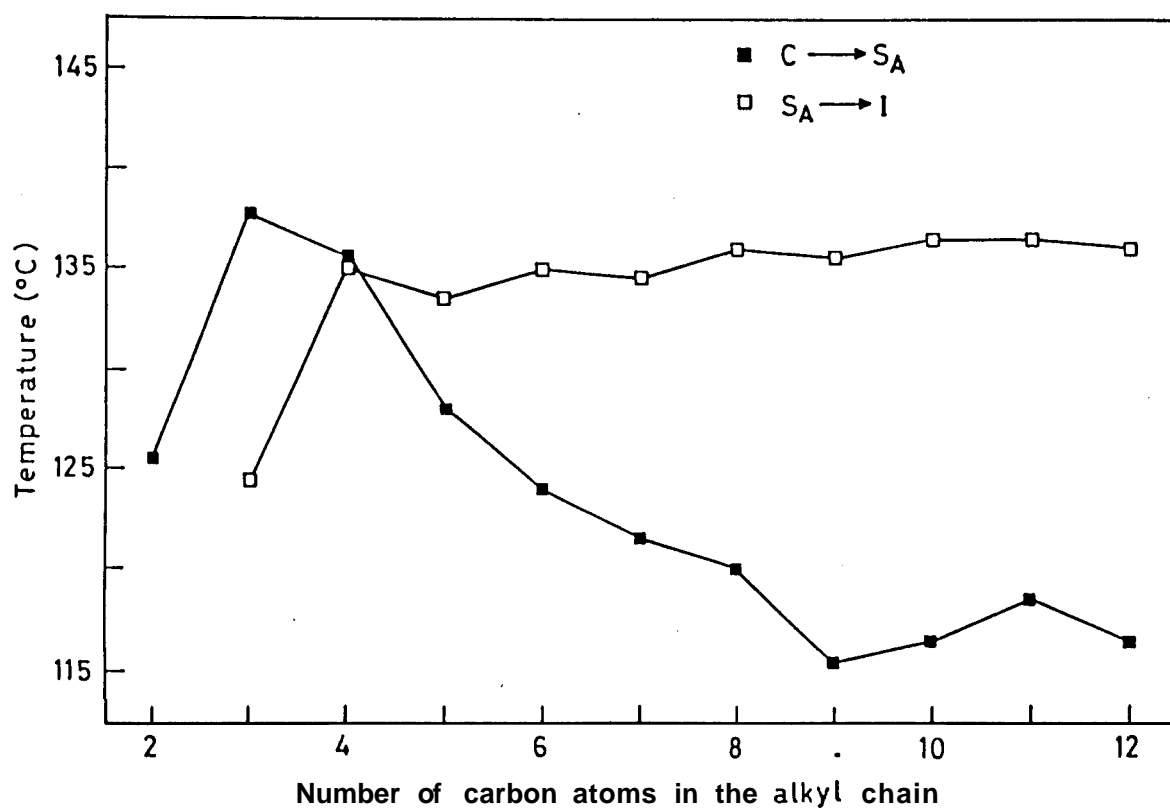


Figure 3.6: A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for series 3.g.

Table 3.3

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for bis[1-(4''-n-alkoxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II), **3.h**

Compound number	n	C ₁	C	N	I
3.h.1	4	. 238.0 <i>1.39</i>	. 263.0 <i>8.66</i>	-	.
3.h.2	5	. 229.0 <i>2.32</i>	. 260.5 <i>11.82</i>	(. 225.5)	.
3.h.3	6		. 255.5 <i>15.79</i>	(. 217.5)	.
3.h.4	7		. 247.0 <i>15.51</i>	(. 208.0)	.
3.h.5	8	. 132.5 <i>2.0</i>	. 235.0 <i>15.67</i>	(. 202.5)	.
3.h.6	9		. 222.0 <i>15.97</i>	(. 195.5)	.
3.h.7	10 ⁺	. 144.5 <i>1.41</i>	. 207.0 <i>11.43</i>	(. 189.0)*	.
3.h.8	11 ⁺	. 187.0 <i>1.93</i>	. 197.0 <i>9.12</i>	(. 183.0)*	.
3.h.9	12 ⁺	. 172.0 <i>1.36</i>	. 195.0 <i>7.7</i>	(. 177.0)'	.

⁺Compounds 3.h.7, 3.h.8 and 3.h.9 have crystal → crystal transitions at 120.5°C (1.0 kcal/mol), 133.0°C (2.69 kcal/mol) and 144.5°C (2.36 kcal/mol) respectively.

*Mesophase is highly unstable due to onset of crystallisation.

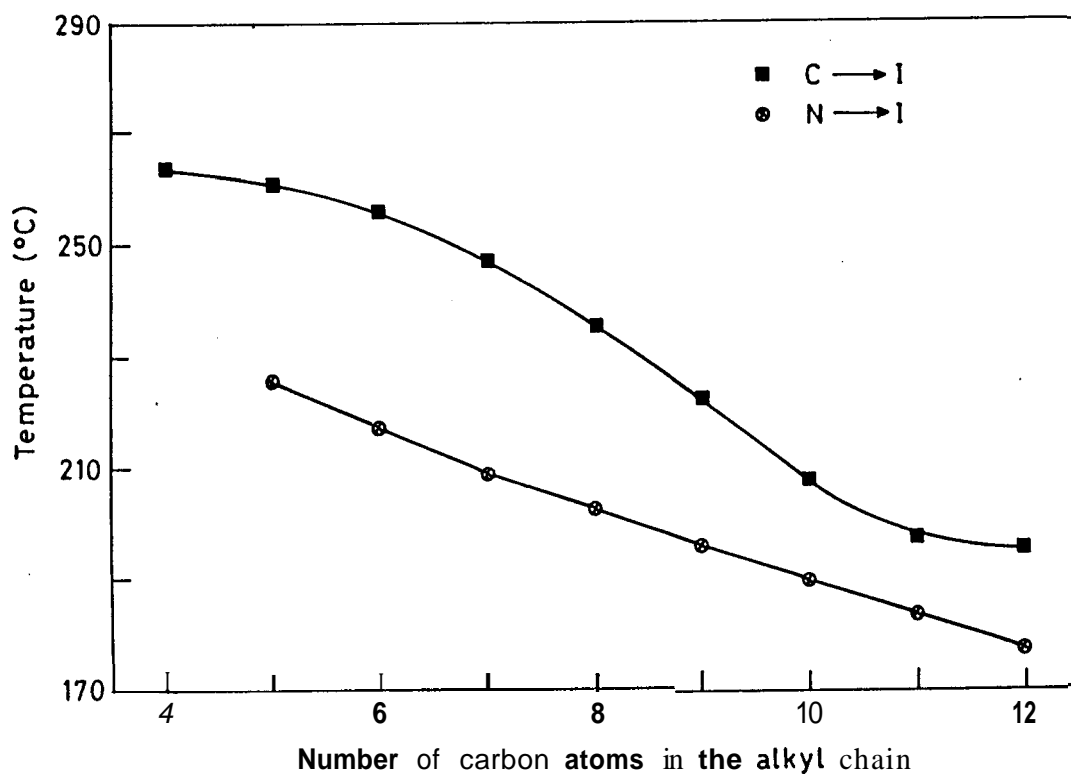


Figure 3.7: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 3.h.

sponding copper(II) complexes are thermally stable and exhibit a nematic phase. The β -diketones of series 3.g, are mesogenic and exhibit only smectic A phase. The copper(II) complexes of this series are nematogenic like their corresponding alkyl derivatives. But in the latter case, the ligands exhibited both nematic as well as smectic A phases.

3.3 Experimental

All the required 4-n-alkyl-4'-acetylbiphenyls were prepared following the standard procedures.¹⁶ Thus, biphenyl was treated with freshly distilled n-alkanoyl chlorides (Friedel-Crafts reaction), which gave the respective 4-n-alkanoylbiphenyls. These compounds were reduced by a Huang-Minlon modification of Wolff-Kishner reduction, to give the corresponding 4-n-alkylbiphenyls. Final acylation was carried out using acetyl chloride and aluminium trichloride under Friedel-Crafts reaction conditions to afford the required 4-n-alkyl-4'-acetylbiphenyls. All these compounds have been characterised by their physical constants as well as spectral data. The observed clearing points of these compounds have been given in table 3.4.

1-(4''-n-Octylbiphenyl)-3-(phenyl)propane-1,3-dione:

In a 100 ml two-necked round bottom flask fitted with a reflux condenser and a nitrogen inlet tube was placed a mixture of 4-n-octyl-4'-acetylbiphenyl (3.08 g, 0.01 mol) and methyl benzoate (1.36 g, 0.01 mol) in dry 1,2-dimethoxyethane (60 ml). This was stirred magnetically and sodium hydride (0.8 g, 0.02 mol, 60% in paraffin oil) was added and the mixture refluxed for four hours and cooled. Ice cold dilute hydrochloric acid (20 ml) was added and the mixture extracted with chloroform (2x100 ml). The combined chloroform solution was washed with water (3x100 ml) and dried (Na_2SO_4). Removal of solvent and chromatography of the residue gave

Table 3.4
Physical constants for 4-n-alkyl-4'-acetylbiphenyls,
 $C_nH_{2n+1}.Ph.Ph.COCH_3$

n	Observed clearing points (°C)	Reported clearing points (°C)	Reference
4	92.5	93.0	18
5	82.0	77.0	18
6	84.0	85.5	18
7	83.0	84.5	18
8	85.0	86.5	18
9	84.0	85.0	18
10	90.5		
11	90.0		
12	94.5		

a pale yellow product. This was crystallised from acetonitrile to constant melting point. Yield, 2.25 g, (54%); m.p. 90.5°C. (Reported¹⁷ m.p. 90.0°C).

The physical constants of the other 1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-diones are given in table 3.5.

Bis[1-(4''-n-octylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II):

A mixture of 1-(4''-n-octylbiphenyl)-3-(phenyl)propane-1,3-dione (0.824 g, 2 mmol), palladium chloride (0.135 g, 1.1 mmol), anhydrous potassium carbonate (0.114 g, 3 mmol) and dry acetonitrile (40 ml) was stirred and refluxed for eighteen hours, cooled and filtered. The yellow precipitate was collected, dissolved in chloroform (150 ml), washed with water (3x100 ml) and dried (Na₂SO₄). Removal of solvent and crystallisation of the residue from butan-2-one gave greenish yellow crystals of the desired complex.

Yield, 0.430 g, (46%); m.p. 214.0°C; IR ν_{max} : 2920, 2850, 1610, 1520, 1385 and 760 cm⁻¹; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 379 (37,100), 325 (53,800), 242 (51,000); NMR δ : 0.9 (t, 6H, 2x-CH₃), 1.0-2.0 (in, 24H, 12x-CH₂), 2.50-2.82 (t, 4H, 2xarCH₂), 6.82 (s, 2H, 2x-C=C(H)), 7.18-8.2 (m, 26H, arH).

Anal. calcd. for C₅₈H₆₂O₄Pd,

C, 74.96 ; H, 6.67 %

Found: C, 74.85 ; H, 6.76 % .

The physical data of the other bis[1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II) complexes are given below:

Bis[1-(4''-n-butylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II):

Yield, 44%; m.p. 244.0°C; IR ν_{max} : 2920, 2850, 1610, 1510, 1380 and 760 cm⁻¹; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (36,900), 325 (53,200), 242 (50,600); NMR δ : 0.96 (t, 6H,

Table 3.5

**Physical constants for 1-(4''-n-alkylbiphenyl)-3-(phenyl)propane-1,3-diones,
C_nH_{2n+1}.Ph.Ph.CO.CH₂.CO.Ph**

n	Observed m.p. (°C)	Reported m.p. (°C)	Reference
4	118.0	118.0	17
5	110.0	110.5	17
6	92.0	93.0	17
7	94.0	95.5	17
8	90.0	90.0	17
9	80.0	81.0	17
10	66.5	67.0	17
11	75.0	74.5	17
12	71.0	72.0	17

2×-CH₃), 1.0–2.0 (m, 8H, 4×-CH₂), 2.54–2.82 (t, 4H, 2×arCH₂), 6.82 (s, 2H, 2×-C=CH), 7.18–8.2 (m, 26H, arH).

Anal. calcd. for C₅₀H₄₆O₄Pd,

C, 73.49 ; H, 5.63 %

Found: C, 73.20 ; H, 5.62 % .

Bis[1-(4''-n-pentylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II):

Yield, 51%; m.p. 254.0°C; IR ν_{max} : 2920, 2850, 1610, 1510, 1380 and 760cm⁻¹; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (36,000), 326 (51,900), 241 (50,600); NMR δ : 0.94 (t, 6H, 2×-CH₃), 1.0–2.0 (m, 12H, 6×-CH₂), 2.54–2.82 (t, 4H, 2×arCH₂), 6.89 (s, 2H, 2×-C=CH), 7.18–8.2 (m, 26H, arH).

Anal. calcd. for C₅₂H₅₀O₄Pd,

C, 73.89 ; H, 5.92 %

Found: C, 73.88 ; H, 6.29 % .

Bis[1-(4''-n-hexylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II):

Yield, 47%; m.p. 230.0°C; IR ν_{max} : 2950, 2850, 1610, 1510, 1380 and 760cm⁻¹; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (37,500), 324 (54,200), 242 (52,400); NMR δ : 0.93 (t, 6H, 2×-CH₃), 1.0–2.0 (m, 16H, 8×-CH₂), 2.5–2.8 (t, 4H, 2×arCH₂), 6.85 (s, 2H, 2×-C=CH), 7.0–8.2 (m, 26H, arH).

Anal. calcd. for C₅₄H₅₄O₄Pd,

C, 74.27 ; H, 6.18 %

Found: C, 74.32 ; H, 6.37 % .

Bis[1-(4''-n-heptylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II):

Yield, 45%; m.p. 230.5°C; IR ν_{max} : 2950, 2850, 1608, 1510, 1380 and 760 cm^{-1} ;
 UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (37,400) 325 (53,600), 242 (51,300); NMR δ : 0.92 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 20H, 10 \times -CH₂), 2.51–2.8 (t, 4H, 2 \times arCH₂), 6.83 (s, 2H, 2 \times -C=CH), 7.2–8.2 (m, 26H, arH).

Anal. calcd. for C₅₆H₅₈O₄Pd,

C, 74.63 ; H, 6.44 %

Found: C, 74.78 ; H, 6.52 % .

Bis[1-(4''-n-nonylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II):

Yield, 53%; m.p. 209.0°C; IR ν_{max} : 2950, 2850, 1608, 1515, 1380 and 760 cm^{-1} ;
 UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (37,200) 325 (53,800), 241 (54,200); NMR δ : 0.89 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 28H, 14 \times -CH₂), 2.5–2.8 (t, 4H, 2 \times arCH₂), 6.83 (s, 2H, 2 \times -C=C), 7.1–8.2 (m, 26H, arH).

Anal. calcd. for C₆₀H₆₆O₄Pd,

C, 75.28 ; H, 6.90 %

Found: C, 75.12 ; H, 6.98 % .

Bis[1-(4''-n-decylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II):

Yield, 49%; m.p. 203.5°C; IR ν_{max} : 2950, 2850, 1610, 1515, 1380 and 760 cm^{-1} ;
 UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (36,400) 325 (52,200), 242 (50,000); NMR δ : 0.88 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 32H, 16 \times -CH₂), 2.52–2.8 (t, 4H, 2 \times arCH₂), 6.83 (s, 2H, 2 \times -C=C), 7.1–8.2 (m, 26H, arH).

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Anal. calcd. for $C_{62}H_{70}O_4Pd$,

C, 75.57 ; H, 7.11 %

Found: C, 75.22 ; H, 7.18 % .

Bis[1-(4'' -n- undecylbiphenyl) -3- (phenyl)propane -1,3- dionato]palladium(II):

Yield, 46%; m.p. 194.0°C; IR ν_{max} : 2950, 2850, 1610, 1510, 1380 and 760 cm^{-1} ; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (37,200), 326 (53,900), 242 (51,700); NMR δ : 0.87 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 36H, 18 \times -CH₂), 2.5–2.8 (t, 4H, 2 \times arCH₂), 6.81 (s, 2H, 2 \times -C=CH), 7.1–8.2 (m, 26H, arH).

Anal. calcd. for $C_{64}H_{74}O_4Pd$,

C, 75.85 ; H, 7.30 %

Found: C, 75.65 ; H, 7.38 % .

Bis[1-(4'' -n- dodecylbiphenyl) -3- (phenyl)propane -1,3- dionato]palladium(II):

Yield, 48%; m.p. 194.5°C; IR ν_{max} : 2950, 2850, 1610, 1510, 1380 and 760 cm^{-1} ; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 378 (36,000), 326 (52,100), 242 (50,100); NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 40H, 20 \times -CH₂), 2.5–2.8 (t, 4H, 2 \times arCH₂), 6.81 (s, 2H, 2 \times -C=CH), 7.1–8.2 (m, 26H, arH).

Anal. calcd. for $C_{66}H_{78}O_4Pd$,

C, 76.12 ; H, 7.49 %

Found: C, 75.77 ; H, 7.59 % .

4-Methyloxybiphenyl:

4-Hydroxybiphenyl (51.0 g, 0.3 mol) was placed in a 500 ml three-necked flask equipped with a pressure equalising separatory funnel, a mechanical stirrer and a reflux condenser. A solution of sodium hydroxide (12.8 g, 0.32 mol) in water (128 ml) and ethyl alcohol (100 ml) was added to it. This mixture was stirred and dimethylsulphate (37.8 g, 0.3 mol) was added dropwise to it over a period of one hour. Then the reaction mixture was refluxed for one and half hours when a clear solution was obtained. This was cooled, the solid product so obtained was filtered, washed with water, dried and crystallised from ethyl alcohol. Yield, 54.2 g (80%); m.p. 89.0°C. (Reported¹⁹ m.p. 91.0°C).

4-Methyloxy-4'-acetylbiphenyl:

In a 500 ml three-necked flask fitted with a mercury sealed stirrer, a pressure equalising separatory funnel and a reflux condenser connected to water trap through anhydrous calcium chloride guard tube, was placed a mixture of 4 - methyloxybiphenyl (18.4 g, 0.1 mol), anhydrous aluminium chloride (18.7 g, 0.14 mol) and carbon disulphide (175 ml). This was cooled in an ice-bath and while stirring freshly distilled acetyl chloride (7.8 g, 0.1 mol) was added dropwise to it. After the addition was complete the reaction mixture was stirred at 35°C for five hours and then refluxed for one hour. After the removal of carbon disulphide, the residue was poured onto a mixture of ice and concentrated hydrochloric acid. The solid formed was filtered and boiled with ether (50 ml) for fifteen minutes and the ethereal solution was decanted off. This operation was repeated thrice and then the ether insoluble portion was crystallised from iso-propanol. Yield, 14.7 g, (65%); m.p. 157.0°C. (Reported²⁰ m.p. 156.5°C).

4-Hydroxy-4'-acetylbiphenyl:

A mixture of 4-methoxy-4'-acetylbiphenyl (10.0 g, 0.044 mol), hydrobromic acid (48 %, 75 ml) and acetic acid (125 ml) was refluxed for sixteen hours. It was then poured into ice-cold water and the precipitate formed was filtered, washed with water and dried. The crude product so obtained was crystallised from ethyl alcohol. Yield, 8.9 g, (95%); m.p. 146.0°C. (Reported^{2'} m.p. 146–147°C).

4-n-Octyloxy-4'-acetylbiphenyl:

A mixture of 4-hydroxy-4'-acetylbiphenyl (4.24 g, 0.02 mol), n-octylbromide (4.63g, 0.024 mol), potassium carbonate (8.28 g, 0.06 mol) and dry acetone (100 ml) was refluxed for eighitecn hours. Then the acetone was distilled off from the reaction mixture and the residue poured onto a mixture of ice and concentrated hydrochloric acid and extracted with chloroform (3x50 ml). The combined chloroform solution was washed with water (3x100 ml) and dried (Na₂SO₄). The solvent was removed and the residue was chromatographed. The required material so obtained was crystallised from iso-propanol. Yield, 4.8 g, (74%); m.p. 95.5°C. (Reported¹⁸ m.p. 95.5°C).

The physical constants of the other 4-n-alkyloxy-4'-acetylbiphenyls are given in table 3.6.

1-(4''-n-Octyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

In a 100 ml two-necked round bottom flask fitted with a reflux condenser and a nitrogen inlet tube, was placed a mixture of 4-n-octyloxy-4'-acetylbiphenyl (3.24 g, 0.01 mol) and methyl benzoate (1.36 g, 0.01 mol) in dry 1,2-dimethoxyethane (60 ml). This was stirred magnetically and sodium hydride (0.8 g, 0.02 mol, 60% in paraffin oil) was added and the mixture refluxed for four hours and cooled. Ice-cold dilute hydrochloric acid (20 ml) was added and the mixture extracted with

Table 3.6

Physical constants for 4-n-alkyloxy-4'-acetylbiphenyls,
 $C_nH_{2n+1}O.Ph.Ph.COCH_3$

n	Observed m.p. (°C)	Reported m.p. (°C)	Reference
2	95.5	96.0	18
3	107.5	107.0	18
4	90.0	91.0	18
5	90.0	90.0	18
6	90.5	89.5	18
7	95.0	95.5	18
8	95.5	95.5	18
9	105.0	104.0	18
10	102.5	103.0	18
11	108.0	109.0	22
12	108.0	108.5	18

chloroform (2x100 ml). The combined chloroform solution was washed with water (3x100 ml) and dried (Na_2SO_4). Removal of solvent and chromatography of the residue gave a pale yellow product. This was crystallised from butan-1-ol.

Yield, 2.8 g, (65%); m.p. 120.0°C ; IR ν_{max} : 2940, 2880, 1608, 1465, 1380, 1205, 830 and 770 cm^{-1} ; NMR δ : 0.96 (t, 3H, $-\text{CH}_3$), 1.0–2.0 (m, 12H, $6 \times -\text{CH}_2$), 4.0 (t, 2H, arOCH_2), 6.8 (s, 1H, $-\text{C}=\text{CH}$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=\text{C}-\text{OH}$).

Anal. calcd. for $\text{C}_{29}\text{H}_{32}\text{O}_3$,

C, 81.30 ; H, 7.47 %

Found: C, 81.01 ; H, 7.48 % .

The physical data of the other 1-(4''-n-alkyloxybiphenyl)-3-(phenyl)propane-1,3-diones are given below:

1-(4''-Ethoxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 71%; m.p. 125.5°C ; IR ν_{max} : 2940, 2860, 1610, 1520, 1460, 1380, 815 and 765 cm^{-1} ; NMR δ : 1.5 (t, 3H, $-\text{CH}_3$), 4.2 (q, 2H, arOCH_2), 6.8 (s, 1H, $-\text{C}=\text{CH}$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=\text{C}-\text{OH}$).

Anal. calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_3$,

C, 80.23 ; H, 5.81 %

Found: C, 80.33 ; H, 5.80 % .

1-(4''-n-Propoxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 67%; m.p. 139.0°C ; IR ν_{max} : 2940, 2860, 1600, 1510, 1460, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.1 (t, 3H, $-\text{CH}_3$), 1.8 (m, 2H, $-\text{CH}_2$), 4.0 (t, 2H, arOCH_2), 6.8 (s, 1H, $-\text{C}=\text{CH}$), 7.0–8.2 (m, 13H, arH), 26.9 (s, 1H, $=\text{C}-\text{OH}$).

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Anal. calcd. for $C_{24}H_{22}O_3$,

C, 80.44 ; H, 6.14 %

Found: C, 80.17 ; H, 6.17 % .

1-(4''-n-Butyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 69%; m.p. 135.5°C; IR ν_{max} : 2940, 2860, 1600, 1460, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.2–2.0 (m, 4H, $2 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{25}H_{24}O_3$,

C, 80.64 ; H, 6.45 %

Found: C, 80.52 ; H, 6.54 % .

1-(4''-n-Pentyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 63%; m.p. 128.0°C; IR ν_{max} : 2940, 2860, 1605, 1465, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.2–2.0 (m, 6H, $3 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{26}H_{26}O_3$,

C, 80.82 ; H, 6.73 %

Found: C, 80.40 ; H, 6.87 % .

1-(4''-n-Hexyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 70%; m.p. 124.0°C; IR ν_{max} : 2940, 2860, 1605, 1510, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.1–2.0 (m, 8H, $4 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

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Anal. calcd. for $C_{27}H_{28}O_3$,

C, 81.0 ; H, 7.0 %

Found: C, 81.5 ; H, 7.11 % .

1-(4''-n-Heptyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 65%; m.p. 121.5°C; IR ν_{max} : 2950, 2870, 1600, 1510, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.1–2.0 (m, 10H, $5 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{28}H_{30}O_3$,

C, 81.15 ; H, 7.24 %

Found: C, 81.53 ; H, 7.37 % .

1-(4''-n-Nonyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 67%; m.p. 115.5°C; IR ν_{max} : 2950, 2880, 1605, 1465, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.0–2.0 (m, 14H, $7 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{30}H_{34}O_3$,

C, 81.44 ; H, 7.69 %

Found: C, 81.17 ; H, 7.85 % .

1-(4''-n-Decyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 73%; m.p. 116.5°C; IR ν_{max} : 2930, 2870, 1600, 1465, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.1–2.0 (m, 16H, $8 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

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Anal. calcd. for $C_{31}H_{36}O_3$,

C, 81.57 ; H, 7.89 %

Found: C, 81.74 ; H, 8.07 % .

1-(4''-n-Undecyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 66%; m.p. 118.5°C; IR ν_{max} : 2930, 2860, 1600, 1465, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.1–2.0 (m, 18H, $9 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{32}H_{38}O_3$,

C, 81.70 ; H, 8.08 %

Found: C, 81.30 ; H, 8.25 % .

1-(4''-n-Dodecyloxybiphenyl)-3-(phenyl)propane-1,3-dione:

Yield, 68%; m.p. 116.5°C; IR ν_{max} : 2940, 2860, 1600, 1465, 1380, 1205, 830 and 765 cm^{-1} ; NMR δ : 1.0 (t, 3H, $-CH_3$), 1.1–2.0 (m, 20H, $10 \times -CH_2$), 4.0 (t, 2H, $arOCH_2$), 6.8 (s, 1H, $-C=CH$), 7.0–8.2 (m, 13H, arH), 16.9 (s, 1H, $=C-OH$).

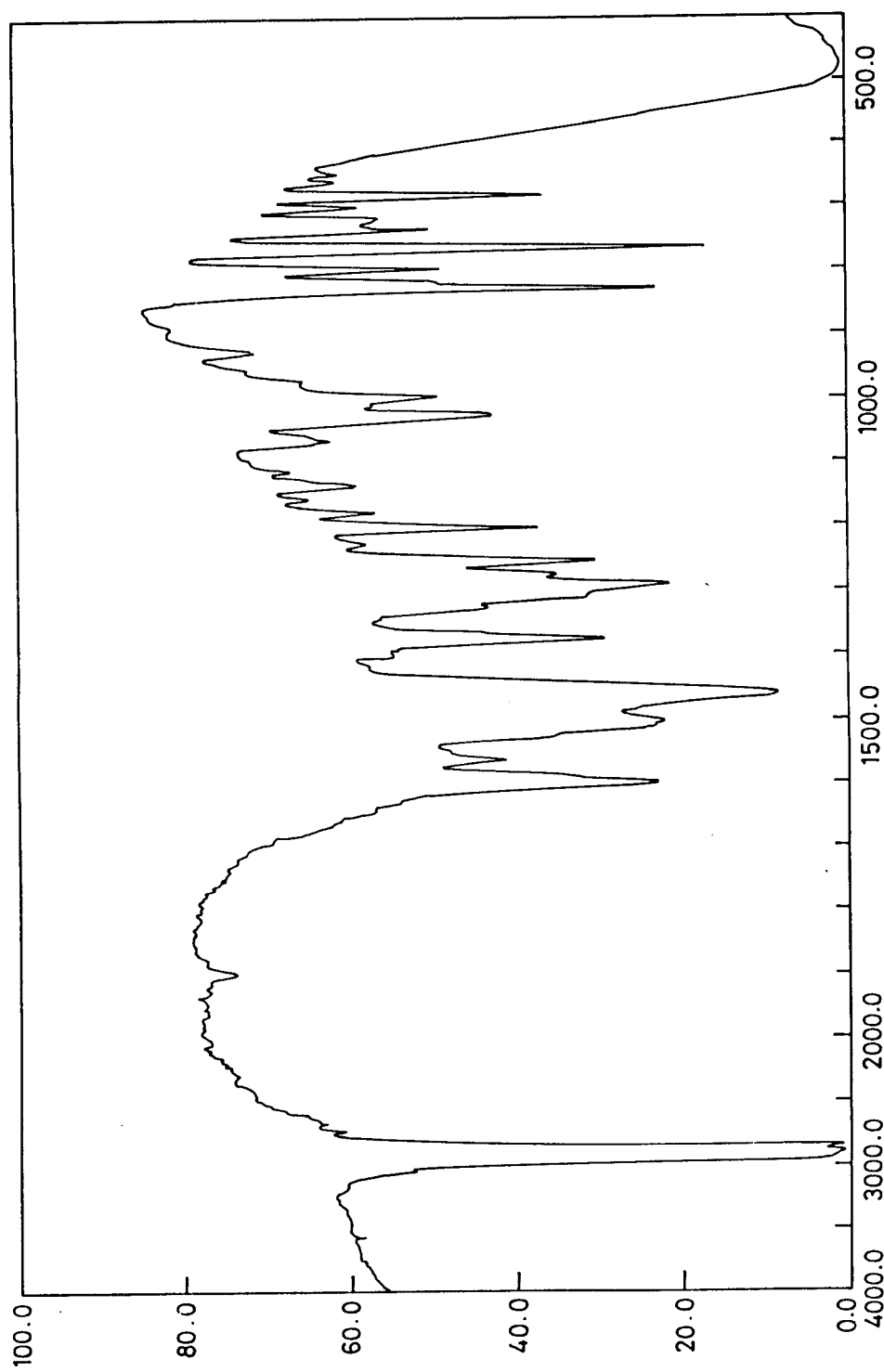
Anal. calcd. for $C_{33}H_{40}O_3$,

C, 81.81 ; H, 8.26 %

Found: C, 81.52 ; H, 8.59 % .

Bis[1-(4''-n-octyloxybiphenyl)-3-(phenyl)propane-1,3-dionato] copper(II):

A mixture of 1-(4''-n-octyloxybiphenyl)-3-(phenyl)propane-1,3-dione (0.428 g, 1 mmol) in tetrahydrofuran (5 ml), cupric chloride dihydrate (0.043 g, 0.5 mmol) in ethyl alcohol (10 ml) and potassium hydroxide (0.056 g, 1 mmol) in ethyl alcohol (20 ml) was stirred for about four hours at room temperature. The green precipitate



IR spectrum for compound 3.g.11

formed was filtered and washed with ethyl alcohol. This was dissolved in chloroform (150 ml), washed with water (4x100 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of the residue using butan-2-one afforded green shining crystals of the desired complex.

Yield, 0.21 g, (46%); m.p. 235.0°C ; IR ν_{max} : 2930, 2870, 1600, 1530, 1485, 1385, 1310, 1200, 825 and 770 cm^{-1} ; UV-Vis $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ (ϵ): 365 (73,900), 316 (36,500), 264 (31,800), 237 (36,800).

Anal. calcd. for $\text{C}_{58}\text{H}_{62}\text{O}_6\text{Cu}$,

C, 75.85 ; H, 6.75 %

Found: C, 75.42 ; H, 6.82 % .

The physical data of the other bis[1-(4''-n-alkyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) complexes are given below:

Bis[1-(4''-n-butyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 52%; m.p. 263.0°C ; IR ν_{max} : 2930, 2860, 1600, 1530, 1485, 1380, 1310, 1190, 825 and 770 cm^{-1} ; UV-Vis $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ (ϵ): 363 (70,100), 323 (39,500), 261 (32,100), 237 (38,900).

Anal. calcd. for $\text{C}_{50}\text{H}_{46}\text{O}_6\text{Cu}$,

C, 74.48 ; H, 5.71 %

Found: C, 74.81 ; H, 5.87 % .

Bis[1-(4''-n-pentyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 41%; m.p. 260.5°C ; IR ν_{max} : 2920, 2860, 1600, 1530, 1485, 1385, 1310, 1200, 825 and 770 cm^{-1} ; UV-Vis $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ (ϵ): 364 (75,100), 320 (38,000), 264 (31,300), 238 (36,300).

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Anal. calcd. for $C_{52}H_{50}O_6Cu$,

C, 74.86 ; H, 5.99 %

Found: C, 74.43 ; H, 6.05 % .

Bis[1-(4''-n-hexyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 45%; m.p. 255.5°C; IR ν_{max} : 2920, 2860, 1600, 1530, 1480, 1385, 1310, 1200, 825 and 770 cm^{-1} ; UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ): 364 (74,500), 316 (36,600), 264 (31,500), 238 (36,400).

Anal. calcd. for $C_{54}H_{54}O_6Cu$,

C, 75.21 ; H, 6.26 %

Found: C, 75.54 ; H, 6.37 % .

Bis[1-(4''-n-heptyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 46%; m.p. 257.0°C; IR ν_{max} : 2920, 2860, 1600, 1525, 1485, 1385, 1310, 1200, 825 and 770 cm^{-1} ; UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ): 365 (73,400), 317 (36,400), 264 (31,100), 237 (35,700).

Anal. calcd. for $C_{56}H_{58}O_6Cu$,

C, 75.54 ; H, 6.52 %

Found: C, 75.08 ; H, 6.52 % .

Bis[1-(4''-n-nonyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 52%; m.p. 222.0°C; IR ν_{max} : 2930, 2860, 1600, 1530, 148.5, 1385, 1310, 1200, 825 and 770 cm^{-1} ; UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ): 365 (74,600), 318 (38,000), 264 (32,100), 237 (37,200).

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Anal. calcd. for $C_{60}H_{66}O_6Cu$,

C, 76.15 ; H, 6.98 %

Found: C, 76.16 ; H, 7.04 % .

Bis[1-(4''-n-decyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 50%; m.p. 207.0°C; IR ν_{max} : 2920, 2850, 1600, 1530, 1485, 1385, 1200, 825 and 770 cm^{-1} ; UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ): 364 (74,000), 318 (39,100), 264 (32,000), 236 (37,100).

Anal. calcd. for $C_{62}H_{70}O_6Cu$,

C, 76.42 ; H, 7.19 %

Found: C, 75.94 ; H, 7.25 % .

Bis[1-(4''-n-undecyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 49%; m.p. 197.0°C; IR ν_{max} : 2920, 2860, 1590, 1530, 1485, 1380, 1200, 825 and 765 cm^{-1} ; UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ): 364 (72,700), 317 (38,400), 263 (32,300), 238 (36,300).

Anal. calcd. for $C_{64}H_{74}O_6Cu$,

C, 76.68 ; H, 7.38 %

Found: C, 76.61 ; H, 7.64 % .

Bis[1-(4''-n-dodecyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II):

Yield, 49%; m.p. 195.0°C; IR ν_{max} : 2920, 2850, 1590, 1530, 1485, 1390, 1200, 825 and 765 cm^{-1} ; UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ): 363 (69,200), 315 (37,300), 265 (33,200), 235 (40,000).

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Anal. calcd. for $C_{66}H_{78}O_6Cu$,

C, 76.93 ; H, 7.57 %

Found: C, 76.50 ; H, 7.75 % .

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