

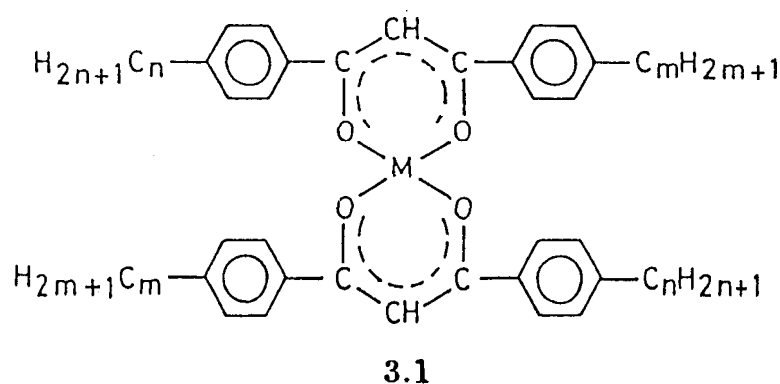
## **CHAPTER III**

**Synthesis and mesomorphic properties  
of a homologous series of**

- i) [1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)  
propane]-1,3-diones, their copper(II)  
and a few palladium(II) complexes, and**
  
- ii) [1-(4-n-alkoxybiphenyl)-3-(4'''-cyanobiphenyl)  
propane]-1,3-diones and their copper(II)  
complexes**

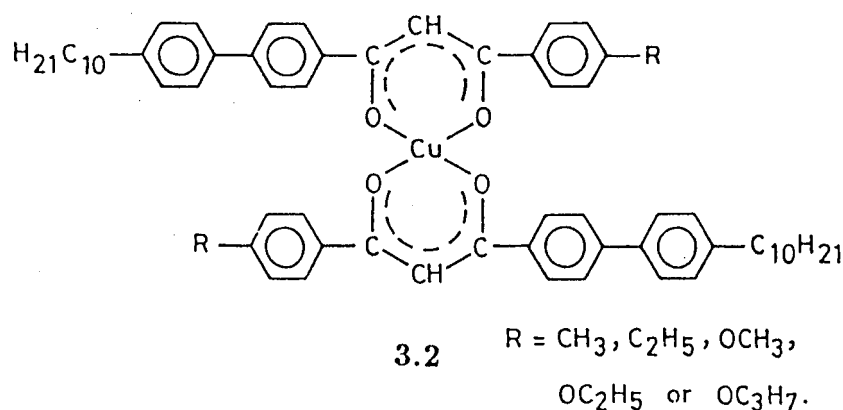
### 3.1 Introduction

Many examples of liquid crystalline substituted metal  $\beta$ -diketonates have been reported over the past few years.<sup>1</sup> Ohta *et al.*<sup>2</sup> reported the first long chain substituted bis( $\beta$ -diketonato)copper(II) complex which was synthesised in an attempt to investigate mesomorphism in a compound containing a transition metal. It did not show any mesogenic property. Around the same time Giroud and Billard<sup>3</sup> reported the first mesogenic transition metal complex (Compound 3.1), but could not identify



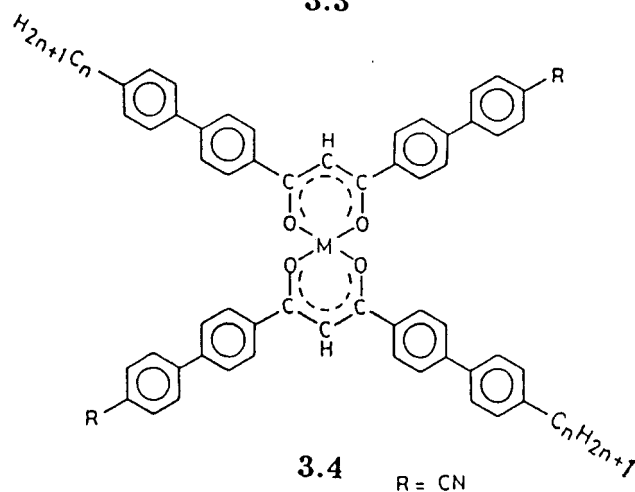
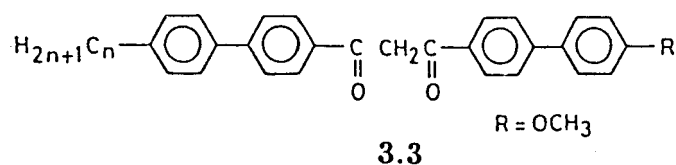
the mesophase. Ohta *et al.*<sup>4</sup> synthesised bis[1,3-di(p-n-alkoxyphenyl)propane-1,3-dionato] copper(II) complexes (same as 3.1 but with four alkoxy chains) and concluded that these have a lamellar structure and termed them *discotic lamellar phase: DL* based on x-ray diffraction and miscibility studies. Since then a large number of similar complexes with variation in chains have been reported. Many of these showed discotic mesophases.<sup>5</sup>

In 1986 Chandrasekhar *et al.*<sup>6</sup> synthesised unsymmetrical complexes of general structure 3.2 which exhibited monotropic nematic phase with a typical schlieren



texture. These represent the first examples of paramagnetic nematic liquid crystals. We<sup>7</sup> have investigated complexes with a similar structure and these have already been discussed in Chapter II. As mentioned in Chapter II the above structure can be considered as an elongated molecule with two *lateral* substituents; the alkylbiphenyl moieties forming the long molecular axis and the two substituted phenyl rings the *lateral* substituents. Thus, while the complexes with four phenyl rings (compound 3.1) mostly showed discotic lamellar mesophases, the unsymmetrical complexes with six phenyl rings (i.e., two biphenyl and two phenyl rings, compound 3.2) exhibited a monotropic nematic phase.

With a view to study the structure-property relationships in metal  $\beta$ -diketonates, we<sup>8</sup> investigated a number of complexes having a structure similar to (3.2). The *breadth* was increased by replacing the phenyl rings with a biphenyl moiety. The resulting complex (3.4) has an unusual molecular structure, in the sense that it is neither rod-like nor disc-like. In this chapter, the synthesis and mesogenic properties exhibited by a number of  $\beta$ -diketones (3.3) and their complexes of type (3.4) where  $R=CN$  have been discussed.

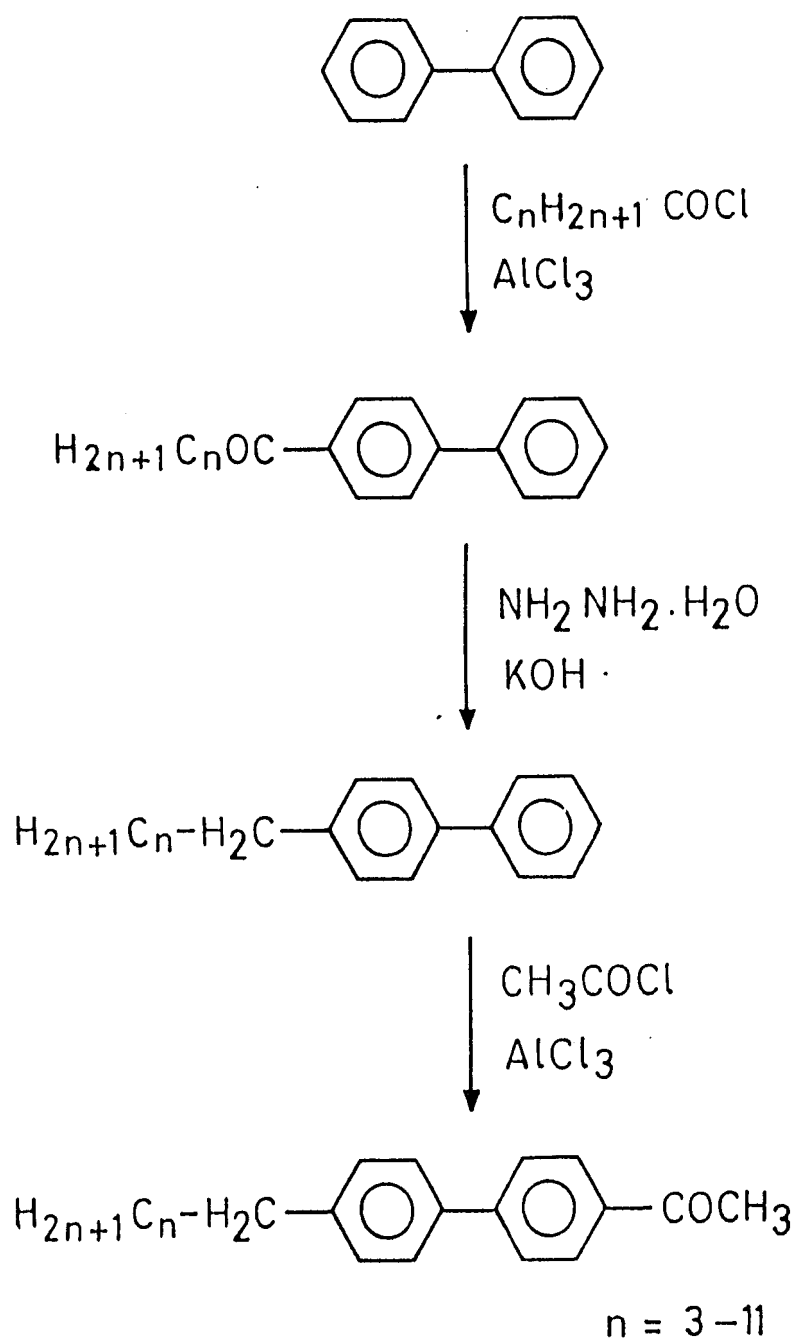


## 3.2 Synthesis

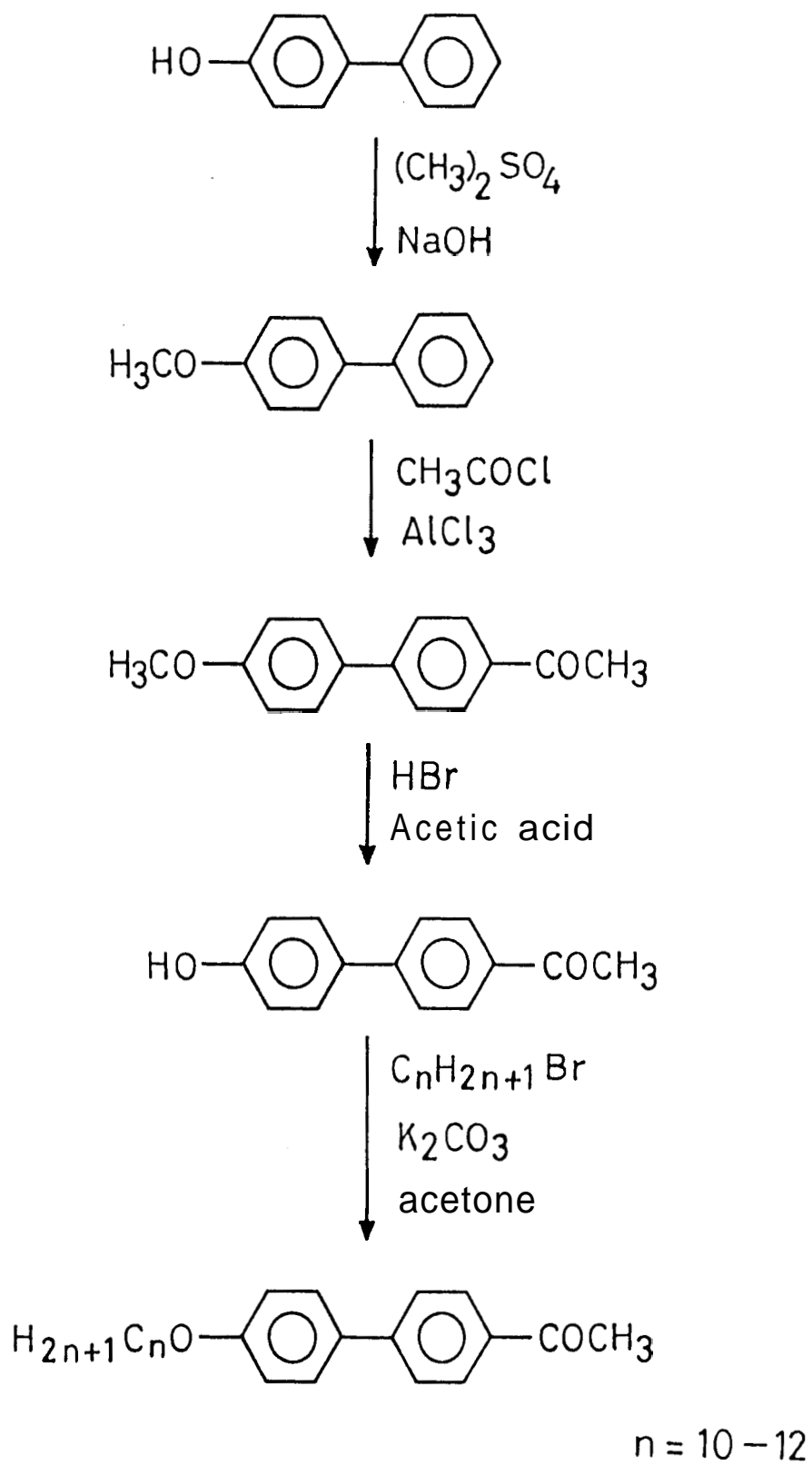
The synthesis of the ligands [1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones was carried out according to the schemes shown in figures 3.1, 3.2, 3.3 and 3.4 respectively. 4-Bromo-4'-acetylbiphenyl was prepared by acetylation of 4-bromobiphenyl using Friedel-Crafts reaction. Oxidation of 4-bromo-4'-acetylbiphenyl with ice-cold sodium hypobromite in 1,4-dioxan gave the corresponding carboxylic acid. This acid was esterified by refluxing it with ethanol in the presence of a catalytic amount of concentrated sulphuric acid for six hours. The cyanation of ethyl-4-bromobiphenyl-4'-carboxylate was carried out by refluxing it with cuprous cyanide in anhydrous dimethylformamide overnight. 4-n-Alkl-4'-acetylbiphenyl was synthesised as already described in chapter II. 4-Methoxybiphenyl was obtained in good yield by methylation of 4-hydroxybiphenyl using dimethylsulphate and sodium hydroxide in ethanol. Acetylation of 4-methoxybiphenyl afforded 4-methoxy-4'-acetylbiphenyl in good yield. This was demethylated with 48% hydrobromic acid and acetic acid to obtain 4-hydroxy-4'-acetylbiphenyl. O-Alkylation of this phenolic compound with n-decyl, n-undecyl or n-dodecylbromide by refluxing it in the presence of potassium carbonate in dry acetone gave the corresponding 4-n-alkoxy-4'-acetylbiphenyls.

The  $\beta$ -diketones were prepared by the reaction of appropriate substituted acetylbiphenyls and ethyl-4-cyanobiphenyl-4'-carboxylate with sodium hydride according to the method of Burr *et al.*<sup>9</sup>.

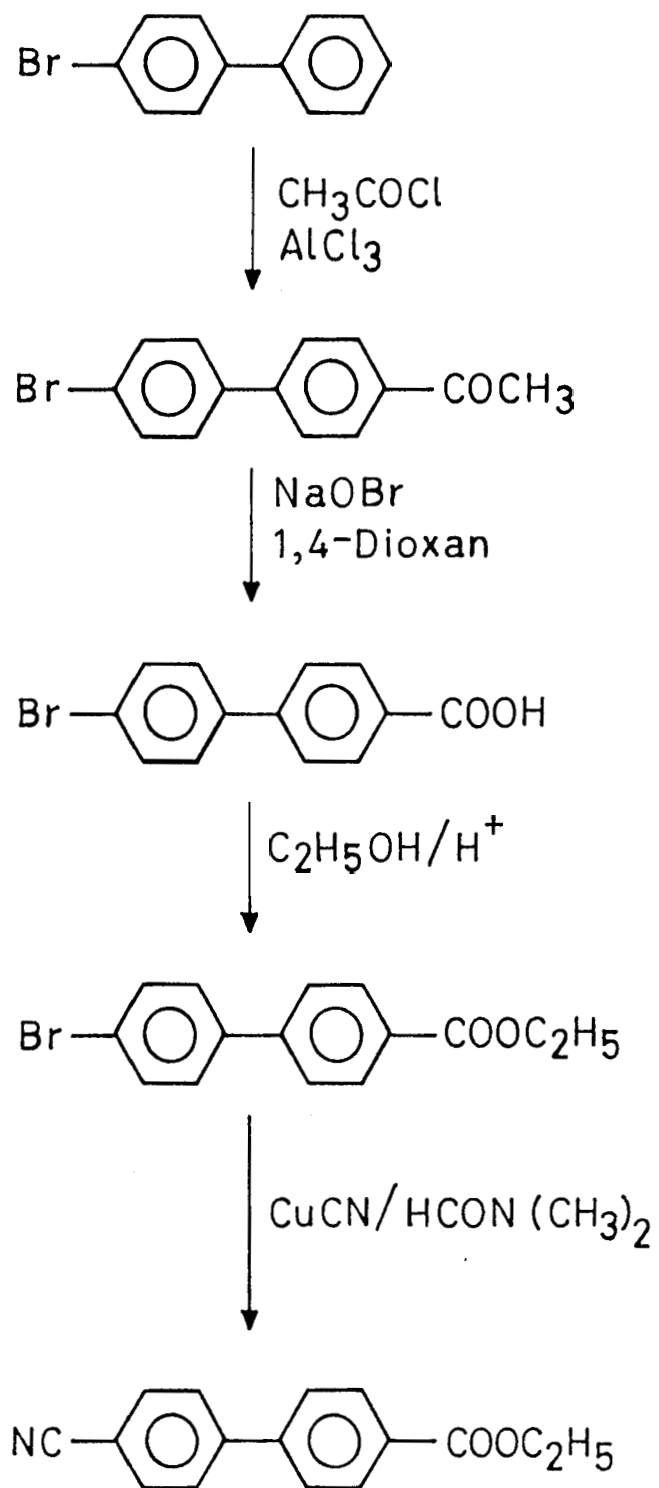
The copper(II) complexes were synthesised by the reaction of a  $\beta$ -diketone ligand with cupric chloride dihydrate in tetrahydrofuran. The crude complexes were purified by several recrystallisations from butan-2-one. The palladium(II) chelates were obtained by refluxing a mixture of the appropriate  $\beta$ -diketones, anhydrous potassium carbonate and palladium chloride in dry acetonitrile.



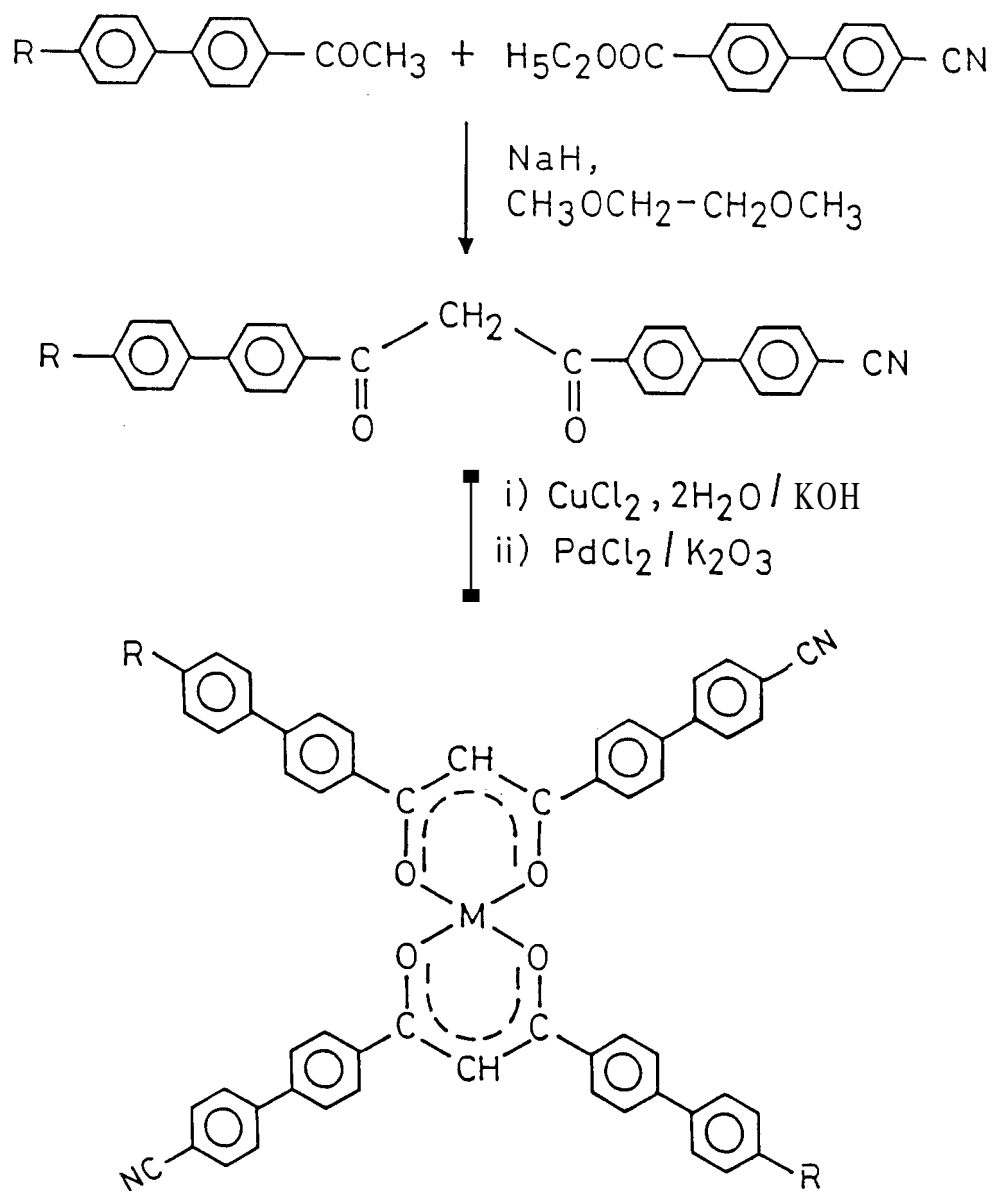
**Figure 3.1**



**Figure 3.2**



**Figure 3.3**



$R = \text{C}_n\text{H}_{2n+1}, \text{OC}_n\text{H}_{2n+1}; n = 4, 5, 6, \dots, 12$

$M = \text{Cu}$  or  $\text{Pd}$ .

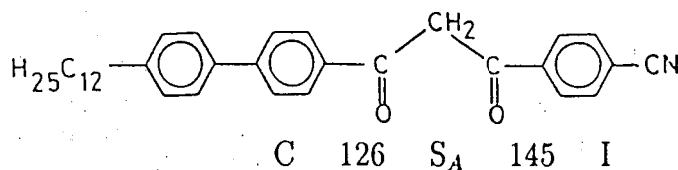
**Figure 3.4**



### 3.3 Results and Discussion

The transition temperatures and the enthalpies of transitions of [1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones are given in table 3.1. It is seen that all the nine compounds exhibit mesophases. The first four lower homologues are nematogenic. Compound 3.a.1, which is the first homologue of the series exhibits a monotropic nematic mesophase, while the remaining three are enantiotropic nematic. Smectic phase appears from the octyl derivative (3.a.5) with a small temperature range of nematic phase. The smectic phase of this and the other higher homologues show a simple fan-shaped texture. The simple fan-shaped texture of the smectic phase exhibited by these is shown in Plate 3.1. This smectic phase has been characterised as smectic A ( $S_A$ ). Higher homologues (3.a.8 and 3.a.9) exhibit a very small range of smectic C phase in addition to  $S_A$  phase. The tendency to exhibit smectic property increases as the chain is lengthened in a homologous series. This is due to increase in lateral intermolecular attractions.

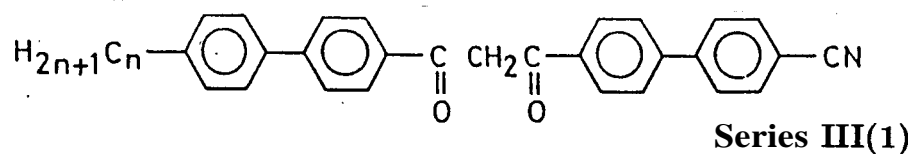
A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for [1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones is shown in figure 3.5. The  $S_A$ -I transition temperature rises with increasing length of alkyl chain and these points fall on a smooth curve. The transition temperatures and the associated enthalpies of [1-(4-n-alkoxybiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones are summarised in Table 3.2. On substituting an n-alkyl chain by an n-alkoxy chain the crystal to  $S_A$  and  $S_A$  to isotropic transition temperatures are raised by 30-34°C and 13-14°C respectively. Compound [1-(4-n-dodecylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-dione (3.a.9) can be compared with [1-(4-n-dodecylbiphenyl)-3-(4''-cyanophenyl)propane]-1,3-dione (compound 3.5) because of



3.5

**Table 3.1**

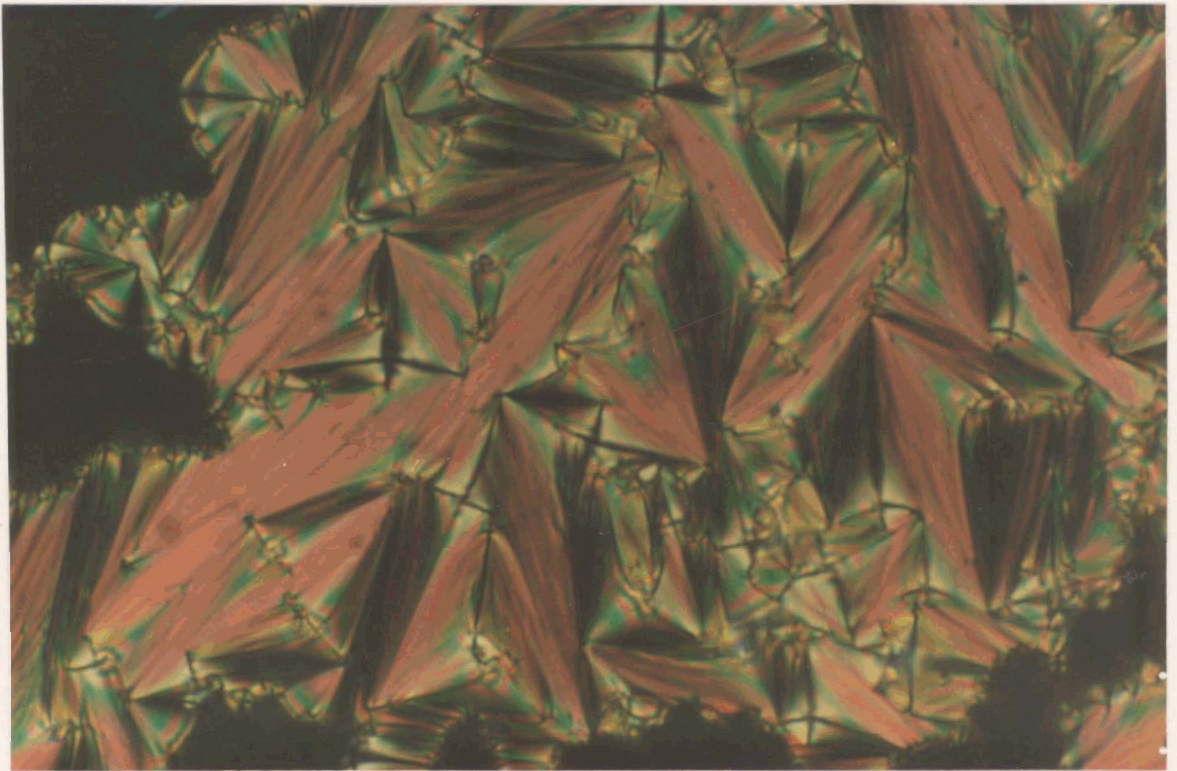
Mesomorphic transition temperatures (°C) and enthalpies (kcal/mol) of



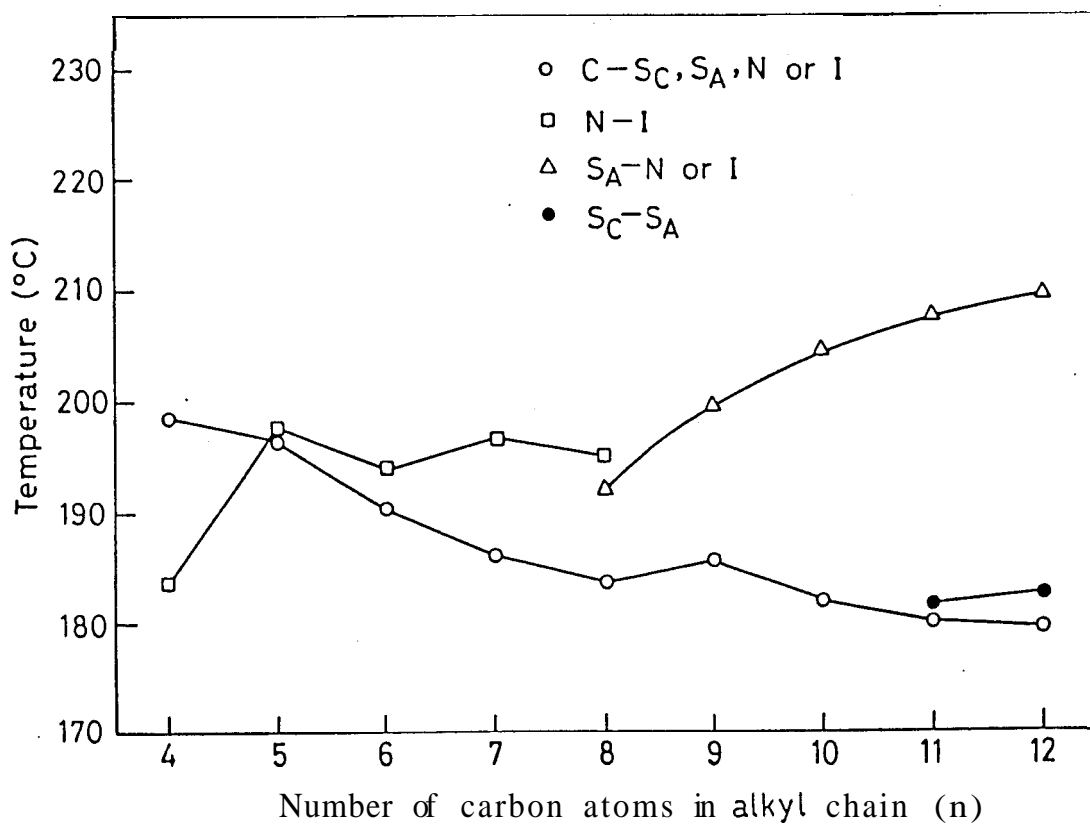
Compound number	n	C	$S_C$	$S_A$	N	I
3.a.1	4	. 198.5 6.29	-	-	(. 184.0) <sup>†</sup>	.
3.a.2	5	. 196.5 7.32	-		. 197.5 <sup>⊙</sup>	.
3.a.3	6	. 190.5 9.01	-		. 194.0 0.03	.
3.a.4	7	. 186.5 6.49	-	-	. 196.5 0.03	.
3.a.5	8	. 183.5 <b>5.49</b>	-	, 192.0 0.10	. 195.0 <b>0.03</b>	.
3.a.6	9	. 185.5 5.49	-	. 199.5 0.51	-	
3.a.7	10	. 182.0 8.28	-	. 204.0 0.51	-	
3.a.8	11	. 180.0 6.86	. 181.5 <sup>⊙</sup>	. 207.0 0.77	-	
3.a.9	12	. 179.5 6.7	. 182.5 <sup>⊙</sup>	. 209.5 1.03	-	

<sup>†</sup>The enthalpy could not be determined because of immediate onset of crystallisation.

<sup>⊙</sup>The enthalpy could not be determined due to very small temperature range of the mesophase.



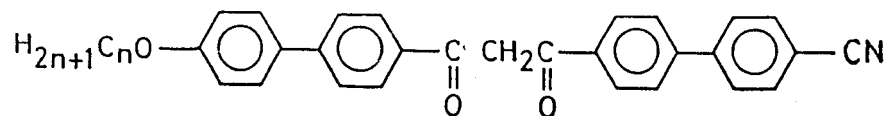
**Plate 3.1.** Focal-conic texture of the smectic A phase of compound 3.a.9 at 190°C.



**Fig.3.5.** A plot of the transition temperatures *versus* the number of carbon atoms (n) in the alkyl chain for a series of 1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)-propane-1,3-diones.

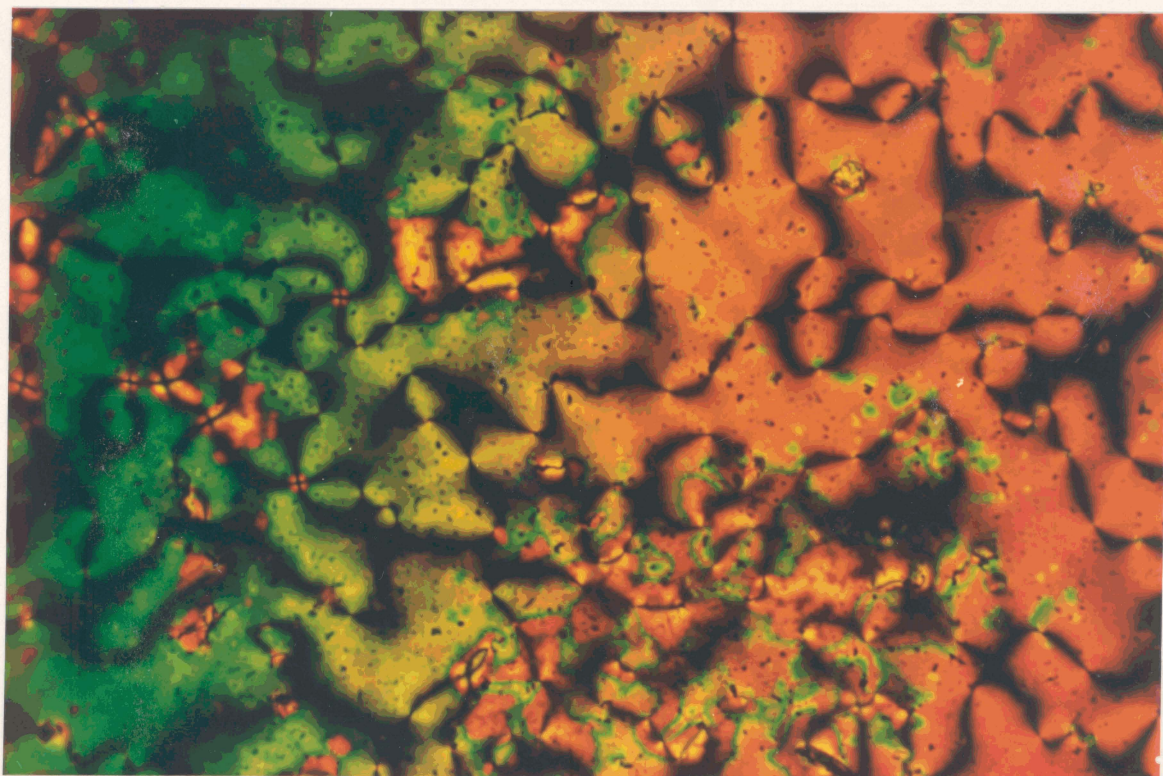
**Table 3.2**

Mesomorphic transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies (kcal/mol) of



**Series III(3)**

Compound number	n	C	$S_A$	I
3.b.1	10	.	215.5 11.95	217.0 0.5
3.b.2	11	.	212.5 8.59	220.0 0.78
3.b.3	12	.	210.0 12.51	223.0 1.18



**Plate 3.2.** Schlieren texture of the nematic phase of compound 3.c.7 at 238°C.

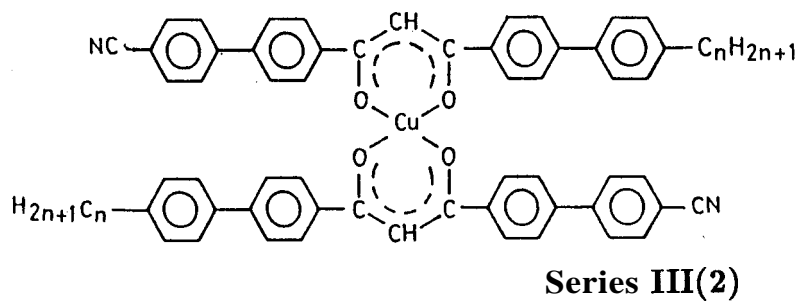
the similarity of their structures. Although a terminal cyano group lies high in the nematic group efficiency order and low in the smectic group efficiency order, it promotes a smectic A phase in these  $\beta$ -diketones. Surprisingly, as a result of extension of the core by a phenyl ring the clearing temperature has increased by  $64.5^\circ\text{C}$  and the smectic A phase is retained in the extended molecule. We have observed in the previous chapter that on extension of the core of [1-(4-n-decylbiphenyl)-3-(methyl)propane]-1,3-dione by the addition of a phenyl ring, the mesophase thermal stability decreases in the resulting compound, but the cyano-substituted ligands (compound 3.5 and 3.a.9) show a different behaviour for this trend.

It is interesting to note that in compounds which are terminally substituted by polar groups such as cyano, antiparallel correlations are commonly encountered.<sup>10</sup> Such a possibility does exist in the above mentioned cyano  $\beta$ -diketones, though none of them exhibit the reentrant phenomenon. It is also possible that antiparallel correlation leads to molecular pairing resulting in different smectic A modifications in the system. It is not clear whether such molecular pairing does occur in this system, as detailed x-ray diffraction studies have not yet been undertaken.

The transition temperatures and enthalpies of transitions of bis[1-(4-n-alkyl biphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]copper(II) complexes are given in table 3.3. The compound with the n-hexyl chain (3.c.1) is non-mesomorphic, hence the lower homologues were not prepared. All higher homologues are nematogenic. Plate 3.2 shows the schlieren texture of the nematic phase of compound 3.c.7. As can be seen they have the temperature range of nematic phase from 15.5 to  $25.5^\circ\text{C}$ . As expected the melting points are raised by about  $70\text{-}78^\circ\text{C}$  upon complexation, while the clearing points are raised by 56 to  $89^\circ\text{C}$ . The enthalpies of nematic to isotropic transitions are of the order of 0.03 to 0.08 kcal/mol. As was mentioned in the previous chapter, this low value may be due to the persistence of nematic-like short range order in the isotropic phase. In figure 3.6 the transition temperatures of these complexes have been plotted against the number of carbon atoms in the alkyl chain. It is clearly seen that the N-I transition temperatures

**Table 3.3**

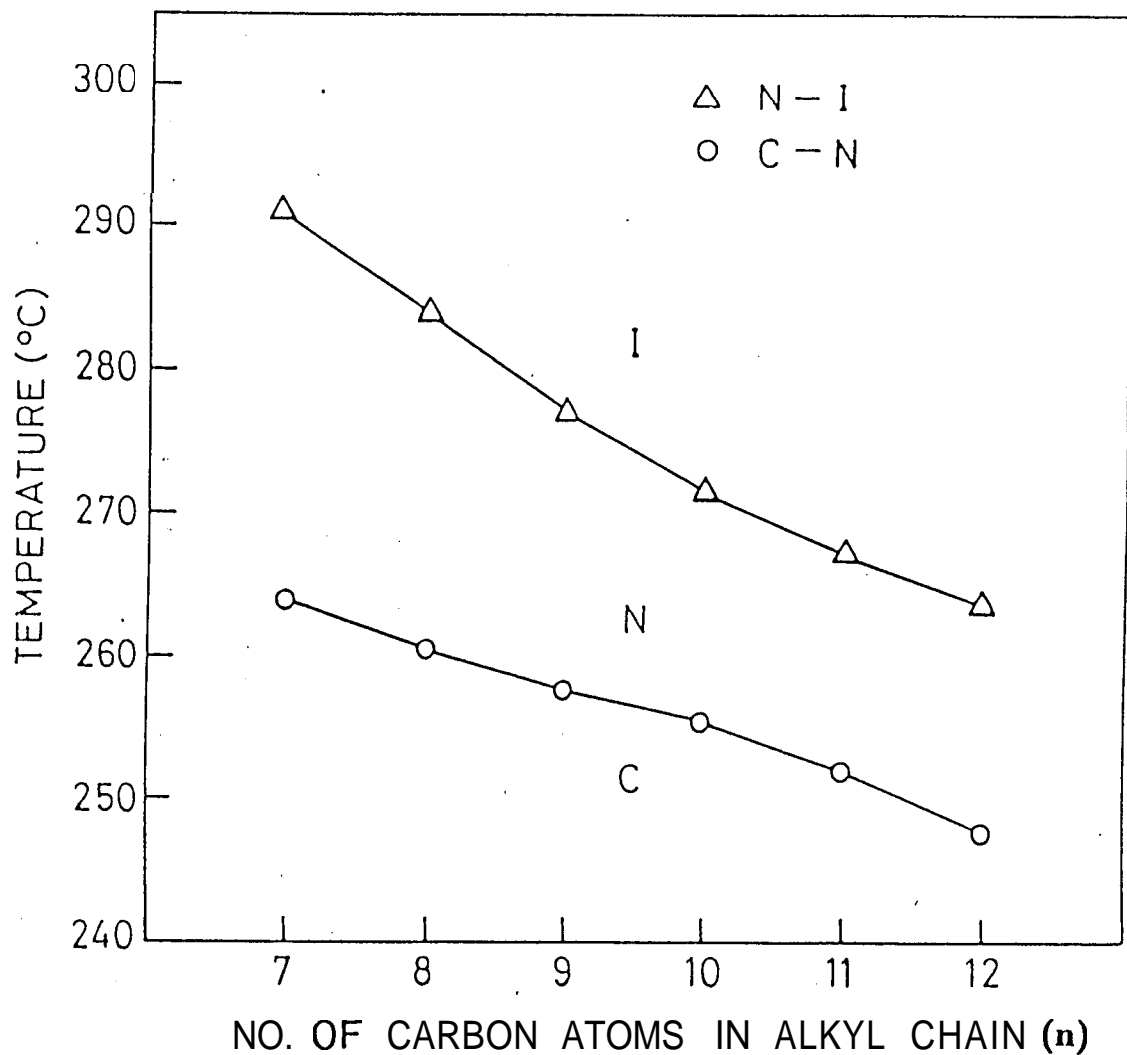
Mesomorphic transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies (kcal/mol) of



Compound number	n	C	N	I
3.c.1	6	. 286.0 5.55	-	
3.c.2	7	. 264.5 5.46	. 291.0*	.
3.c.3	8	. 260.5 9.36	. 284.0	. 0.08
3.c.4	9	. 257.5 4.99	. 277.0	. 0.10
3.c.5	10	. 255.5 11.46	. 271.5	. 0.03
3.c.6	11	. 252.0 13.66	. 267.5	. 0.07
3.c.7	12	. 250.2 5.34	. 266.0	. 0.05

\* The enthalpy could not be determined because of sample decomposition.

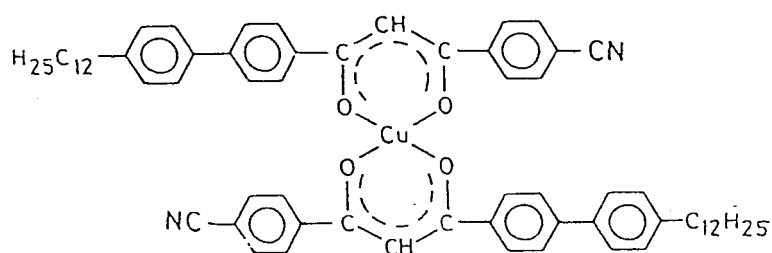




**Fig.3.6.** A plot of the transition temperatures *versus* the number of carbon atoms ( $n$ ) in the alkyl chain for a series of bis[1-(4- $n$ -alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]copper(II).

for this series decrease as the number of carbon atoms increase in the alkyl chain. Similar trend has been observed in homologous series of bis[1-(4-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) complexes, reported by Sadashiva *et al.*<sup>6</sup> The melting points for the entire series is quite high and is in the range of 250 to 264°C. It is found that replacement of alkyl chains with alkoxy chains in a few higher homologues of the above described homologous series of copper(II) complexes, the crystal to nematic temperatures decrease by 12 to 22°C, while the nematic to isotropic temperatures are raised by 7 to 10°C. The decrease in melting points for the alkoxy derivatives is contrary to what has been observed for other homologous series of compounds.<sup>11</sup> The raise of N-I transition temperature for alkoxy substituted complexes can be attributed to an increase in polarisability. The transition temperatures and heats of transitions of bis[1-(4-n-alkoxybiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]copper(II), [series III(4)] have been given in table 3.4. As compared to the ligands [series III(2)] the melting points are raised by about 18 to 24°C upon complexation while the clearing points are raised by 50 to 57°C. A plot of the transition temperatures *versus* the number of carbon atoms in the alkoxy chain is shown in figure 3.7. The melting points for these three complexes are in the range of 230-239°C and clearing points are >270°C. At such high temperatures thermal decomposition generally occur.

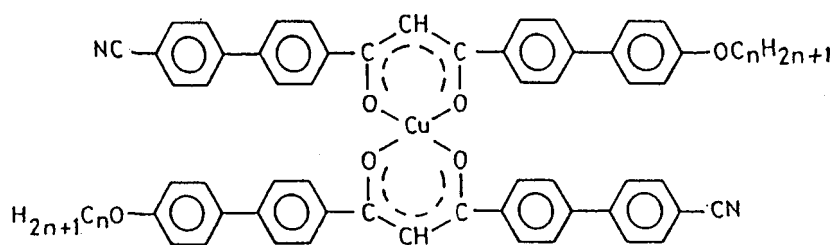
The mesogenic behaviour of bis[1-(4-n-dodecylbiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]copper(II) complex (3.c.7) can be compared with bis[1-(4-n-dodecylbiphenyl)-3-(4''-cyanophenyl)propane-1,3-dionato] copper(II) complex (compound 3.6) as the structures of the two are similar. The melting point of



C 212 (S<sub>A</sub> 197.5) I

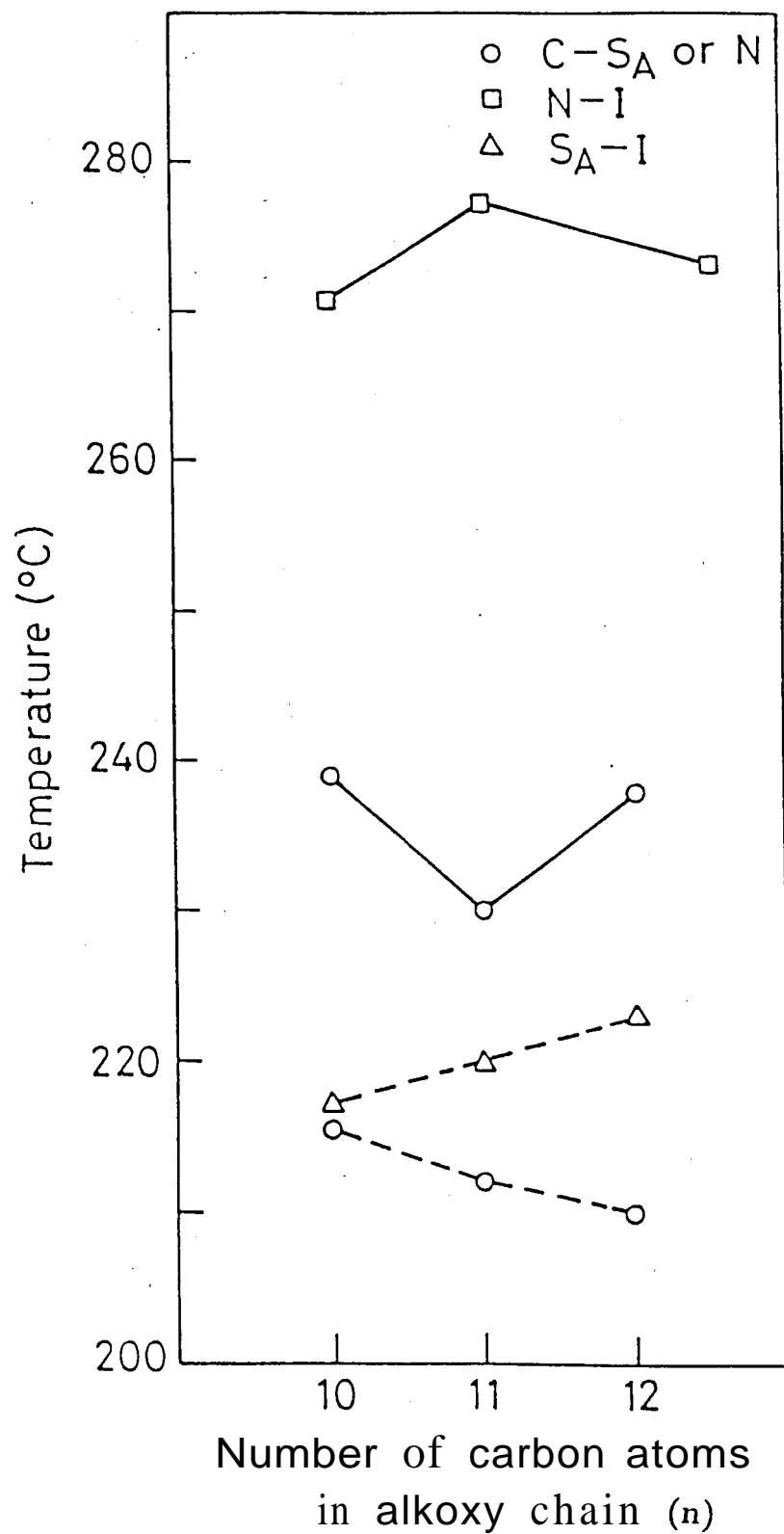
**Table 3.4**

Mesomorphic transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies (kcal/mol) of

**Series III(4)**

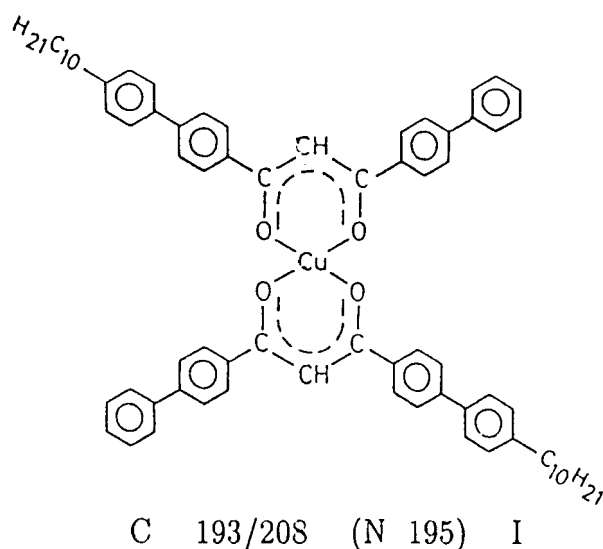
Compound number	n	C	N	I
3.d.1	10	239.0 12.78	270.5 <sup>®</sup>	.
3.d.2	11	230.0 3.94	277.0' 0.07	.
3.d.3	12	238.0 11.81	273.0' 0.09	.

<sup>®</sup> Partial decomposition takes place before clearing.



**Fig.3.7.** A plot of the transition temperatures *versus* the number the carbon atoms (n) in the alkoxy chain for series 3.b and 3d. Dotted and solid lines denote transitions for ligands (series 3b) and complexes (series 3d) respectively.

compound 3.c.7 is  $38.2^{\circ}\text{C}$  higher than that of compound 3.6. Compound 3.6 exhibited a monotropic smectic A phase and remarkably complex 3.c.7 is purely nematogenic. It is interesting to compare the mesogenic properties of bis[1-(4-n-decylbiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]copper(II) complex, (3.c.5) with bis [1-(4-n-decylbiphenyl)-3-(biphenyl-4yl) propane-1,3-dionato] copper (II) complex,<sup>12</sup> (compound 3.7) as this can be considered to be a parent compound of 3.c.5. A comparison of these two compounds shows that in 3.c.5 cyano substitution

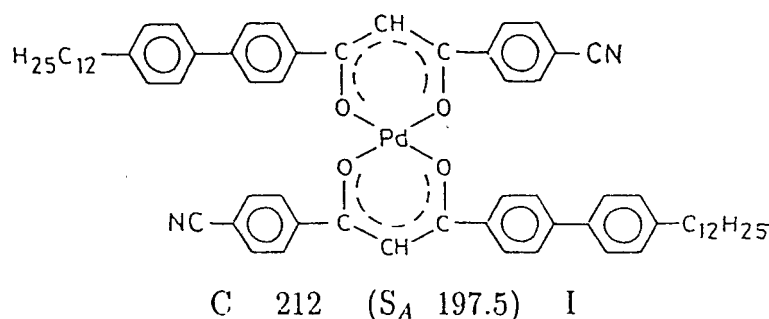


### 3.7

promotes mesogenicity and it exhibits an enantiotropic nematic phase, while the parent compound shows a monotropic nematic phase. This group also increases nematic thermal stability by  $78^{\circ}\text{C}$ , when compared with its parent compound.

We have also investigated the properties of a few palladium chelates of the above discussed  $\beta$ -diketones. The palladium(II) complexes of [1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones do not exhibit any mesomorphism. The atomic radius of palladium is  $137\text{\AA}$  which is more than that of copper ( $128\text{\AA}$ ). The polarisability of an atom increases with increase in its atomic radius.<sup>13</sup> Thus the polarisability of the complexes in this system increases the intermolecular attractions, to such

an extent that the melting point increases and no mesophase is observed. But in the system incorporating two biphenyl and two phenyl moieties, for example, bis[1-(4-n-dodecylbiphenyl)-3-(4''-cyanophenyl)propane-1,3-dionato] palladium(II) complex (compound 3.8), monotropic smectic **A** phase is observed. Thus, it is difficult to predict the influence of a metal atom on the nature of the mesophase.



### 3.8

To summarise, the above described  $\beta$ -diketones show interesting behaviour, the terminal cyano-substitution showed enhanced smectic character and has promoted mesogenicity in the compounds. The extended core of these compounds resulted in higher melting and clearing temperatures. On substituting the terminal n-alkyl chain in the compound by n-alkoxy chain, the melting and clearing points are raised and the smectic A phase of the alkoxy substituted compound became thermally more stable. Thus the introduction of alkoxy chains seems to affect only the thermal stabilities of the smectic **A** phase. This is reflected in tables 3.2 and 3.4. The copper(II) complexes of the above described alkyl and alkoxy ligands, exhibited enantiotropic nematic phase with higher clearing temperatures as compared to the corresponding complexes with six phenyl rings (two biphenyl and two phenyl moieties). On moving from six phenyl rings system (two biphenyl and two phenyl rings) to eight phenyl rings system (four biphenyl moieties) monotropic mesophases become enantiotropic. Thus the nature of the ligand is important for the formation and/or stability of a mesophase in these systems.

### 3.4 Experimental

#### 4-Bromo-4'-acetylbiphenyl

This was prepared by the Friedel-Crafts acylation on 4-bromobiphenyl. Thus, powdered aluminium chloride (32.0 g, 0.23 mol) was added to a cooled and stirred solution of 4-bromobiphenyl (46 g, 0.19 mol) in dry carbon disulphide (300 ml). To this mixture acetyl chloride (15.4 g, 0.19 mol) in dry carbon disulphide (100 ml) was added dropwise, over a period of one hour. Stirring was continued for two hours and the mixture was then refluxed for a further four hours. Carbon disulphide was removed by distillation and the residue was added slowly to ice-water and hydrochloric acid (10 ml). The organic material was extracted into ether (3x200 ml). The combined ethereal solution was washed with water until the aqueous washings were neutral and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a pale brown product, which was purified by column chromatography and the required product was recrystallised from ethyl alcohol.

Yield (42 g, 77.5%); m.p.128.4°C (Reported<sup>14</sup> 98%; m.p.127.5°C).

#### 4-Bromobiphenyl-4'-carboxylic acid

This was prepared following the procedure of Johnson et al.<sup>15</sup> A solution of sodium hypobromite was prepared by the addition of bromine (66.4 g, 0.41 mol) in small portions to an aqueous solution of sodium hydroxide (58 g, 1.45 mol in 290 ml water) maintained at 0°C. This was added to a vigorously stirred solution of 4-bromo-4'-acetylbiphenyl (23.0 g, 0.08 mol) in 1,4-dioxan (400 ml). The addition was carried out at room temperature, during one hour. The temperature of the reaction mixture was slowly raised to 55°C to ensure completion of the reaction and stirring was continued for a further 2 hours. Enough quantity of sodium metabisulphite solution was added to remove the excess of hypobromite and the mixture was diluted with water (1200 ml). About 500 ml of the liquid was distilled, the reaction

mixture was cooled and acidified with hydrochloric acid. Pale yellow precipitate so obtained was filtered and washed with water and air dried. Recrystallisation of this material from 2-methoxyethyl alcohol gave colourless crystals of 4-bromobiphenyl-4'-carboxylic acid.

Yield (23 g, 99.0%); m.p. >280.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1680, 1630, 1570, 1460, 1360, 820, 780  $\text{cm}^{-1}$ .

### **Ethyl-4-bromobiphenyl-4'-carboxylate**

A mixture of 4-bromobiphenyl-4'-carboxylic acid (23 g, 0.083 mol), concentrated sulphuric acid (5 ml) and ethyl alcohol (300 ml) was heated under reflux for 4 hours. The excess of ethyl alcohol was removed under reduced pressure and the residue poured into water. The organic material was extracted into chloroform (3×150 ml) and the combined organic extracts was washed with saturated aqueous sodium bicarbonate solution (2×100ml), water (2×200 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a pale yellow solid, which was purified by crystallisation from ethyl alcohol.

Yield (15.4 g, 61%); m.p.75.0°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 1720, 1610, 1590, 1460, 1280, 1000, 820, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  1.4(t,3H,  $-\text{CH}_3$ ), 4.2-4.6 (q, 2H,  $\text{COOCH}_2$ ), 7.12-8.2 (m,16H, ArH).

*Elemental analysis:* Found, C,59.47; H,4.18%  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}$  requires  
C,59.01; H,4.26%.

### **Ethyl-4-cyanobiphenyl-4'-carboxylate**

A mixture of ethyl-4-bromobiphenyl-4'-carboxylate (11.9 g, 0.039 mol), cuprous cyanide (7 g, 0.078 mol) and dry dimethyl formamide (200 ml) was heated under reflux for twelve hours. The cooled reaction mixture was poured into a mixture of hydrated ferric chloride (12.7 g), concentrated hydrochloric acid (3.7 ml) and water (158 ml) and the resultant mixture was heated at 60-70°C for 20 minutes. The



organic material was extracted into chloroform (3x200 ml). The combined chloroform solution was washed successively with 5N-hydrochloric acid (3x50 ml), water (5x150 ml), 10% aqueous sodium hydroxide (3x50 ml) and water until the aqueous washing was neutral and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed by distillation and the solid residue was purified by column chromatography. The required product was crystallised from petroleum ether.

Yield (6 g, 61.5%); m.p.117.0°C, IR  $\nu_{\text{max}}^{\text{nujol}}$  2900, 2850, 1720, 1610, 1460, 1250, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  1.3(t,3H, -CH<sub>3</sub>), 4.2-4.5 (q, 2H, COOCH<sub>2</sub>), 6.8-8 (m,8H, ArH).

Elemental analysis: Found, C,76.33; H,5.19; N,5.75% C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>N requires  
C,76.40; H,5.10; N,5.50%.

#### 4-Methoxybiphenyl

in a 500 ml three-necked flask fitted with a pressure equalising separatory funnel, a mechanical stirrer and a reflux condenser was placed 4-hydroxybiphenyl (40 g, 0.23 mol), a solution of sodium hydroxide (0.6 g, 0.24 mol) in water (96 ml) and ethyl alcohol (275 ml). The reaction flask was cooled in an ice-bath and while stirring dimctliyl sulphate (28.98 g, 0.23 mol) was added dropwise to it over a period of forty minutes. After the addition, the reaction mixture was refluxed for one hour when a clear solution was obtained. The reaction flask was cooled to room temperature which resulted in the precipitation of the product. It was filtered, washed with water and air dried. This was crystallised from ethyl alcohol.

Yield (40 g, 92.5%); m.p.89.5°C (Reported<sup>16</sup> m.p.91.0°C).

#### 4-Methoxy-4'-acetylbiphenyl

In a 500 ml three-necked flask equipped with a mechanical stirrer, a pressure equalising funnel and a reflux condenser carrying an anhydrous calcium chloride guard tube, a mixture of 4-methoxybiphenyl (36 g, 0.19 mol), anhydrous aluminium chloride (35.5 g, 0.26 mol) and dry carbon disulphide (200 ml) was placed. This was

stirred, cooled in an ice-bath and acetyl chloride (14.8 g, 0.19 mol) was added dropwise during thirty minutes. After the completion of addition, the reaction mixture was stirred at room temperature for 5 hours and then refluxed for one hour. Carbon disulphide was removed by distillation and the sticky residue was added slowly to a mixture of ice-water (500 ml) and hydrochloric acid (10 ml). The solid formed was filtered and boiled with ether (50 ml) for fifteen to twenty minutes and the ethereal solution was decanted off. This operation was repeated thrice and then the ether insoluble portion was crystallised from isopropanol.

Yield (28 g, 63%); m.p.157.0°C (Reported<sup>17</sup> m.p.156.5°C).

#### **4-Hydroxy-4'-acetylbiphenyl**

A mixture of 4-methoxy-4'-acetylbiphenyl (25 g, 0.11 mol), hydrobromic acid (48%, 150 ml) in glacial acetic acid (250 ml) was refluxed for ten hours. The reaction mixture was cooled and poured slowly into ice-water. The precipitate so obtained was filtered off, washed with water and air dried. This was crystallised from ethyl alcohol using activated charcoal to give crystals of 4-hydroxy-4'-acetylbiphenyl.

Yield (20 g, 85%); m.p. 206°C. (Reported<sup>18</sup> m.p. 206°C. °C).

#### **4-n-Dodecyloxy-4'-acetylbiphenyl**

This was prepared from 4-hydroxy-4'-acetylbiphenyl (4.24 g, 0.02 mol), n-dodecyl bromide (7.47 g, 0.03 mol) and potassium carbonate (4.24 g, 0.03 mol) by refluxing the mixture in dry acetone (200 ml) for 18 hours with stirring. The reaction mixture was cooled and poured very carefully into a mixture of ice-cold water (300 ml) and HCl (50 ml). This was extracted with chloroform (3x100 ml). The combined chloroform solution was washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of solvent afforded a product which was purified by column chromatography and crystallised from isopropyl alcohol.

Yield (4.5 g, 59.2%); m.p.108.4°C (Reported<sup>19</sup> m.p.108.5°C).

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

#### **4-n-Undecyloxy-4'-acetylbiphenyl**

Yield 80%; m.p.108.0°C (Reported<sup>19</sup> m.p.109.0°C).

#### **4-n-Decyloxy-4'-acetylbiphenyl**

Yield (63.5%); m.p.103.2°C (Reported<sup>20</sup> m.p.103.0°C).

The method of preparation and physical data of other 4-n-alkyl-4'-acetylbiphenyls have been discussed in Chapter II.

#### **[1-(4-n-Undecylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-dione, (3.a.8)**

A mixture of 4-n-undecyl-4'-acetylbiphenyl (1.2 g, 3.4 mmol), ethyl-4-cyanobiphenyl-4'-carboxylate (0.86 g, 3.4 mmol) and anhydrous 1,2-dimethoxyethane (150 ml) was placed in a 250 ml two-necked round bottom flask fitted with a reflux condenser, carrying a calcium chloride guard tube and an inlet tube for dry nitrogen. To this was added sodium hydride (0.2 g, 6.8 mmol, 80% dispersed in oil) and the mixture was refluxed under nitrogen for ten hours and left at room temperature overnight. The reaction mixture was then cooled in ice and while stirring, dilute hydrochloric acid was added until it became acidic. The solid material so obtained was filtered and washed with water until the washings were neutral to litmus. This was dried and chromatographed over silica gel and the pale yellow product thus obtained was recrystallised from butan-2-one several times until the melting point was constant. Yield (1.87 g, 34%); m.p. 180.0°C; IR  $\nu_{max}^{nujol}$  2900,2850, 2230, 1606, 1590, 1380, 825, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 371 (49,800), 285 (22,100), 305 (19,950), 259 (17,950); NMR  $\delta$ 0.89(t,3H, -CH<sub>3</sub>), 1-1.85(m,18H, 9×-CH<sub>2</sub>), 2.62(t,2H,ArCH<sub>2</sub>), 6.92(s,1H, -

C=CH), 7.85-8.65(m,16H, ArH), 16.9(s,1H, enol OH).

*Elemental analysis:* Found, C,84.63; H,7.45; N,2.47% C<sub>39</sub>H<sub>41</sub>O<sub>2</sub>N requires  
C,84.32; H,7.38; N,2.52%.

The physical data of the cognate preparations of other [1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones are given below.

**[1-(4-n-Butylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-dione,  
(3.a.1)**

Yield 54.5%; m.p. 198.5°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2230, 1605, 1590, 1380, 830, 790 cm<sup>-1</sup>; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 369.5 (50,200), 284.5 (22,500), 257.5 (15,900), 305 (19,200); NMR  $\delta$  0.96(t,3H, -CH<sub>3</sub>), 1.24-1.8(m,4H, 2×-CH<sub>2</sub>), 2.68(t,2H,ArCH<sub>2</sub>), 6.92(s,1H, -C=CH), 7.2-8.3(m,16H, ArH), 16.9(s,1H, enol OH).

*Elemental analysis:* Found, C,84.26; H,5.80; N,3.12% C<sub>32</sub>H<sub>27</sub>O<sub>2</sub>N requires  
C,84.02; H,5.90; N,3.06%.

**[1-(4-n-Pentylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-dione,  
(3.a.2)**

Yield 53%; m.p. 196.5°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2225, 1605, 1590, 1380, 830, 790 cm<sup>-1</sup>; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 369(50,860), 285 (23,000), 257 (15,900), 305 (19,200); NMR  $\delta$  0.87(t,3H, -CH<sub>3</sub>), 1.2-1.66(m,6H, 3×-CH<sub>2</sub>), 2.6(t,2H,ArCH<sub>2</sub>), 6.9 (s,1H, -C=CH), 7.2-8.2(m,16H, ArH), 16.8(s,1H, enol OH).

*Elemental analysis:* Found, C,79.16; H,5.60; N,2.89% C<sub>33</sub>H<sub>29</sub>O<sub>2</sub>N requires  
C,78.92; H,5.50; N,2.79%.

**[1-(4-n-Hexylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,**  
**(3.a.3)**

Yield 41%; m.p. 190.5°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2225, 1604, 1590, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 369.5 (50,930), 284.5 (22,000), 257 (16,000), 305 (19,300); NMR  $\delta$  0.96(t,3H, -CH<sub>3</sub>), 1.2-1.64(m,8H, 4×-CH<sub>2</sub>), 2.68(t,2H,ArCH<sub>2</sub>), 6.92(s,1H, -C=CH), 7.2-8.2(m,16H, ArH), 16.8(s,1H, enol OH).

*Elemental analysis:* Found, C,79.17; H,5.77; N,2.50% C<sub>34</sub>H<sub>31</sub>O<sub>2</sub>N requires  
C,79.10; H,5.80; N,2.59%.

**[1-(4-n-Heptylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,**  
**(3.a.4)**

Yield 52%; m.p. 186.5°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2230, 1605, 1590, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 369.5 (51,000), 286.5 (23,800), 257 (16,000), 305 (19,300); NMR  $\delta$  0.84(t,3H, -CH<sub>3</sub>), 1.2-1.8(m,10H, 5×-CH<sub>2</sub>), 2.68(t,2H,ArCH<sub>2</sub>), 6.92(s,1H, -C=CH), 7.16-8.32(m,16H, ArH), 16.9(s,1H, enol OH).

*Elemental analysis:* Found, C,78.98; H,5.95; N,3.17% C<sub>35</sub>H<sub>33</sub>O<sub>2</sub>N requires  
C,79.28; H,6.04; N,2.64%.

**[1-(4-n-Octylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,**  
**(3.a.5)**

Yield 50.5%; m.p. 183.5°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2230, 1605, 1585, 1380, 800, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 370.5 (49,900), 285 (24,000), 257 (16,000), 305 (19,400); NMR  $\delta$  0.84(t,3H, -CH<sub>3</sub>), 1.1-1.6(m,12H, 6×-CH<sub>2</sub>), 2.6(t,2H,ArCH<sub>2</sub>), 6.92(s,1H, -C=CH), 7.2-8.2(m,16H, ArH), 16.9(s,1H, enol OH).

*Elemental analysis:* Found, C,83.85; H,6.85; N,2.27% C<sub>36</sub>H<sub>35</sub>O<sub>2</sub>N requires  
C,84.21; H,6.82; N,2.72%.

**[1-(4-n-Nonylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,**  
**(3.a.6)**

Yield 47.5%; m.p. 185.5°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2230, 1605, 1580, 1380, 840, 790  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 370 (52,000), 285 (23,000), 258 (17,100), 305 (19,500); NMR  $\delta$  0.88(t,3H, -CH<sub>3</sub>), 1.0-1.6(m,14H, 7×-CH<sub>2</sub>), 2.68(t,2H,ArCH<sub>2</sub>), 6.9(s,1H, -C=CH), 7.1-8.2(m,16H, ArH), 16.9(s,1H, enol OH).

*Elemental analysis:* Found, C,84.67; H,7.13; N,2.58% C<sub>37</sub>H<sub>37</sub>O<sub>2</sub>N requires  
C,84.25; H,7.02; N,2.65%.

**[1-(4-n-Decylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,**  
**(3.a.7)**

Yield 37%; m.p. 182.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2230, 1605, 1590, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 370.5 (51,000), 285.5 (22,800), 305 (20,000), 258 (18,700); NMR  $\delta$  0.9(t,3H, -CH<sub>3</sub>), 1.1-1.9(m,16H, 8×-CH<sub>2</sub>), 2.6(t,2H,ArCH<sub>2</sub>), 6.9(s,1H, -C=CH), 7.2-8.4(m,16H, ArH), 16.9(s,1H, enol OH).

*Elemental analysis:* Found, C,84.20; H,7.29; N,2.29% C<sub>38</sub>H<sub>39</sub>O<sub>2</sub>N requires  
C,84.28; H,7.20; N,2.58%.

**[1-(4-n-Dodecylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,**  
**(3.a.9)**

Yield 44%; m.p. 179.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2230, 1605, 1590, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 370 (49,800), 285 (22,000), 305 (19,950), 259 (17,950); NMR  $\delta$  0.88(t,3H, -CH<sub>3</sub>), 1.2-1.6(m,20H, 10×-CH<sub>2</sub>), 2.66(t,2H,ArCH<sub>2</sub>), 6.94(s,1H, -C=CH), 7.2-8.14(m,16H, ArH), 16.9(s,1H, enol OH).

*Elemental analysis:* Found, C,84.41; H,7.66; N,2.13% C<sub>40</sub>H<sub>43</sub>O<sub>2</sub>N requires  
C,84.30; H,7.55; N,2.13%.

**[1-(4-n-Undecyloxybiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,  
(3.b.2)**

This compound was prepared from 4-n-undecyloxy-4'-n-acetylbiphenyl (2.81 g, 7.6 mmol), ethyl-4-cyanobiphenyl-4'-carboxylate (1.93 g, 7.6 mmol), dry 1,2-dimethoxyethane (100 ml) and sodium hydride (0.45 g, 15 mmol, 80% dispersion in oil) using a procedure similar to the one described for the preparation of compound 3.a.8.

Yield (1.5 g, 34%); m.p. 216.0°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2250, 1608, 1580, 1200, 825, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 375 (49,800), 280 (25,950), NMR  $\delta$  0.88(t,3H, -CH<sub>3</sub>), 1.2-2.16(m,18H, 9×-CH<sub>2</sub>), 4.07 (t,2H, -OCH<sub>2</sub>), 6.85(s,1H, -C=CH), 7.0-8.25(m,16H, ArH), 16.9(s,1H, enol OH).

Elemental analysis: Found, C,81.83; H,7.26; N,2.10% C<sub>39</sub>H<sub>41</sub>O<sub>3</sub>N requires  
C,81.96; H,7.26; N,2.10%.

The physical data of the cognate preparations of other [1-(4-n-alkoxybiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones are given below.

**[1-(4-n-Decyloxybiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dione,  
(3.b.1)**

Yield 46.5%; m.p. 215.5°C; IR  $\nu_{max}^{nujol}$  2920, 2870, 2250, 1602, 1590, 1200, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 375.0 (49,000), 279.5 (31,200); NMR  $\delta$  0.88(t,3H, -CH<sub>3</sub>), 1.27-2.17(m,16H, 8×-CH<sub>2</sub>), 4.01 (t,2H, -OCH<sub>2</sub>), 6.9(s,1H, -C=CH), 7.0-8.1(m,16H, ArH), 16.9(s,1H, enol OH).

Elemental analysis: Found, C,82.33; H,7.07; N,2.28% C<sub>38</sub>H<sub>39</sub>O<sub>2</sub>N requires  
C,81.86; H,7.00; N,2.51%.

**[1-(4-n-Dodecyloxybiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-dione,  
(3.b.3)**

Yield 55.5%; m.p. 210.0°C; IR  $\nu_{max}^{nujol}$  2920, 2850, 2250, 1602, 1590, 1200, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 375 (52,000), 283 (25,200), NMR  $\delta$  0.92(t,3H, -CH<sub>3</sub>), 1.1-1.9(m,20H, 10×-CH<sub>2</sub>), 4.0 (t,2H, -OCH<sub>2</sub>), 6.8(s,1H, -C=CH), 7-8.2(m,16H, ArH), 16.9(s,1H, enol OH).

Elemental analysis: Found, C,81.95; H,7.43; N,2.21% C<sub>40</sub>H<sub>43</sub>O<sub>3</sub>N requires  
C,82.05; H,7.35; N,2.39%.

**Bis[1-(4-n-undecylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3-dionato  
copper(II), (3.c.6)**

To a stirred solution of [1-(4-n-Undecylbiphenyl)-3-(4'''-cyanobiphenyl) propane]-1,3 dione (0.2 g, 0.36 mmol) in warm THF (50 ml) was added a solution of potassium hydroxide (0.02 g, 0.36 mmol) in ethyl alcohol (8 ml). To this was added a solution of cupric chloride dihydrate (0.031 g, 0.18 mmol) in ethyl alcohol (8 ml). The reaction mixture turned dark-green in colour. This was refluxed for four hours and cooled. The greenish precipitate was filtered and washed with ethanol. This precipitate was dissolved in chloroform (100 ml) and washed with water (3x75 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of solvent and crystallisation of the residue repeatedly from butan-2-one gave green shining crystals of the complex.

Yield (0.01 g, 40%); m.p. 252.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2225, 1610, 1580, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 371 (69,600), 307 (54,900), 242 (34,800).

Elemental analysis: Found, C,84.63; H,7.45; N,2.47% C<sub>78</sub>H<sub>80</sub>O<sub>4</sub>N<sub>2</sub>Cu requires  
C,84.32; H,7.38; N,2.52%.

The physical data of the cognate preparations of other bis[1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato] copper(II) complexes are given below.



**Bis[1-(4-n-hexylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato]  
copper(II), (3.c.1)**

Yield 61.5%; m.p. 286.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2250, 1610, 1585, 1380, 830, 785  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 371 (96,450), 309 (72,500), 240 (46,200).

*Elemental analysis:* Found, C,79.17; H,5.77; N,2.59%  $\text{C}_{68}\text{H}_{60}\text{O}_4\text{N}_2\text{Cu}$  requires  
C,79.10; H,5.81; N,2.71%.

**Bis[1-(4-n-heptylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato]  
copper(II), (3.c.2)**

Yield 42%; m.p. 264.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2250, 1610, 1580, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 370.5 (96,300), 309.5 (71,500), 245 (43,100).

*Elemental analysis:* Found, C,78.98; H,5.95; N,3.17%  $\text{C}_{70}\text{H}_{64}\text{O}_4\text{N}_2\text{Cu}$  requires  
C,79.28; H,6.04; N,2.64%.

**Bis[1-(4-n-octylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato]  
copper(II), (3.c.3)**

Yield 66.5%; m.p. 260.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2250, 1610, 1590, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 371.5 (95,000), 308.5 (70,900), 240.5 (43,100).

*Elemental analysis:* Found, C,79.72; H,6.63; N,2.45%  $\text{C}_{74}\text{H}_{72}\text{O}_4\text{N}_2\text{Cu}$  requires  
C,79.60; H,6.45; N,2.51%.

**Bis[1-(4-n-nonylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato]  
copper(II), (3.c.4)**

Yield 44.5%; m.p. 257.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2250, 1610, 1590, 1380, 840, 790  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 371.5 (91,700), 309 (71,000), 240 (43,900).

Elemental analysis: Found, C,79.72; H,6.63, N,2.45%  $C_{74}H_{72}O_4N_2Cu$  requires  
C,79.60; H,6.45; N,2.51%.

**Bis[1-(4-n-decylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato]  
copper(II), (3.c.5)**

Yield 60%; m.p. 255.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2250, 1610, 1590, 1380, 850, 780  
 $cm^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 371.5 (89,600), 307.5 (66,000), 242.5 (44,800).

Elemental analysis: Found, C,79.47; H,6.69; N,2.14%  $C_{76}H_{76}O_4N_2Cu$  requires  
C,79.75; H,6.64; N,2.44%.

**Bis[1-(4-n-dodecylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato]  
copper(II), (3.c.7)**

Yield 50%; m.p. 250.2°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2210, 1608, 1585, 1380, 830, 780  
 $cm^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 371.5 (92,500), 306.5 (66,500), 243.5 (43,000).

Elemental analysis: Found, C,79.75; H,7.14; N,2.06%  $C_{80}H_{84}O_4N_2Cu$  requires  
C,80.04; H,6.99; N,2.30%.

**Bis[1-(4-n-undecyloxybiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato]  
copper(II), (3.d.2)**

This complex was prepared from [1-(4-n-undecyloxybiphenyl)-3-(4'''-cyanobiphenyl)  
propane-1,3-dione (0.22 g, 0.38 mmol), potassium hydroxide (0.022 g, 0.39 mmol),  
cupric chloride dihydrate (0.034 g, 0.19 mmol) and ethyl alcohol (10 ml) by following  
a procedure similar to the one described for the synthesis of compound 3.c.6.

Yield (0.72 g, 40%); m.p. 230.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610 1585, 1380, 825, 780  
 $cm^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 375 (89,800), 300 (61,000), 244 (40,200).

Elemental analysis: Found, C,77.57; H,6.19; N,2.71%  $C_{78}H_{80}O_6N_2Cu$  requires  
C,77.77; H,6.64; N,2.32%.

**Bis[1-(4-n-dodecyloxybiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]  
copper(II), (3.d.3)**

Yield 38.2%; m.p. 238.0°C; IR  $\nu_{max}^{nujol}$  2920, 2850, 2230, 1610 1590, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  (c) 375.5 (90,900), 300 (61,000), 244.5 (40,200).

*Elemental analysis:* Found, C,77.57; H,6.93; N,1.95%  $\text{C}_{80}\text{H}_{84}\text{O}_6\text{N}_2\text{Cu}$  requires  
C,77.94; H,6.82; N,2.27%.

**Bis[1-(4-n-decyloxybiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]  
copper(II), (3.d.1)**

Yield 33.5%; m.p. 239.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 2230, 1610 1590, 1380, 830, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 375.8 (90,800), 295 (62,100), 244.5 (40,100).

*Elemental analysis:* Found, C,77.58; H,6.46; N,2.38%  $\text{C}_{76}\text{H}_{76}\text{O}_6\text{N}_2\text{Cu}$  requires  
C,77.58; H,6.46; N,2.38%.

**Bis[1-(4-n-undecylbiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]  
palladium(II), (3.e.1)**

A mixture of [1-(4-n-undecylbiphenyl)-3-(4'''-cyanobiphenyl)-propane]-1,3-dione (0.194 g, 0.34 mmol), palladium chloride (0.043 g, 0.19 mmol) dry acetonitrile (50 ml) and anhydrous potassium carbonate (0.072 g, 0.52 mmol) was stirred and heated at 80°C for twenty hours. The cooled reaction mixture was filtered and the solid material was washed with acetonitrile (50 ml). This was taken up in chloroform (75 ml) and washed with water (3x50 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a yellow product which was crystallised from butan-2-one several times until the melting point was constant.

Yield 0.12 g, 60%; m.p. 269.5°C; IR  $\nu_{max}^{nujol}$  2950, 2850, 2230, 1610, 1580, 1380, 825, 770  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  (c) 384 (51,100), 326 (90,200), 260 (55,900); NMR  $\delta$  0.84(t,6H, 2x -CH<sub>3</sub>), 1.07-1.62 [m,36H, (9x-CH<sub>2</sub>)<sub>2</sub>], 2.7 [t,4H, (ArCH<sub>2</sub>)<sub>2</sub>], 6.8 (s,2H,

2× -C=CH), 7.15-8.22 (m,32H, ArH).

*Elemental analysis:* Found, C,76.80; H,6.69; N,1.88% C<sub>78</sub>H<sub>80</sub>O<sub>4</sub>N<sub>2</sub>Pd requires  
C,77.07; H,6.58; N,2.30%.

Following the above procedure, bis[1-(4-n-dodecylbiphenyl)-3-(4'''-cyanobiphenyl) propane-1,3-dionato] palladium(II) complex, (3.e.2) was prepared and the physical data is given below.

Yield 38.5%; m.p.264.0°C, IR  $\nu_{max}^{nujol}$  2900, 2850, 2230, 1610, 1580, 1370, 825, 770 cm<sup>-1</sup>; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 384 (48,000), 325.5 (89,000), 260 (55,000); NMR  $\delta$  0.88(t,6H, 2× -CH<sub>3</sub>), 1.26-1.66 [m,40H, (10×-CH<sub>2</sub>)<sub>2</sub>], 2.6 [t,4H, (ArCH<sub>2</sub>)<sub>2</sub>], 6.8 (s,2H, 2× -C=CH), 7.1-8.1 (m,32H, ArH).

*Elemental analysis:* Found, C,77.04; H,6.93; N,2.05% C<sub>80</sub>H<sub>84</sub>O<sub>4</sub>N<sub>2</sub>Pd requires  
C,77.26; H,6.76; N,2.25%.

## References

- [1] A.M.Giroud-Godquin and P.M.Maitlis, *Angew. Chem., Int. Edn. Engl.*, 30, 375 (1991); P.Epsinet, M.A.Esteruelas, L.A.Oro, J.L.Serrano and E.Sola, *Coord. Chem. Rev.*, 117, 215 (1992).
- [2] K.Ohta, M.Yokoyama, S.Kusabayashi and M.Mikawa, *J. Chem. Soc. Chem. Commun.*, 392 (1981).
- [3] A.M.Giroud-Godquin and J.Billard, *Mol. Cryst. Liq. Cryst.*, 66, 147 (1981).
- [4] K.Ohta, H.Muroki, A.Takagi, K.Hatada, H.Ema, I.Yamamoto and K.Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 140, 131 (1986).
- [5] A.M.Giroud-Godquin, M.M.Gauthier, G.Sigaud, F.Hardouin and M.F.Achard, *Mol. Cryst. Liq. Cryst.*, 132, 35 (1986).
- [6] S.Chandrasekhar, B.K.Sadashiva, S.Ramesha and B.S.Srikanta, *Pramana - J. Phys.*, 27, L-713 (1986); S.Chandrasekhar, B.K.Sadashiva and B.S.Srikanta, *Mol. Cryst. Liq. Cryst.*, 151, 93 (1987).
- [7] B.K.Sadashiva, Archana Ghode and P.Rani Rao, *Mol. Cryst. Liq. Cryst.*, 200, 187 (1991).
- [8] Archana Ghode and B.K.Sadashiva, Paper presented at the Third Annual General Meeting of the Materials Research Society of India, 9-11 February 1992 (Abst. No.PD13).
- [9] J.G.Burr, W.F.Holten and G.N.Webb, *J. Am. Chem. Soc.*, 72, 4903 (1950).
- [10] G.Sigaud, N.H.Tinh, F.Hardouin and H.Gasparoux, *Mol. Cryst. Liq. Cryst.*, 69, 81 (1981); W.Weissflog, G.Pelzl and D.Demus, *Mol. Cryst. Liq. Cryst.*, 110, 309 (1984).
- [11] G.W.Gray, K.J.Harrison and T.W.Nash, *Abstract of the 166th National Meeting of the American Chemical Society, Chicago, 1973*, (Abst. No.Coll-142).

- [12] N.J.Thompson, J.W.Goodby and K.J.Toyne, *Mol. Cryst. Liq. Cryst.*, **213**, 187 (1992).
- [13] G.W.Gray, *Molecular Structure and the Properties of Liquid Crystals*, (Academic Press, London and New York, 1962),p.149.
- [14] D.J.Cram and M.F.Antar, *J. Am. Chem. Soc.*, **80**, 3103 (1958)
- [15] W. S.Johnson, C.D.Gutsche and R.D.Offenhauer, *J. Am. Chem. Soc.*, **68**, 1648 (1946)
- [16] *Dictionary of Organic Compounds*, Fifth Edition (Chapman and Hall, 1982).
- [17] G.W.Gray, J.B.Hartley and B.Jones, *J. Chem. Soc.*, 1412 (1955)
- [18] **Chem. Abst. 43, 1034e (1949)** ~~See, 13, 640 (1964)~~
- [19] B.Shivkumar, Ph.D.Thesis (Bangalore University, 1991), p.174.
- [20] D.Demus, H.Demus and H.Zaschke, *Flussige Kristalle in Tabellen*, Vol.1 (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974), p.189.