CHAPTER IV

Synthesis and mesogenic properties of

i) bis[1-(4-n-alkylbiphenyl)-3-(4‴-substituted-biphenyl)propane-1,3-dionato]copper(II) and a few palladium complexes, and

ii) bis[1-(4-n-alkoxybipheny1)-3-(4"'-methoxy-biphenyl)propane-1,3-dionato]copper(II) complexes

4.1 Introduction

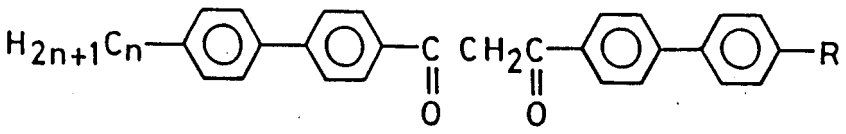
As we have seen in earlier chapters, many metallo β-diketonates, exhibiting liquid crystalline properties, mainly contain two biphenyl moieties and two phenyl rings.[1-5] In Chapter II, we have discussed the effect of substituents on the mesogenic properties of bis[1-(4-n-dodecylbiphenyl)-3-(4″-substitutedphenyl) propane-1,3-dionato]metal(II) complexes by incorporating different substituents on the pheriyl ring and observed that cyano and bromo substituents promote smectic A phase in the complexes, while methoxy, ethoxy, methyl, ethyl and chloro substituents enhance nematic phase in the complexes. On extension of the core of bis[1-(4-n-dodecylbiphenyl)-3-(4″-cyanophenyl) propane-1,3-dionato]copper(II) complex exhibited enantiotropic nematic phase. Mesogenic properties of these were discussed in Chapter III.

With a view to study the effect of substituents on the mesogenic properties of a metal-β-diketonate system containing four biphenyl moieties, a number of bis[1-(4-n-alkylbiphenyl)-3-(4‴-substitutedbiphenyl) propane-1,3-dionato]copper(II) complexes were synthesised and their mesogenic properties have been discussed in the present chapter.

4.2 Synthesis

The ligands that have been used to synthesise these complexes are [1-(4-n-alkylbiphenyl)-3-(4‴-methoxybiphenyl)propane]-1,3-diones, [1-(4-n-alkoxybiphenyl)-3-(4‴-methoxybiphenyl)propane]-1,3-diones, and [1-(4-n-alkylbiphenyl)-3-(4‴-substitutedbiphenyl)propane]-1,3-diones. The molecular structures of these ligands and their corresponding metal clielates are shown in figure 4.1.

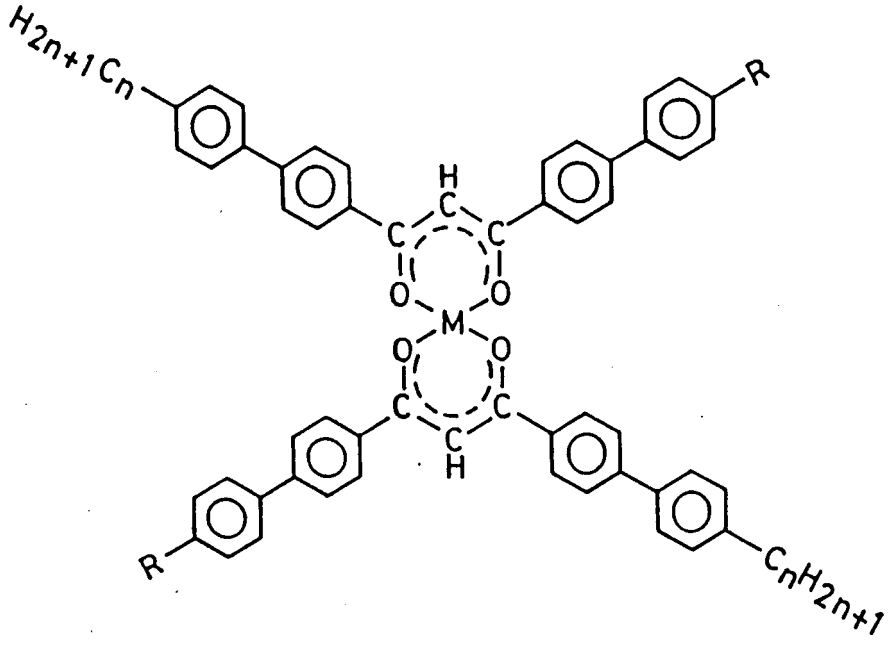
These compounds were synthesised by following a series of reactions sequence as shown in figures 4.2 to 4.7. Methylation of 4-hydroxybiphenyl using diriietliyl sulphate in a solution of ethanolic sodium hydroxide followed by Fiiedel-Crafts acetylation with acctyl chloride using anhydrous aluminium chloride in carbon disulphide



R = OC_2H_5, C_2H_5, C_3H_7, C_4H_9 or Br, n = 12

R = OCH_3, n = 10–12

Series IV.1



R = OCH_3, M = Cu, n = 10–12

R = OCH_3, M = Pd, n = 10–12

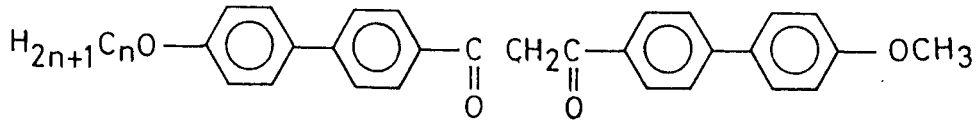
R = OC_2H_5, C_2H_5, C_3H_7, C_4H_9 or Br

M = Cu, n = 12

Series IV.3

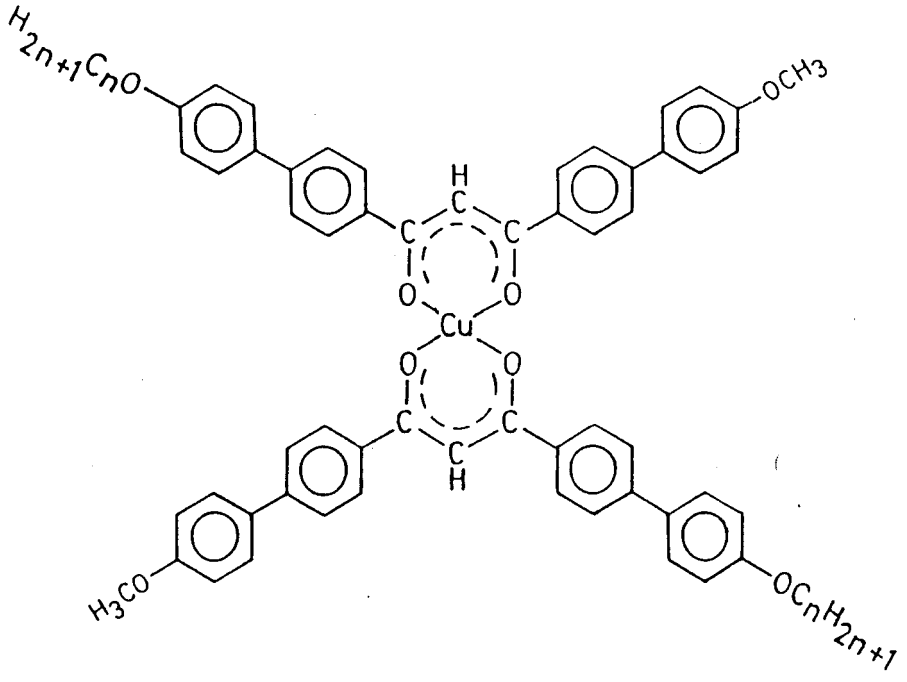
Figure 4.1

(continued ...)



n = 10 – 12

Series IV.2



n = 10 – 12

Series IV.4

Figure 4.1

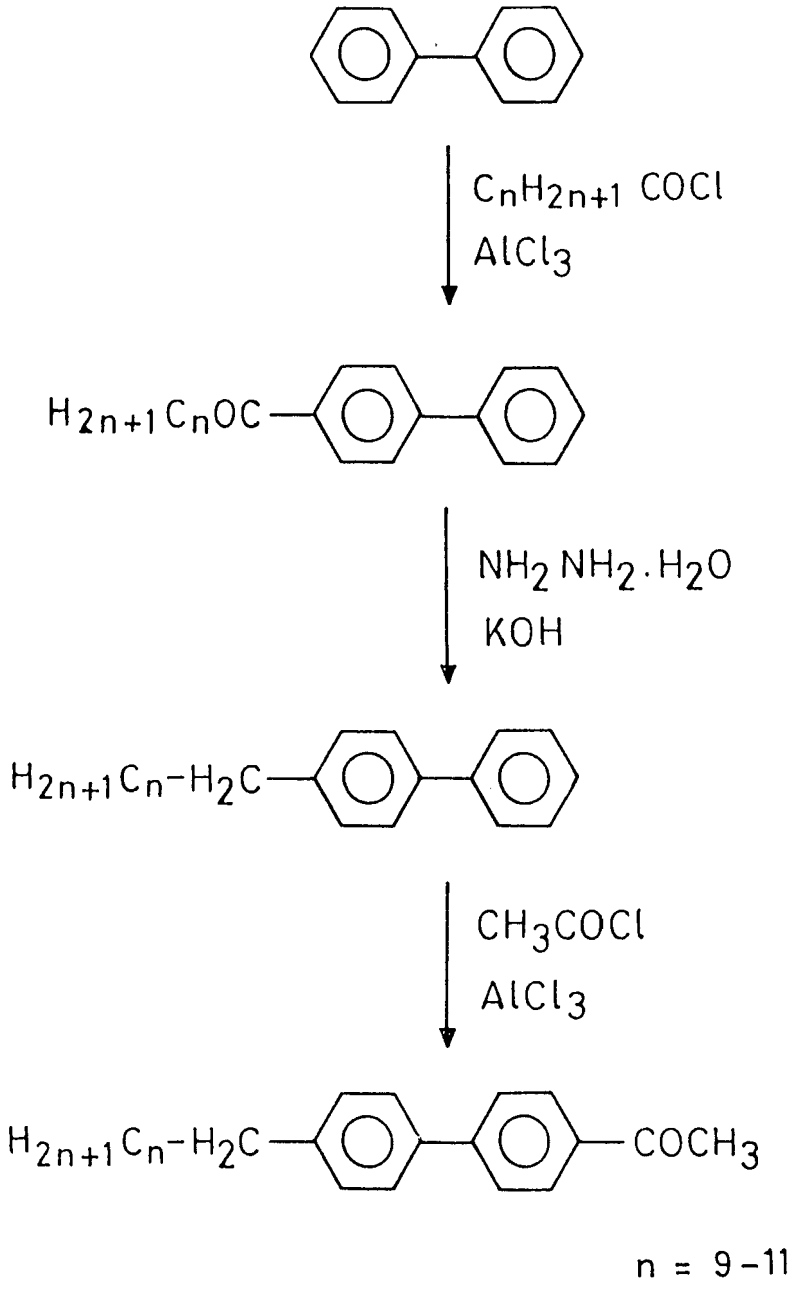

$C_nH_{2n+1}COCl$
$AlCl_3$
$H_{2n+1}C_nOC$
$NH_2NH_2.H_2O$
KOH
$H_{2n+1}C_n-H_2C$
CH_3COCl
$AlCl_3$
$H_{2n+1}C_n-H_2C$
$COCH_3$
n = 9-11

Figure 4.2

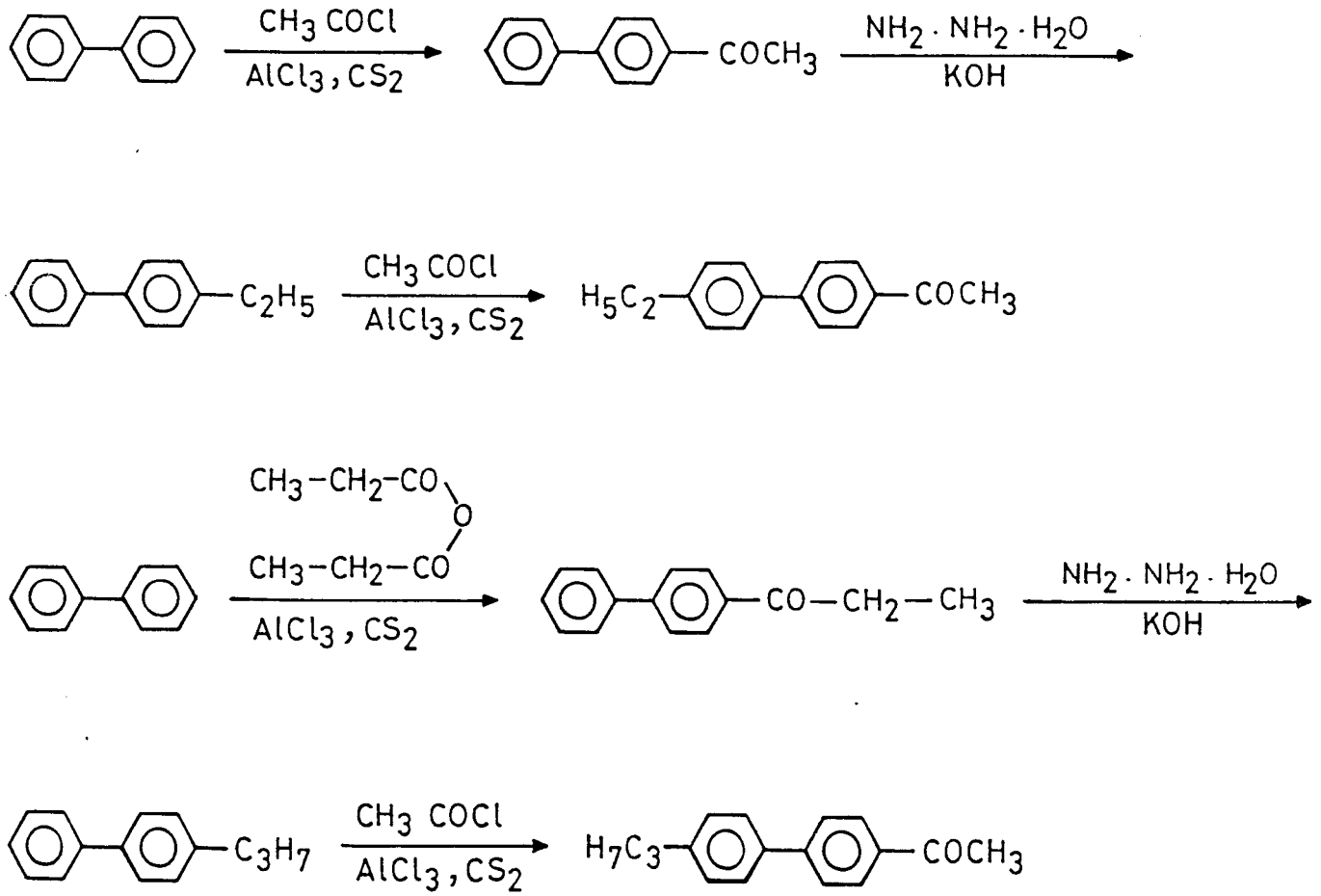


Figure 4.3 (continued)

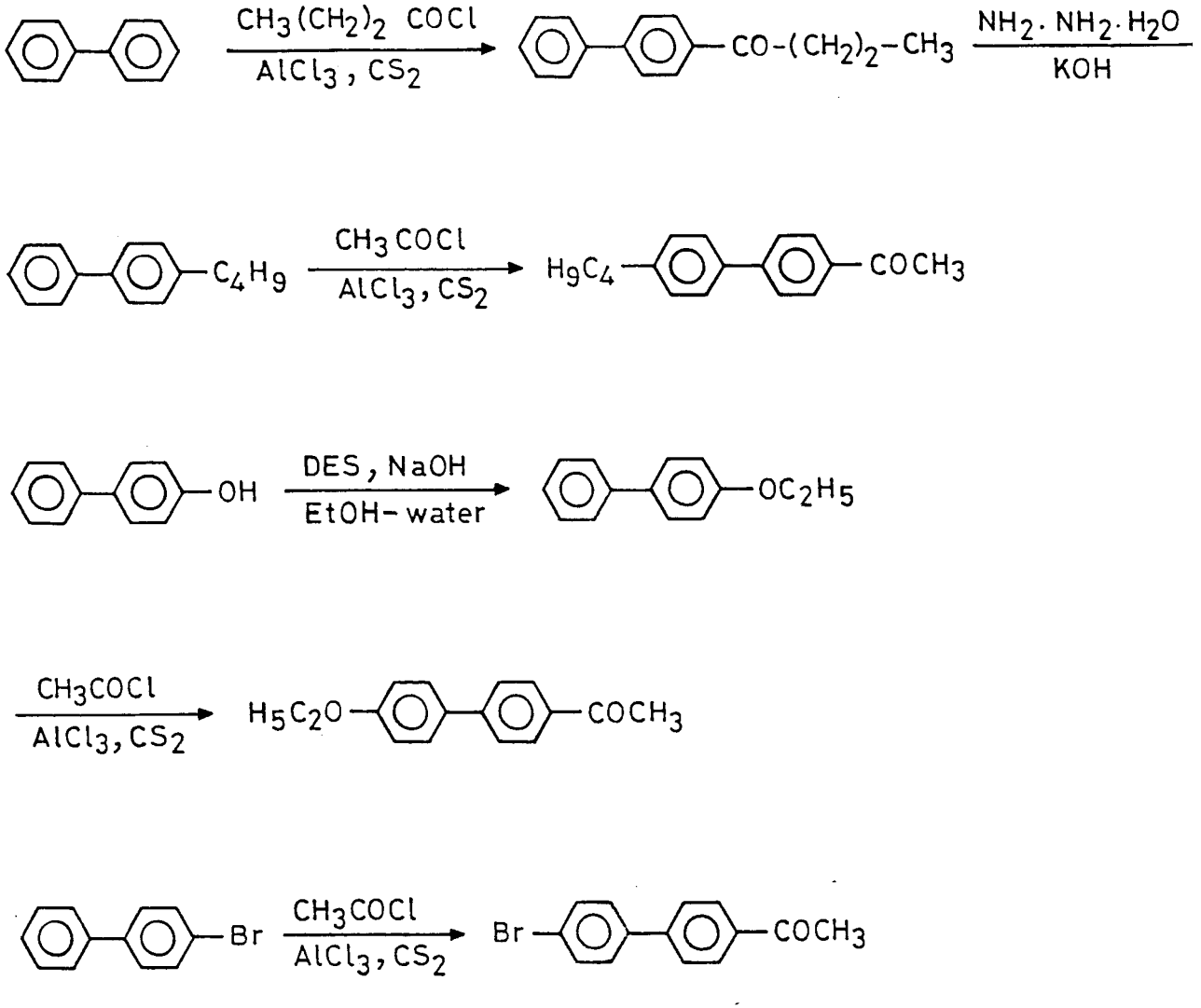

CH3(CH2)2 COCl
AlCl3, CS2
CO-(CH2)2-CH3
NH2. NH2. H2O
KOH
C4H9
CH3COCl
AlCl3, CS2
H9C4
COCH3
OH
DES, NaOH
EtOH-water
OC2H5
CH3COCl
AlCl3, CS2
H5C2O
COCH3
Br
CH3COCl
AlCl3, CS2
Br
COCH3

Figure 4.3

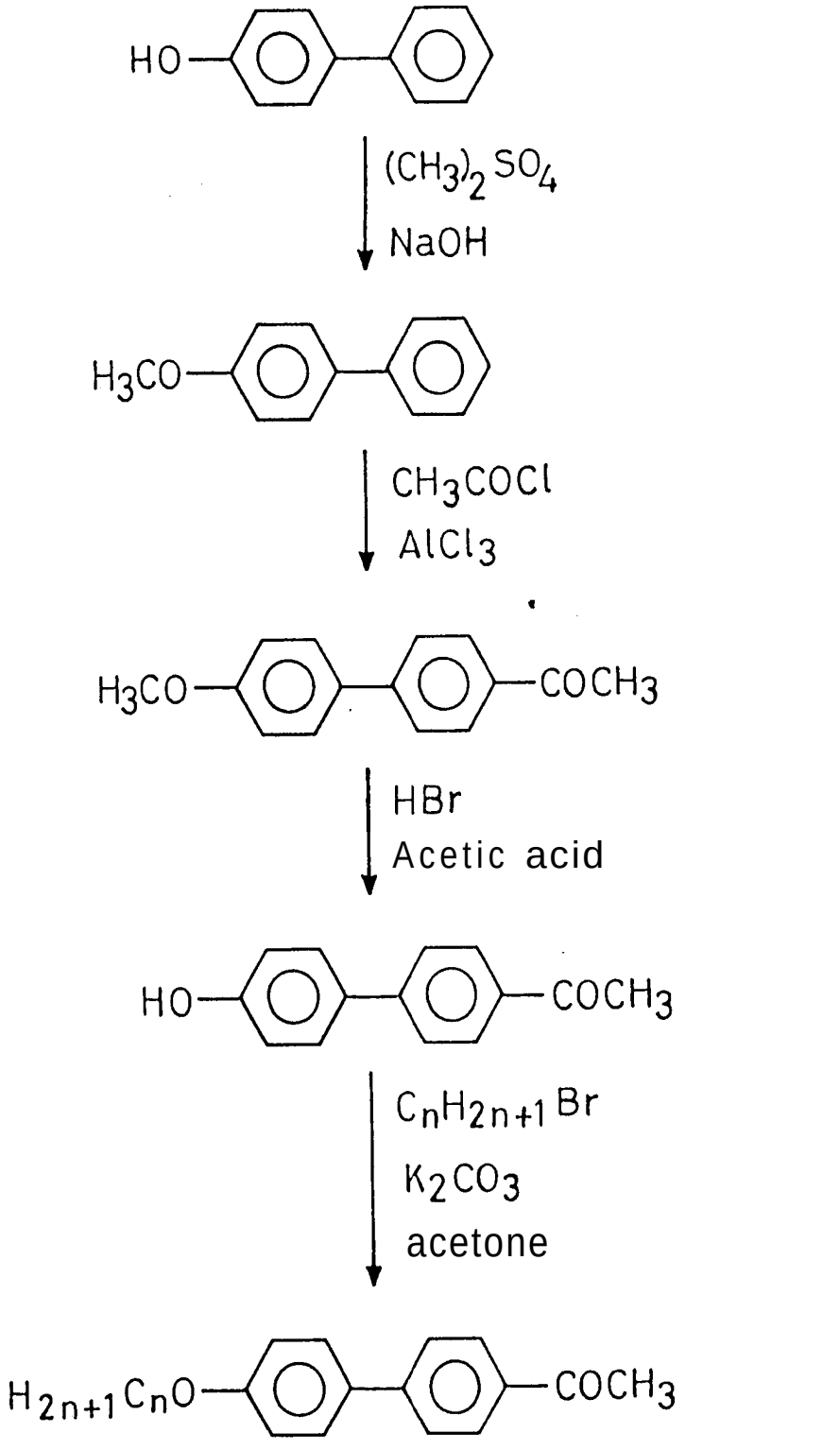

HO
$(CH_3)_2SO_4$
NaOH
H_3CO
CH_3COCl
$AlCl_3$
H_3CO
$COCH_3$
HBr
Acetic acid
HO
$COCH_3$
$C_nH_{2n+1}Br$
K_2CO_3
acetone
$H_{2n+1}C_nO$
$COCH_3$
n = 10 – 12

Figure 4.4

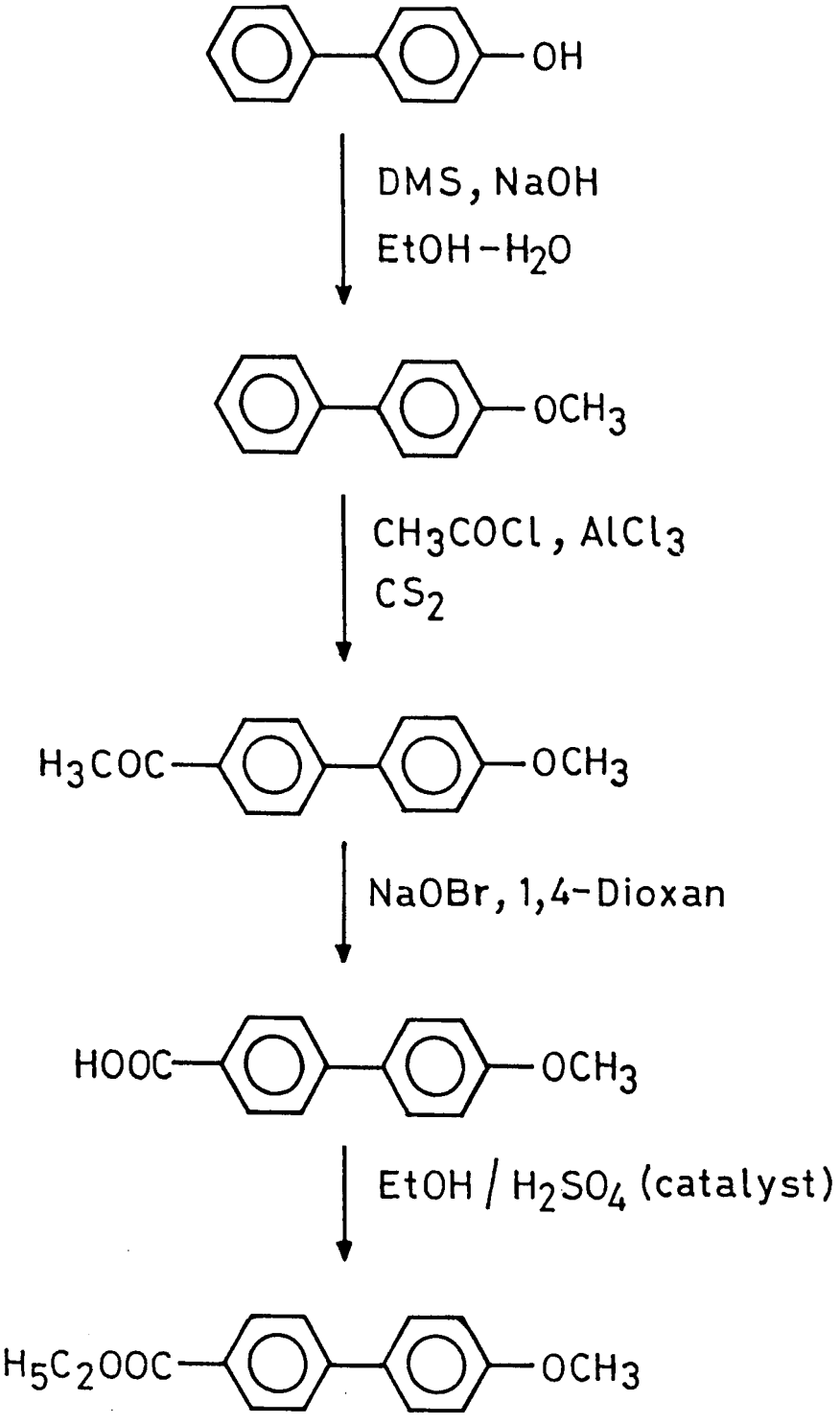

OH
DMS, NaOH
EtOH–H2O
OCH3
CH3COCl, AlCl3
CS2
H3COC
OCH3
NaOBr, 1,4-Dioxan
HOOC
OCH3
EtOH / H2SO4 (catalyst)
H5C2OOC
OCH3

Figure 4.5

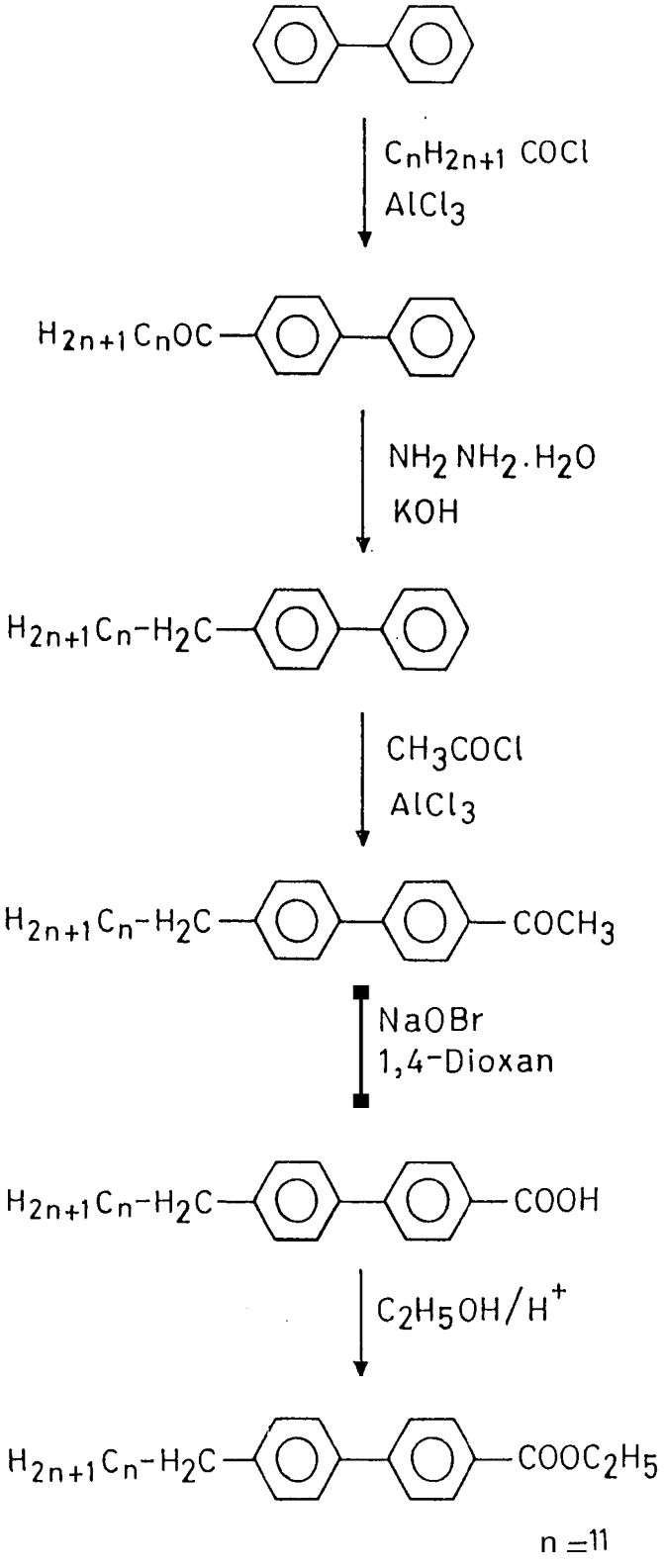
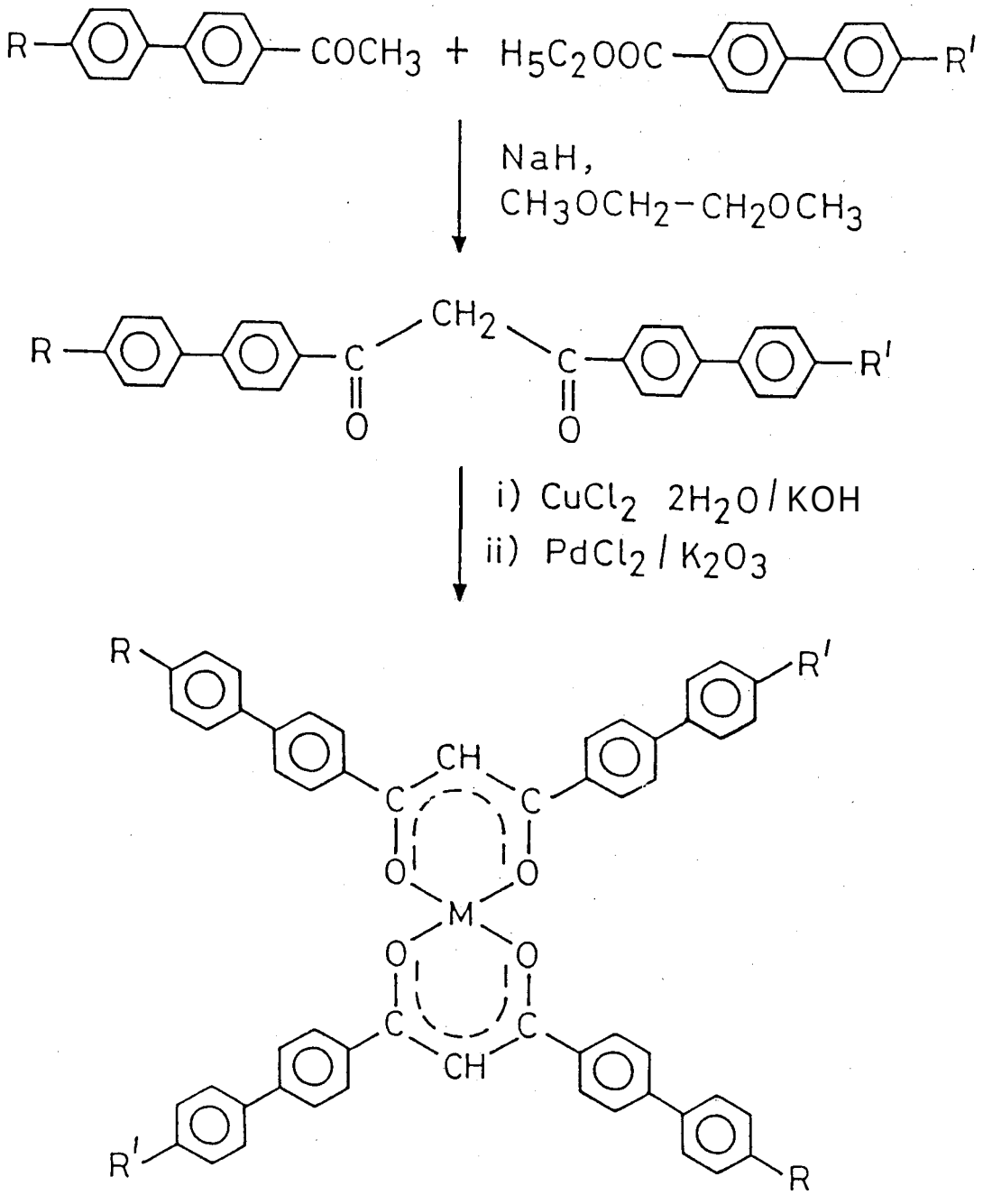

CnH2n+1 COCl
AlCl3
H2n+1CnOC
NH2 NH2.H2O
KOH
H2n+1Cn-H2C
CH3COCl
AlCl3
H2n+1Cn-H2C
COCH3
NaOBr
1,4-Dioxan
H2n+1Cn-H2C
COOH
C2H5OH/H+
H2n+1Cn-H2C
COOC2H5
n =11

Figure 4.6



R = C_nH_{2n+1} , OC_nH_{2n+1} , OC_2H_5 , C_2H_5 , C_3H_7 , C_4H_9 or Br

R = OCH_3 or $C_{12}H_{25}$

M = Cu or **Pd**

Figure 4.7

afforded **4-methoxy-4'-acetylbiphenyl.** This was converted into 4-methoxybiphenyl-4'-carboxylic acid, using sodium hypobromite as an oxidising agent.[6] This carboxylic acid, on esterification with ethyl alcohol in the presence of a catalytic amount of sulphuric acid yielded ethyl-4-methoxybiphenyl-4'-carboxylate. Demethylation of 4-methoxy-4′-acetylbiphenyl with 48% hydrobromic acid and acetic acid, followed by o-alkylation using an appropriate n-alkyl bromide in the presence of anhydrous potassium carbonate in dry acetone gave the corresponding 4-n-alkoxy-4'-acetylbiphenyls.

4-n-Alkyl-4'-acetylbiphenyl was prepared by acylating biphenyl with an appropriate acylhalide using Friedel-Crafts reaction to furnish 4-n-alkanoylbiphenyl. This on Huang-Minlon modification of Wolff-Kishner reduction afforded 4-n-alkylbiphenyl, which was again acylated using acetyl chloride to yield 4-n-alkyl-4'-acetylbiphenyl. The **4-n-dodecyl-4'-acetylbiphenyl** was converted to the corresponding carboxylic acid by hypobromite oxidation and esterified with ethyl alcohol in the presence of a catalytic amount of concentrated sulphuric acid to give ethyl-4-n-dodecylbiphenyl-4'-carboxylate. Claisen condensation of the above esters and methyl ketones yielded the respective β-diketones in good yields. These β-diketones exist in enolic form as shown by the PMR spectra. A typical PMR spectrum is shown in figure 4.8.

The copper(II) complexes were obtained by treating the potassium salt of the β-diketones in tetrahydrofuran with cupric chloride dihydrate in ethanol at room temperature. All the palladium complexes were obtained by refluxing a mixture of palladium chloride, a β-diketone, and anhydrous potassium carbonate in acetonitrile.

4.3 Results and Discussion

The melting points of [1-(4-n-alkylbiphenyl)-3-(4‴-methoxybiphenyl)propane]-1,3-diones, and their alkoxy analogues have been summarised in table 4.1. The melting points vary from 207 to 234°C and the enthalpies for crystal to isotropic transition are of the order of 11 to 13 kcal/mol. The melting points of [1-(4-n-dodecylbiphenyl)-

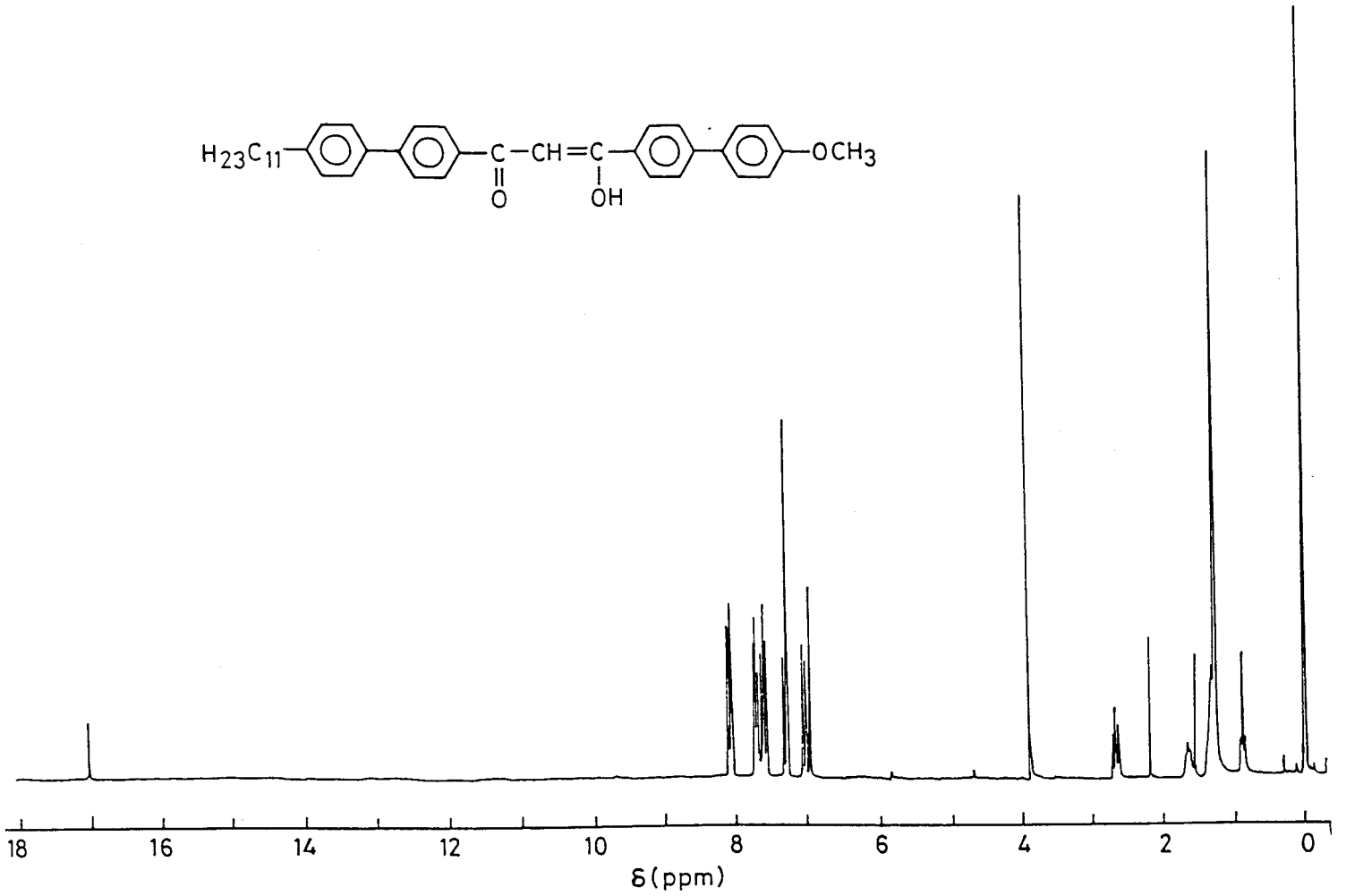
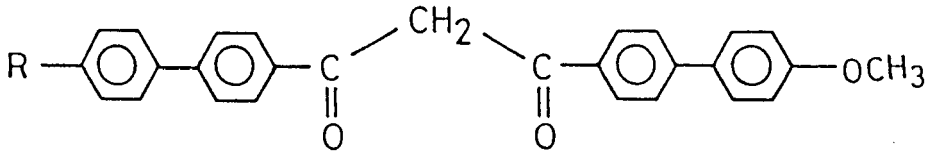


Fig.4.8. 200 MHz PMR spectrum of the compound 4.a.2 in $CDCl_3$ containing 1% TMS.

Table 4.1

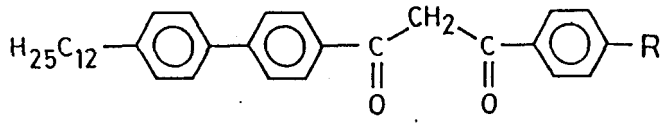
Mesomorphic **transition temperatures** (°C) **and enthalpies** (kcal/mol) **of**



Compound number	R	C		I
4.a.1	$C_{10}H_{21}$	.	210.50 11.10	.
4.a.2	$C_{11}H_{23}$	.	211.50 13.05	.
4.a.3	$C_{12}H_{25}$	.	207.50 12.58	.
4.a.4	$OC_{10}H_{21}$	.	234.00 11.30	.
4.a.5	$OC_{11}H_{23}$	.	233.50 11.57	.
4.a.6	$OC_{12}H_{25}$	.	234.00 12.28	.

3-(4‴-substitutedbiphenyl)propane]-1,3-diones, are given in table 4.2. Surprisingly all these ligands are non-mesogenic. Ligands with terminal polar substituents show relatively higher melting points.

As mentioned in Chapter II, all the derivatives of a compound of structure 4.1



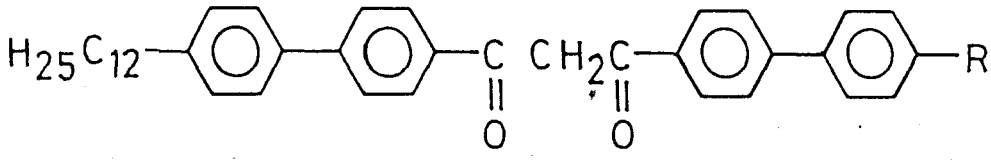
4.1 R = OC_2H_5, C_2H_5 or Br

exhibit smectic phases. If we compare the mesogenic behaviour of these [1-(4-n-dodecylbiphenyl)-3-(4″-substitutedphenyl)propane]-1,3-diones, (4.1) with [1-(4-n-dodecylbiphenyl)-3-(4‴-substitutedbiphenyl)propane]-1,3-diones, [series IV(1)], then it is observed that addition of a phenyl ring results in elimination of mesophase and the compounds so obtained are non-mesogenic. To explain this behaviour change in molecular geometry may be considered. Molecules of structure 4.1 can be imagined to be bent as shown in figure 4.9a. The addition of a phenyl ring to such a molecule increases the molecular lateral dimensions even more, as shown in figures 4.9b and 4.9d. Compounds of series IV(1) can exist in keto or enol form. In the keto form there are two possible configurations, 4.9b and 4.9c. It is possible that the two keto groups can either be on the same side or on opposite sides as shown in figures 4.9b and 4.9c respectively. In the latter case the molecule has a linear structure and is conducive to the formation of a mesophase. However this compound is found to be non-mesogenic and hence this possibility is ruled out.

Enolic form of this conipound is shown in figure 4.9d. As can be seen the molecule is very much broadened after the addition of a phenyl ring. This broad structure is not suitable for the formation of a mesophase. The PMR spectra of these compounds in $CDCl_3$ clearly show that they exist in the enol form even in solution and a typical spectrum is shown in figure 4.8. Thus the evidence from the results obtained shows

Table 4.2

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



Compound number	R	C		I
4.b.1	C_2H_5	.	186.8 6.94	.
4.b.2	C_3H_7	.	187.4 7.77	.
4.b.3	C_4H_9	.	235.0 9.31	.
4.b.4	Br	.	235.0 9.31	.
4.b.5	OC_2H_5	.	205.0 9.76	.

Compounds 4.b.1, 4.b.2, 4.b.3, 4.b.4 and 4.b.5 have crystal-crystal transitions at 119.5, 91.0, 91.5, 101.5 and 169.6°C respectively.

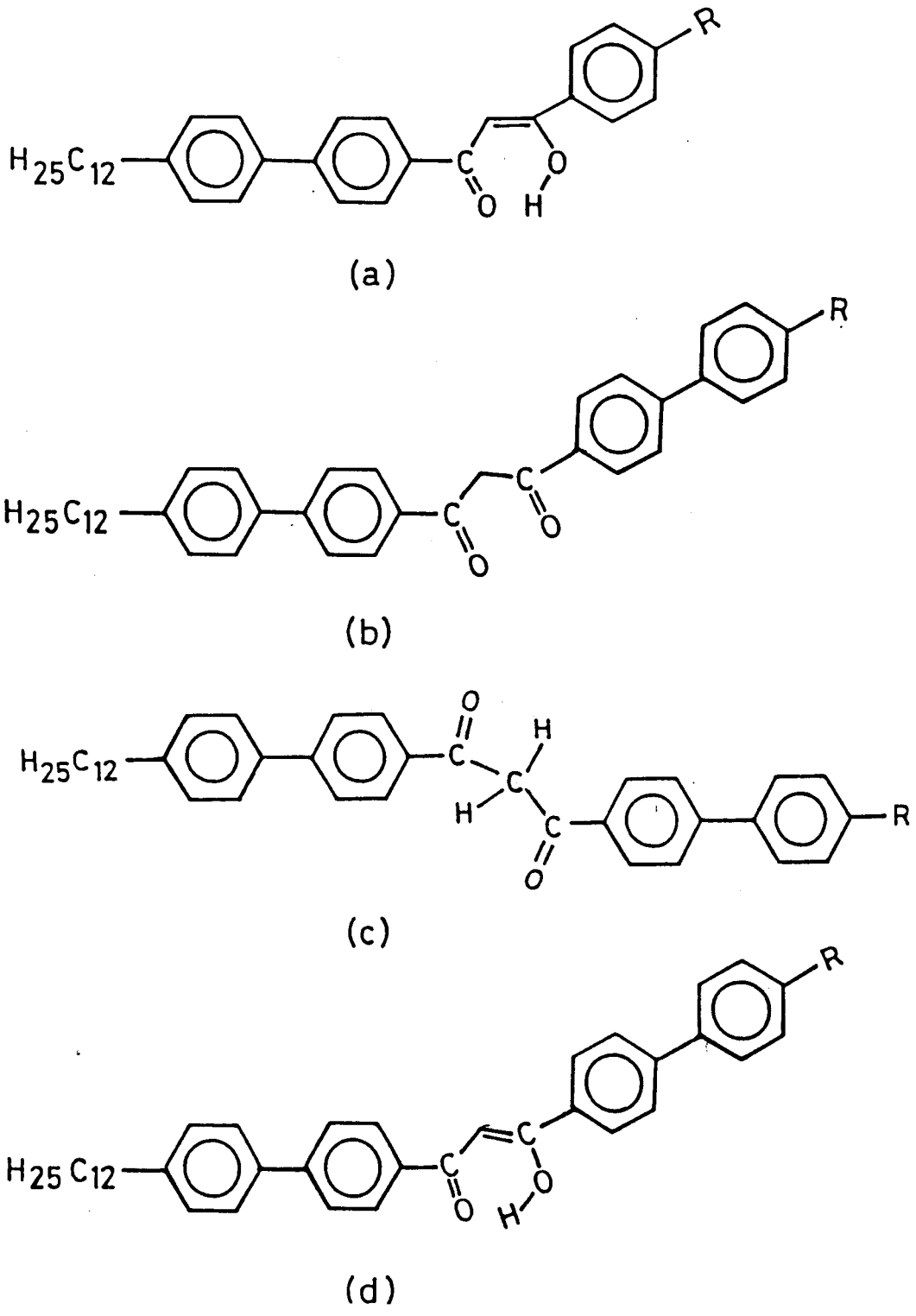
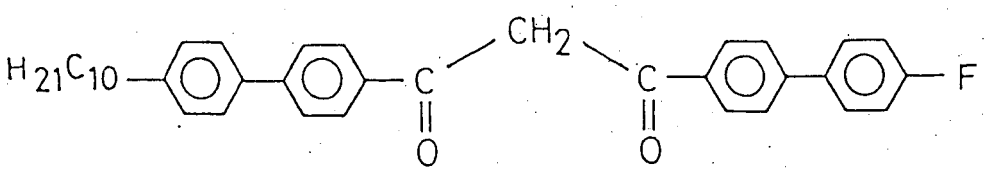


Figure 4.9: Different possible conformations of compounds 4.1 and [1-(4-n-dodecylbiphenyl)-3-(4‴-substitutedbiphenyl) propane]-1,3-diones.

that these β-diketones exist in the *enolic* form. The increase in the breadth as a result of introducing a phenyl group would affect the thermal stability of the mesophase considerably and sometimes renders the compound non-mesogenic.

Recently Thompson et *al.*[7] have reported a compound 4.2 terminally substitutcd with a fluoro group. This is also non-mesogenic. They obtained a virtual transition



C 199 [S_A 135] I

4.2

temperature for this compound by mixing it with 4-n-pentyl-4″-octyloxy-p-terphenyl. It is quite probable that the β-diketones discussed above may also have virtual mesogenic transition temperatures.

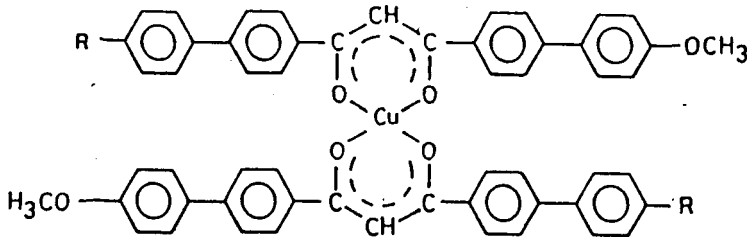
The transition temperatures of bis[1-(4-n-alkylbiphenyl)-3-(4‴-methoxybiphenyl) propane-1,3-dionato]copper(II) complexes and bis[1-(4-n-alkoxybiphenyl)-3-(4‴-methoxybiphenyl) propane-1,3-dionato] copper (II) complexes are shown in table **4.3.** All the six complexes exhibit an enantiotropic nematic phase. The range of the nematic pliase varies from 7 to 33°*C* and exhibits a schlieren texture.

Figures 4.10 and 4.11 show plots of the transition temperatures ***versus*** the number of carbon atoms in the alkyl and alkoxy chains of these copper complexes [series IV(3) and series IV(4)] respectively. It can be clearly seen that there is a gradual fall in nematic-isotropic transition temperatures as the series is ascended in both cases. These clearing points lie on a smooth curve in both the series. A comparison of these two series of compounds reveals that alkoxy substitution favours thermal stabilization of the nematic phase.

Mesomorphic transition temperatures and heats of transitions of bis[1-(4-n-dodecylbiphenyl)-3-(4‴-substitutedbiphenyl) propane-1,3-dionato]copper(II) complexes have

Table 4.3

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



Compound number	R	C	N	I
4.c.1	$C_{10}H_{21}$	. 215.5 10.03	. 247.0 0.07	.
4.c.2	$C_{11}H_{23}$	. 210.0 5.93	. 243.0 0.09	.
4.c.3	$C_{12}H_{25}$	. 202.0 5.6	. 235.0 0.08	.
4.c.4	$OC_{10}H_{21}$	. 235.0 16.7	. 257.5 0.08	.
4.c.5	$OC_{11}H_{23}$	. 225.0 9.5	. 253.5 0.07	.
4.c.6	$OC_{12}H_{25}$	. 237.0 7.25	. 244.0 0.07	.

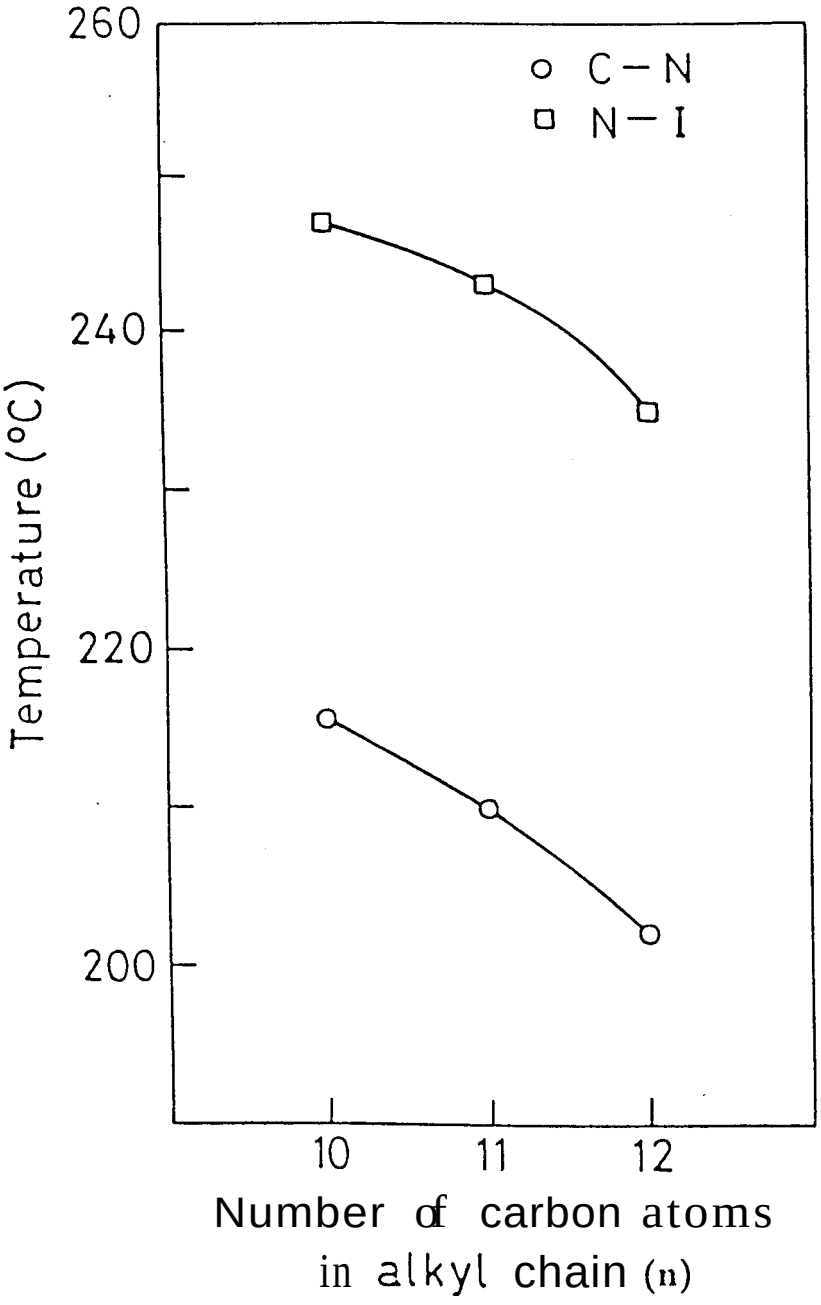


Plate 4.10.A plot of the transition temperatures versus the number of carbon atoms (n) in the alkyl chain for bis[1-(4-n-alkyl-biphenyl)-3-(4‴-methyloxybiphenyl)propane-1,3-dionato]-copper(II) complexes.

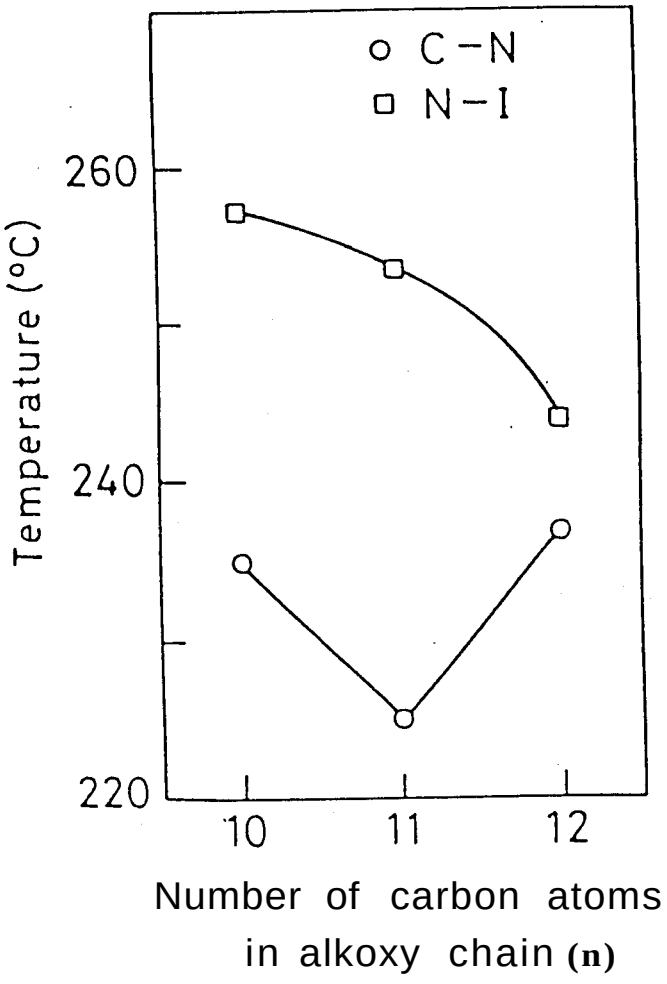


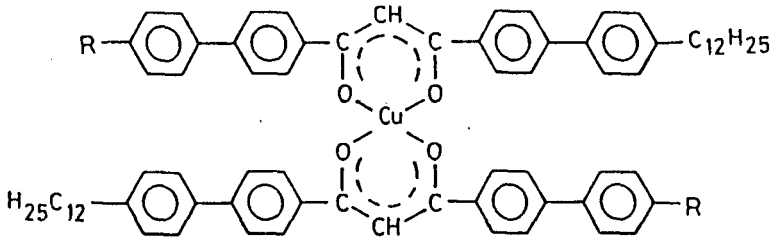
Figure 4.11. A plot of the transition temperatures versus the number of carbon atoms (n) in the alkoxy chain for bis[1-(4-n-alkoxybiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]copper(II) complexes.

been summarised in table 4.4. The bis[1-(4-n-dodecylbiphenyl)-3-(4‴-ethylbiphenyl) propane-1,3-dionato]copper(II) complex, (4.d.l) exhibits an enantiotropic nematic phase and bis[1-(4-n-dodecylbiphenyl)-3-(4‴-bromobiphenyl) propane-1,3-dionato] copper(II) complex, (4.d.4) shows an enantiotropic smectic A phase. Rest of the complexes exhibit a monotropic nematic phase. The smectic character of 4.d.4 is perhaps due to the polarity of bromo group. The enthalpy of smectic A-isotropic transition for this compound is of the order of 1.6 kcal/mol. This value is in general agreement with those obtained for smectic A-isotropic transition in calarnitic mesogens. But the enthalpies of nematic-isotropic transition is of the order 0.07 to 0.09 kcal/mol for all the metallonematogens which is quite low as compared to those obtained for the calamitic mesogens. The DSC thermogram of compound 4.d.1 is given in figure 4.12.

A comparison of the liquid crystalline properties of bis[1-(4-n-dodecylbiphenyl)-3-(4‴-ethylbiphenyl) propane-1,3-dionato]copper(II) complex, (4.d.l) with bis[1-(4-n-dodecylbiphenyl)-3-(4‴-ethoxybiphenyl) propane-1,3-dionato]copper(II) complex, (4.d.5) shows that compound 4.d.l exhibits an enantiotropic nematic phase, while a monotropic nematic phase was observed in the latter compound (4.d.5). A possible explanation for this behaviour could be that alkoxy substituted compounds generally have significantly higher melting points than their alkyl analogues. Although there is an increase in the polarisability of the molecule, which is an important factor for enhancement of thermal stability of the mesophases, compound 4.d.5 exhibits only a monotropic nematic phase. The mesomorphic properties of bis[1-(4-n-dodecylbiphenyl)-3-(4‴-ethoxybiphenyl) propane-1,3-dionato]copper(II) complex, (4.d.5) can be compared with those for bis[1-(4-n-dodecyl- biphenyl)-3-(4‴-propylbiphenyl) propane-1,3-dionato]copper(II) complex, (4.d.2), as the two have similar length of substituents at the terminal position. Both the compounds exhibit a monotropic nematic phase almost at the same temperature. Similarly the mesogenic behaviour of compounds 4.c.3 and 4.d.1 can be explained. On moving frorn n-propyl substituted complex (4.d.2) to n-butyl substituted complex (4.d.3), it is found that

Table 4.4

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



Compound number	R	C	S_A	N	I
4.d.1	C_2H_5	. 211.5 6.30	-	. 218.5 0.10	.
4.d.2	C_3H_7	. 234.0 7.24	-	(. 217.0) 0.06	.
4.d.3	C_4H_9	. 241.5 8.52	-	(. 227.0) 0.06	.
4.d.4	Br	. 177.0 10.5	. 271.5 1.69	-	
4.d.5	OC_2H_5	. 241.0 8.21	-	(. 220.5) 0.14	.

Note: Compounds 4.d.1, 4.d.2 and 4.d.4 have crystal-crystal transitions at 102.5, 210.0 and 166.0°C respectively.

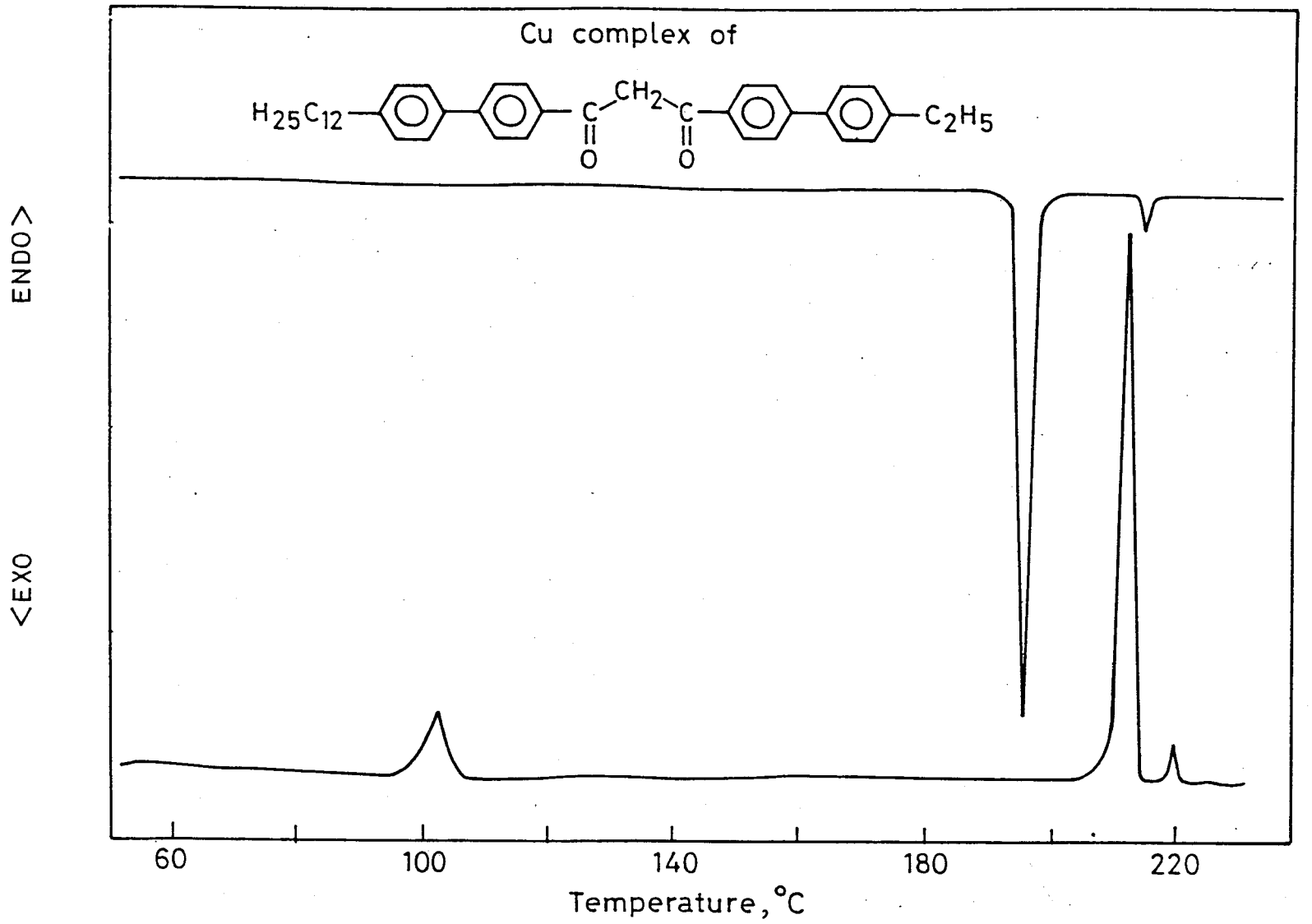
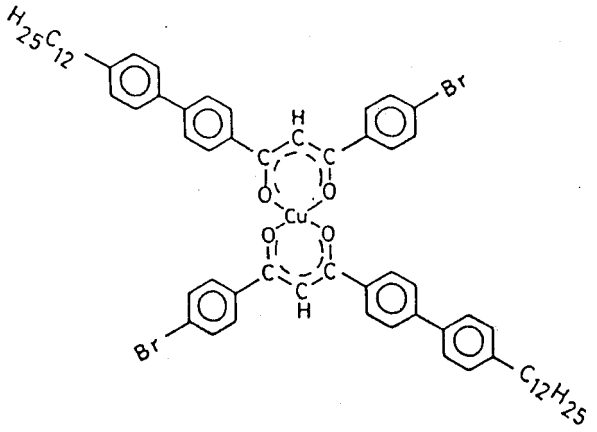


Fig.4.12. DSC thermogram of compound 4.d.1.

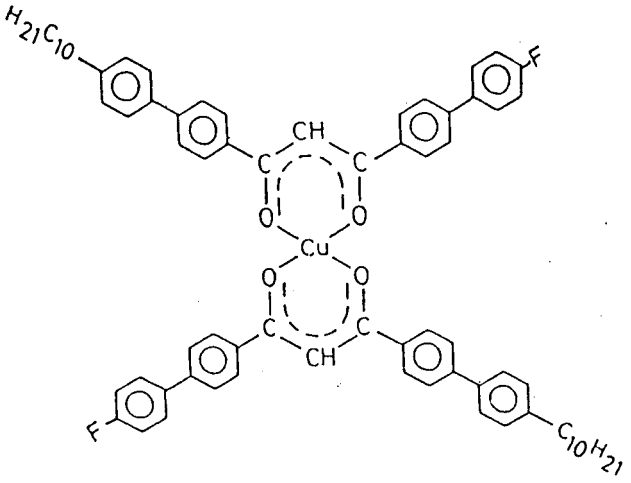
nematic thermal stability of the latter increases by $10°C$. Compound, bis[1-(4-n-dodecylbiphenyl)-3-(4″-bromophenyl) propane-1,3-dionato]copper(II), (4.3) exhibits a monotropic S_A phase.



C 201 (S_A 170.5) I

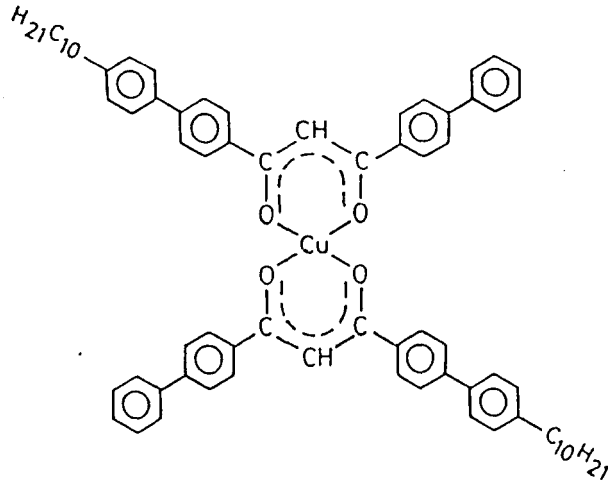
4.3

On introducing a phenyl ring (complex 4.d.4), the molecule broadens and it becomes enantiotropic smectic A, with an increase in its clearing ternperature by $101°C$. Similarly, fluoro substituted complex (4.4) which was recently reported,[7] exhibits a smectic A and a monotropic smectic C phases. It appears therefore that the smectic phases are stabilised in brorno and fluoro substituted complexes.



C 155 (S_C 122) S_A 250 I

Thompson *et al.*[5] have reported that bis[1-(4-n-decylbiphenyl)-3-(biphenyl-4-yl) propane-1,3-dionato]copper(II) complex, (4.5) exhibited a monotropic nematic phase and this can be considered to be the parent compound.



C 193/208 (N 195) I

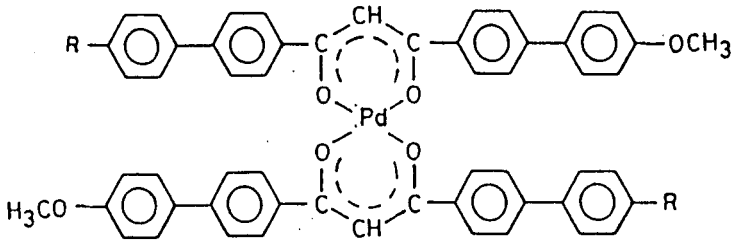
4.5

By introducing different terminal substituents we can observe the effect of these groups on the mesophase with respect to the parent compound (4.5). For example ethyl substituent (compound 4.d.1) increases both melting point (3°C) and nematic-isotropic temperature (23°*C*). Similarly the replacement of terminal hydrogen in 4.5 by ethoxy, n-propyl or n-butyl groups (4.d.5, 4.d.2, 4.d.3) the melting points are raised by about 26 to 34°*C*, while the nematic-isotropic temperatures are raised by 22 to 32°*C*. All these complexes exhibit a monotropic nematic phase. The bromo substituted complex (4.d.4) exhibits a smectic A phase and has a lower melting point (31°C) than the parent compound.

In order to examine the influence of a palladium(II) metal atom, instead of a copper(II) atom, a few of the former complexes were synthesised. The transition temperatures of bis[1-(4-n-alkylbiphenyl)-3-(4‴-methoxybiphenyl) propane-1,3-dionato]palladium(II) complexes are summarised in table 4.5. These complexes exhibit a nematic mesophase over a narrow temperature range. The transition temperatures for all the three complexes are very high. As a result of replacing copper

Table 4.5

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



Compound number	R	C	N	I
4.e.1	$C_{10}H_{21}$	. 236.8 5.46	. 237.2⊙	.
4.e.2	$C_{11}H_{23}$	. 227.6 5.59	. 227.8⊙	.
4.e.3	$C_{12}H_{25}$	. 227.2 5.46	. 227.6⊙	.

⊙The enthalpy could not be determined due to a very small temperature range of the mesophase.

with palladium, the melting points are raised by 17 to 25°C. The PMR spectra of these diamagnetic palladium(II) complexes in $CDCl_3$ solution is consistent with their expected structures. .Figure 4.13 shows the PMR spectrum of the complex 4.e.2.

We can summarise that in the above discussed complexes each terminal substituent promotes mesophase thermal stability as compared to the unsubstituted parent compound. Halogen substituents have a dramatic effect on smectic phase stability, whereas the other substituents such as methoxy, ethoxy, ethyl, propyl or butyl groups promote a nematic phase in these complexes. When the alkyl chain in series IV(3) is replaced by an alkoxy chain, the thermal stability of the nematic phase increases. Replacement of copper atom by palladium increases melting points. Complexes with four biphenyl moieties are enantiotropic mesomorphic while those with two biphenyl and two phenyl groups are monotropic mesomorphic.

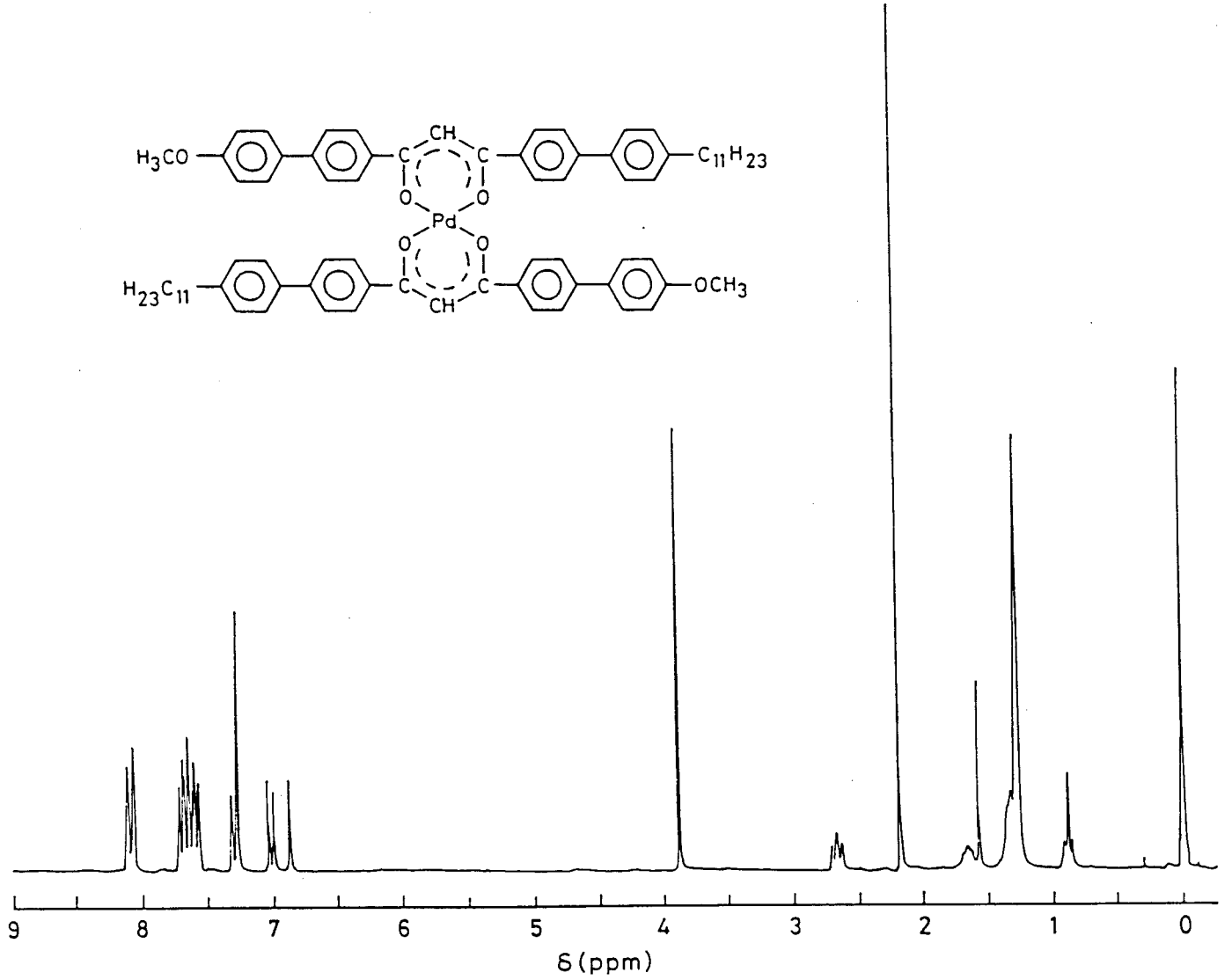


Fig.4.13. 200 MHz PMR spectrum of the complex 4.e.2 in $CDCl_3$ containing 1% TMS.

4.4 Experimental

4-Acetylbiphenyl

This was prepared following a procedure similar to the one described in Chapter II for the preparation of 4-n-dodecanoylbiphenyl. Thus,from biphenyl (62 g, 40.25 mmol), anhydrous aluminium chloride (64 g, 47.94 mmol), dry carbon disulphide (250 ml) and acetyl chloride (32 g, 40.7 mmol), 4-acetylbiphenyl was obtained.
Yield (58 g, 73.5%); m.p. 116-117.5° C (Reported[8] m.p.120-121°C).

4-Ethylbiphenyl

This compound was synthesised from 4-acetylbiphenyl(58 g, 29.59 mmol), hydrazine hydrate (80%, 24.5 g, 48.94 mmol), potassium hydroxide (34 g, 60.71 mmol) and digol (500 ml) by following a procedure similar to the one described in chapter II for tlie preparation of 4-n-dodecylbiplienyl.
Yield (38 g, 70.5%); b.p. 115-118' C/1 mm (Reported[g] b.p.146-147°C/11mm).

4-Ethyl-4′-acetylbiphenyl

This was prepared from 4-ethylbiphenyl (38 g, 20.87 mmol), acetyl chloride (16.5 g, 21.09 mmol), anhydrous aluminium chloride (35 g, 26.21 mmol) and dry carbon disulpliide (250 ml) by following a procedure similar to the one described in chapter II for the preparation of **4-n-dodecyl-4'-acetylbiphenyl.** Crystallisation from petroleum ether gave colourless crystals of 4-ethyl-4'-acetylbiphenyl.
Yield (22 g, 47.0%); m.p. 118-119° C (Reported[1'] yield 45%, m.p.117.5°C).

4-Ethoxybiphenyl

This was prepared from 4-hydroxybiphenyl (32 g, 18.82 mmol), diethyl sulphate (30.8 g, 20 mmol), sodium hydroxide (16 g, 40 mmol), water (180 ml) and ethyl

alcohol (350 ml) following the same procedure as described for 4-methoxybiphenyl in chapter III. The required product was crystallised from ethyl alcohol.
Yield (34 g, 91.0%); m.p. 71-72" C.

4-Ethoxy-4′-acetylbiphenyl

This was prepared from 4-ethoxybiphenyl (34 g, 17.17 mmol), acetyl chloride (13.5 g, 17.19 mmol), anhydrous aluminium chloride (30 g, 22.47 mmol) and dry carbon disulphide (500 ml) by following a procedure described for 4-methoxy-4'-acetyl biphenyl in chapter III. This material was crystallised from ethyl alcohol.
Yield (12 g, 29%); m.p. 96.0° C (Reported[1'] m.p.96.0°*C*).

4-n-Propanoylbiphenyl

This was prepared from biphenyl (77 g, 50 mmol), propionic anhydride (65 g, 50 mmol), anhydrous aluminium chloride (80 g, 59.92 mmol) and carbon disulphide (300 ml) by following a procedure similar to the one described in chapter II for the preparation of 4-n-dodecanoylbiphenyl. The required product was crystallised from petroleum ether.
Yield (42 g, 40%); m.p. 96.0° C (Reported[12] yield 79%; m.p.89°*C*).

4-n-Propylbiphenyl

This was prepared from 4-n-propanoylbiphenyl (42 g, 19.90 mmol), hydrazine hydrate (80%, 18 g, 35.95 mmol), potassium hydroxide (26 g, 46.42 mmol) and digol (400 ml) by following a procedure described in chapter II for the preparation of 4-n-dodecylbiphenyl.
Yield (28 g, 39%); b.p. 112-115°*C*/0.2 mm (Reported[13] b.p.300°*C*/760 mm).

4-n-Propyl-4′-acetylbiphenyl

This compound was synthesised from 4-n-propylbiphenyl (28 g, 14.28 mmol), acetyl chloride (11.1 g, 14.14 mmol), aluminium chloride (24 g, 18 mmol) and dry carbon disulphide (200 ml) by following a procedure described in chapter II for the preparation of 4-n-dodecyl-4'-acety lbiplienyl.

Yield (7 g, 20.5%); m.p. 95.0" C (Reported[14] yield 55%; m.p.97.0°C).

4-n-Butanoylbiphenyl

This was prepared from biphenyl (77g, 50 mmol), butanoyl chloride (53 g, 50 mmol), anhydrous aluminium chloride (80 g, 60 mmol) and carbon disulphide (200 ml) by following a procedure similar to the orie described in chapter II for the preparation of 4-n-dodecanoylbiphenyl. The required product was crystallised from petroleum ether.

Yield (75 g, 67%); m.p. Y5.0°C (Reported[12] yield 78%; m.p.94.0°C).

4-n-Butylbiphenyl

This was prepared from biphenyl (75 g, 50 mmol), 4-n-butylbiphenyl (75 g, 33 mmol), liydrazine hydrate (80%, 60 ml, 47 mmol), potassium hydroxide (45 g, 80 mmol) and digol (500 ml) by following a procedure described in chapter II for the preparation of 4-n-dodecylbiphenyl.

Yield (50 g, 71%); b.p.128-130°C/0.5 mm (Reported[13] b.p.310.0°C/760 mm).

4-n-Butyl-4′-acetylbiphenyl

This compound was synthesised from 4-n-butylbiphenyl (50 g, 23 mmol), acetylchloride (20 g, 25 mmol), aluminium chloride (40 g, 30 mmol) and dry carbon disulphide (200 ml) by following a procedure similar to the one described in chapter II for the preparation of 4-n-dodecyl-4'-acetylbiphenyl.

Yield (31 g, 51%); m.p. 91.0°C (Reported[15] m.p.93.0°C).

The procedure to synthesise **4-methoxy-4'-acetylbiphenyl** has already been described in chapter III.

4-Methoxybiphenyl-4'-carboxylic acid

This was synthesised from **4-methoxy-4'-acetylbiphenyl** (13.2 g, 5.84 mmol), dioxan (200 ml) bromine (24 g, 13.33 mmol), sodium hydroxide (42 g, 105 mrnol) and water (210 ml), following the procedure of Johnson *et al.*.[6] The required product was crystallised from acetic acid.

Yield (11.2 g, 84%); m.p. 254.5° C (Reported[16] m.p. 254.0°C.)

Ethyl-4-methoxybiphenyl-4′-carboxylate

A mixture of 4-methoxybiphenyl-4'-carboxylic acid (11 g, 4.82 mmol), ethyl alcohol (300 ml) and concentrated sulphuric acid (1.5 ml) was heated under reflux for 12 hours at the end of which the excess of ethyl alcohol was removed under reduced pressure. The organic material was extracted into chloroform (3×150 ml) and the combined organic extracts was washed with saturated aqueous sodium bicarbonate solution (2×100 ml), water (2x200 ml) and dried (Na_2SO_4). Solvent was removed and the residue was purified by column chromatography. The required compound was crystallised from ethyl alcohol.

Yield (9 g, 72.5%); m.p. 105.0" C; IR ν_{max}^{nujol} 2920, 2850, 1710, 1605, 1440, 1290, 1200, 830, 765 cm^{-1}; NMR δ 1.41 (t, 3H, -C<u>H</u>$_3$), 3.8 (s, 311, -OC<u>H</u>$_3$), 4.2-4.5 (q, 211, C<u>H</u>$_2$), 6.91-8.2 (m, 8H, Ar<u>H</u>).

Elemental analysis: Found, C,83.89; H,7.98% $C_{39}H_{44}O_3$ requires C,83.57; H,7.85%.

4-n-Dodecylbiphenyl-4'-carboxylic acid

This was synthesised by the oxidation of 4-n-dodecyl-4'-acetylbiphenyl (27.6 g, 7.58 mmol), using dioxan (300 ml), bromine (59.2 g, 37 mmol), sodium hydroxide (53.2 g, 133 mmol) and water (245 ml) as described in chapter III for the preparation of 4-bromobiphenyl-4'-carboxylic acid. The required product was crystallised from acetic acid.

Yield (24.5 g, 88%); m.p. 119.0" C; IR ν_{max}^{nujol} 2900, 2850, 2700, 2580, 1680, 1610, 1470, 1300, 770 cm^{-1}; NMR δ(DMSO-d_6) 0.92 (t, 3H, C$\underline{H}_3$), 1.6-1.7 (m, 16H, 8×C$\underline{H}_2$), 2.6 (q, 2H, ArC$\underline{H}_2$), 3.5 (s, 1H, COO$\underline{H}$), 7-8.2 (m, 8H, Ar$\underline{H}$).

Ethyl-4-n-dodecylbiphenyl-4'-carboxylate

A mixture of 4-n-dodecylbiphenyl-4'-carboxylic acid (23.8 g, 650 mmol), ethyl alcohol (400 ml) and concentrated sulphuric acid (2.5 ml) was refluxed for 12 hours. The excess of ethyl alcohol was distilled under reduced pressure. The organic material was extracted into diethyl ether (3×150 ml) and the combined organic extracts was washed with saturated aqueous sodium bicarbonate solution (3×100 ml), water (3×150 ml) and dried (Na_2SO_4). Removal of solvent afforded a white residue which was crystallised from ethyl alcohol.

Yield (20 g, 78%); m.p. 57.5" C; IR ν_{max}^{nujol} 2900, 2825, 1715, 1605, 1460, 1280, 765 cm^{-1}; NMR 6 0.84 (t, 6H, 2×C$\underline{H}_3$), 1.15-1.72 (m, 20H, 10×C$\underline{H}_2$), 2.66 (t, 211, ArC$\underline{H}_2$), 4.24-4.5 (q, 2H, C$\underline{H}_2$), 7.1-8.2 (m, 8H, Ar$\underline{H}$).

Elemental analysis: Found, C,81.87; H,9.79% $C_{27}H_{38}O_2$ requires C,82.23; H,9.64%.

The method of preparation and the physical data for 4-bromo-4'-acetylbiphenyl, 4-n-dodecyl-4'-acetyl biphenyl and 4-methoxy-4'-acetylbi phenyl have already been given in previous chapters.

[1-(4-n-Undecylbiphenyl)-3-(4‴-methoxybiphenylpropane]-1,3-dione, (4.a.2)

A mixture of 4-n-undecyl-4′acetylbiphenyl (1.16 g, 3.3 mmol), ethyl-4-methoxybiphenyl-4′-carboxylate (0.85 g, 3.3 mmol) and anhydrous 1,2-dimethoxyethane (100 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 (0.198 g, 6.6 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 on silica gel and the pale yellow product thus obtained was crystallised from butan-2-one several times until the melting point was constant.

Yield (1 g, 38%); m.p. 210.5°C; IRν_{max}^{nujol} 2920, 2850, 1608, 1585, 1465, 780 cm^{-1}; NMR δ 0.88 (t, 3H, -C$\underline{H}_3$), 1-2.1 (m, 18 H, 9×C$\underline{H}_2$), 2.6 (t, 2H, ArC$\underline{H}_2$), 3.87 (s, 3H, -OC$\underline{H}_3$), 6.9 (s, 1H, -C=C$\underline{H}$), 7-8 (rn, 16H, Ar$\underline{H}$), 17.01 (s, 1H, enol O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 375 (56,800), 243 (22,100) and 308 (18,400).

Elemental **analysis:** Found, C,83.89; H,7.98% $C_{39}H_{44}O_3$ requires C,83.57; H,7.85%.

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

[1-(4-n-Decylbiphenyl)-3-(4‴-methoxybiphenyl)propane]-1,3-dione, (4.a.1)

Yield 39%; m.p. 210.5°C; IRν_{max}^{nujol} 2920, 2850, 1602, 1583, 1462, 780 cm^{-1}; NMR 6 0.88 (t, 3H, -C$\underline{H}_3$), 1-2 (m, 16 H, 8×C$\underline{H}_2$), 2.66 (t, 2H, ArC$\underline{H}_2$), 3.8 (s, 3H, -OC$\underline{H}_3$),

6.9 (s, 1H, -C=C<u>H</u>), 7-8.1 (m, 16H, Ar<u>H</u>), 17.0 (s, 1H, enol O<u>H</u>); UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 374.5 (56,000), 243.5 (21,800) and 307 (17,800).

Elemental analysis: Found, C,83.72; H,7.81% $C_{38}H_{42}O_3$ requires C,83.51; H,7.70%.

[1-(4-n-Dodecylbiphenyl)-3-(4‴-methoxybiphenyl)propane]-1,3-dione, (4.a.3)

Yield 44.5%; m.p. 207.5°C; IR ν_{max}^{nujol} 2920, 2850, 1602, 1585, 1462, 780 cm^{-1}; NMR δ 0.88 (t, 3H, -C<u>H</u>$_3$), 1.2-2.1 (m, 20H, 10×C<u>H</u>$_2$), 2.66 (t, 2H, ArC<u>H</u>$_2$), 3.8 (s, 3H, -OC<u>H</u>$_3$), 6.9 (s, 1H, -C=C<u>H</u>), 7-8 (m, 16H, Ar<u>H</u>), 17.0 (s, 1H, enol O<u>H</u>); UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 375 (56,800), 242.5 (22,200) and 306 (17,000).

Elemental analysis: Found, C,83.20; H,8.10% $C_{40}H_{46}O_3$ requires C,83.62; H,8.01%.

[1-(4-n-Dodecyloxybiphenyl)-3-(4‴-methoxybiphenyl)propane]-1,3-dione, (4.a.6)

This compound was synthesised from 4-n-dodecyl-4′-acetylbiphenyl (1.9 g, 0.5 mmol), ethyl-4-methoxybiphenyl-4′-carboxylate (1.28 g, 0.5 mmol), dry 1,2-dimethoxyethane (150 ml) and sodium hydride (0.24 g, 1 mmol, 80% dispersed in oil), following the same procedure as described for the preparation of the compound 4.a.2.
Yield (1 g, 34%); m.p. 234.0°C; IR ν_{max}^{nujol} 2920, 2850, 1602, 1505, 1470, 780 cm^{-1}.

Elemental analysis: Found, C,81.23; H,7.77% $C_{40}H_{46}O_4$ requires C,81.35; H,7.79%.

The physical data of the cognate preparations of other [1-(4-n-alkoxybiphenyl)-3-(4‴-methoxybiphenyl) propane]-1,3-diones are given below and due to insolubility of these compounds in $CDCl_3$, C_6D_6, CD_3COCD_3 and in DMSO-d_6, the PMR spectra could not be recorded.

[1-(4-n-Decyloxybiphenyl)-3-(4'''-methoxybiphenyl)propane]-1,3-dione, (4.a.4)

Yield 33.5%; m.p. 234.0°C; IR ν_{max}^{nujol} 2920, 2850, 1602, 1585, 1462, 780 cm^{-1}.

Elemental analysis: Found, C,80.99; H,7.49% $C_{38}H_{42}O_4$ requires C,81.13; H,7.47%.

[1-(4-n-Undecyloxybipheny1)-3-(4'''-met hoxybiphenyl)**propane]-1,3-dione,** (4.a.5)

Yield 36.5%; m.p. 233.5°C; IR ν_{max}^{nujol} 2920, 2850, 1602, 1585, 1460, 780 cm^{-1}.

Elemental analysis: Found, C,81.49; H,7.73% $C_{39}H_{44}O_4$ requires C,81.25; H,7.63%.

[1-(4-n-Dodecylbiphenyl)-3-(4'''-ethylbiphenyl)propane]-1,3-dione, (4.b.1)

This compound **was** prepared from 4-ethyl-4'-acetylbiphenyl(2 **g**, 0.89 mmol), ethyl-**4-n-dodecylbiphenyl-4'-carboxylate** (3.5 **g**, 0.89 mmol), dry 1,2-dimethoxyethane (150 ml) and sodium hydride (0.42 **g**, 1.75 mmol, 80% dispersed in oil) using a procedure **similar** to the one described for the preparation of compound 4.a.2.

Yield (1.5 **g**, 51.5%); m.p. 186.5°C; IR ν_{max}^{nujol} 2920,2850, 1602, 1585, 1460, 780 cm^{-1}; NMR δ 0.87(t, 6H, 2×-C<u>H</u>$_3$), 1.2-2 (m, 20H, 10×C<u>H</u>$_2$), 2.65 (t, 4H, 2×ArC<u>H</u>$_2$), 6.9 (s, 1H, -C=C<u>H</u>), 7.2-8 (m, 1611, Ar<u>H</u>), 17.02 (s, 1H, enol O<u>H</u>); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 371 (51,600), 241.5 (21,800), 305 (17,100).

Elemental analysis: Found, C,86.01; H,8.39% $C_{41}H_{48}O_2$ requires C,85.92; H,8.58%.

The physical data of the cognate preparations of other **[1-(4-n-dodecylbipheny1)-**3-(4'''-alkylbiphenyl) propane]-1,3-diones are given below.

[1-(4-n-Dodecylbiphenyl)-3-(4‴-n-propylbiphenyl)propane]-1,3-dione, (4.b.2)

Yield 36%; m.p. 187.5°C; IR ν_{max}^{nujol} 2900, 2850, 1602, 1582, 1465, 780 cm^{-1}; NMR 6 0.8 (t, 6H, 2×-C<u>H</u>$_3$), 1.1-1.8 (m, 20H, 10×C<u>H</u>$_2$), 2.6 (t, 4H, 2×ArC<u>H</u>$_2$), 6.9 (s, 1H, -C=C<u>H</u>), 7.1-8.2 (m, 16H, Ar<u>H</u>), 17 (s, 1H, enol O<u>H</u>); UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 371.5 (51,900), 241.5 (22,000), 306.5 (18,000).

Elemental analysis: Found, C,85.80; H,8.65% $C_{42}H_{50}O_2$ requires C,86.00; H,8.53%.

[1-(4-n-Dodecylbiphenyl)-3-(4‴-n-butylbiphenyl)propane]-1,3-dione, (4.b.3)

Yield 34.5%; m.p. 184.0°C; IR ν_{max}^{nujol} 2920, 2850, 1602, 1585, 1470, 780 cm^{-1}; NMR 6 0.8 (t, 6H, 2×-C<u>H</u>$_3$), 1.1-2.1 (m, 2011, 10×C<u>H</u>$_2$), 2.6 (t, 4H, 2×ArC<u>H</u>$_2$), 6.9 (s, 1H, -C=C<u>H</u>), 7.05-8.5 (m, 16H, Ar<u>H</u>), 17.0 (s, 1H, enol O<u>H</u>); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 371.5 (50,900), 240.8 (21,300), 305 (16,900).

Elemental analysis: Found, C,86.42; H,8.85% $C_{43}H_{52}O_2$ requires C,86.00; H,8.66%.

[1-(4-n-Dodecylbiphenyl)-3-(4‴-bromobiphenyl)propane]-1,3-dione, (4.b.4)

This was prepared from ethyl-4-bromobiphenyl-4′-carboxylate (2.03 g, 0.66 mmol), 4-n-dodecyl-4'-acetylbiphenyl(2.42 g, 0.66 mmol), dry 1,2-dimethoxyethane (150 ml) and sodium hydride (0.4 g, 1.66 mmol, 80% dispersed in oil) following the procedure described for the preparation of compound 4.a.2.

Yield (1.6 g, 49.5%); m.p. 235.0°C; IR ν_{max}^{nujol} 2920, 2885, 1600, 1580, 1460, 1000, 780 cm^{-1}; NMR 6 0.9 (t, 3H, C<u>H</u>$_3$), 1.3-1.6 (m, 20H, 10×C<u>H</u>$_2$), 2.6 (t, 2H, ArC<u>H</u>$_2$), 6.8 (s, 1H, -C=C<u>H</u>), 7.2-8.2 (m, 16H, Ar<u>H</u>), 16.95 (s, 1H, enol OH); UV-Vis $\lambda_{max}^{CHCl_3}$

(ϵ) 369 (51,300), 305.5 (18,000), 244 (18,800).

Elemental analysis: Found, C,75.14; H,6.93% $C_{39}H_{43}O_2Br$ requires C,75.12; H,6.90%.

[1-(4-n-Dodecylbiphenyl)-3-(4‴-ethoxybiphenyl)propane]-1,3-dione, (4.b.5)

This compound was prepared from 4-ethoxy-4'-acetylbipheliyl (1.21 g, 0.5 mrnol), **ethyl-4-n-dodecylbiphenyl-4'-carboxylate** (2 g, 0.5 mmol), dry 1,2-dimethoxyethane (150 ml) and sodium hydride (0.4 g, 1 mmol, 60% dispersion in paraffin oil) following a procedure similar to the one described for the preparation of compound 4.a.2.

Yield (1 g, 33.5%); m.p. 205.0°C; IR ν_{max}^{nujol} 2920, 2850, 1600, 1580, 1460, 780 cm^{-1}; NMR δ 0.88 (t, 611, 2×-C$\underline{H}_3$), 1.2-1.6 (m, 2011, 10×C$\underline{H}_2$), 2.66 (t, 2H, 2×ArC$\underline{H}_2$), 4.08 (q, 2H, -OC$\underline{H}_2$), 6.9 (s, 1H, -C=C$\underline{H}$), 7-8.1 (m, 16H, Ar$\underline{H}$), 16.95 (s, 1H, enol O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 375.5 (49,100), 242 (20,950), 308 (14,700).

Elemental analysis: Found, C,83.80; H,8.29% $C_{41}H_{48}O_3$ requires C,83.67; H,8.16%.

Bis[1-(4-n-undecylbiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]copper(II), (4.c.2)

To a stirred solution of [1-(4-n-undecylbiphenyl)-3-(4‴-methoxybiphenyl) propane]-1,3-dione (0.2 g, 0.35 mmol) in warm tetrahydrofuran (50 ml) was added a solution of potassiutn hydroxide (0.019 g, 0.35 mmol) in ethyl alcohol (8 ml). To this was added a solution of cupric chloride dihydrate (0.029 g, 0.17 mmol) in ethyl alcohol (8 ml). The reaction mixture turned dark green in colour. This was refluxed for four hours and cooled. The green precipitate was filtered and washed with ethyl alcohol. This precipitate was dissolved in chloroform (100 ml) and washed with water (3x75 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of tlie residue repeatedly from butan-2-one gave green shining crystals.

Yield (0.084 g, 40%); m.p. 210.0°C; IR ν_{max}^{nujol} 2900, 2850, 1610, 1585, 1520, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 373 (88,600), 327 (56,500)) 243 (48,100).

Elemental analysis: Found, C,79.20; H,7.73% $C_{78}H_{86}O_6Cu$ requires C,79.19; H,7.32%.

Bis[1-(4-n-decylbiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]copper(II), (4.c.1)

Yield 47%; m.p. 215.5°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1585, 1520, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 374 (89,000), 327 (57,000), 243.5 (49,000).

Elemental analysis: Found, C,78.79; H,7.49% $C_{76}H_{82}O_6Cu$ requires C,79.07; H,7.15%.

Bis[1-(4-n-dodecylbiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]copper(II), (4.c.3)

Yield 35%; m.p. 202.0°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1583, 1520, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 373.5 (89,500))327 (57,000)) 243 (48,500).

Elemental analysis: Found, C,78.81; H,7.44% $C_{80}H_{90}O_6Cu$ requires C,79.38; H,7.43%.

Bis[1-(4-n-undecyloxybiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]copper(II), (4.c.5)

This complex was prepared from [1-(4-n-undecyloxybiphenyl)-3-(4‴-methoxybiphenyl) propane- 1,3-dione] (0.32 g, 0.55 mmol), potassium hydroxide (0.031 g, 0.55 mmol), cupric chloride dihydrate (0.047 g, 0.29 mmol) and ethyl alcohol (16 ml) following a procedure similar to the one described for the preparation of compound 4.a.2.
Yield (0.1 g, 43.5%); m.p. 225.0°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1585, 1525, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 376.5 (81,000), 336.5 (60,700), 244 (51,900).

Elemental analysis: Found, C,77.65; H,7.17% $C_{78}H_{86}O_8Cu$ requires C,77.13; H,7.08%.

The physical data of the cognate preparations of other [1-(4-n-alkoxybipheny1)-3-(4‴-methoxybiphenyl) propane-1,3-dionato]copper(II) complexes are given below.

Bis[1-(4-n-decyloxybiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]copper(II), (4.c.4)

Yield 47.5%; m.p. 235.0°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1590, 1525, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 376.5 (82,000), 336 (59,000), 242 (50,600).

Elemental analysis: Found, C,76.76; H,6.91% $C_{76}H_{82}O_8Cu$ requires C,76.92; H,6.90%.

Bis[1-(4-n-dodecyloxybiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]copper(II), (4.c.6)

Yield 38%; m.p. 237.0°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1585, 1518, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 376.5 (82,200), 336.5 (58,800), 243.4 (50,800).

Elemental analysis: Found, C,77.17; II,7.50% $C_{80}II_{90}O_8Cu$ requires C,77.32; H,7.24%.

Bis[1-(4-n-dodecylbiphenyl)-3-(4‴-ethylbiphenyl)propane-1,3-dionato]copper(II), (4.d.1)

This complex was prepared from [1-(4-n-dodecylbiphenyl)-3-(4‴-ethylbiphenyl) propane-1,3-dione (0.2 g, 0.035 mmol), potassium hydroxide (0.019 g, 0.035 mmol), cupric chloride dihydrate (0.03 g, 0.175 mmol) and ethyl alcohol (16 ml) following a procedure similar to the one described for the preparation of compound 4.c.2.

Yield (0.1 g, 47.5%); m. p. 211.5°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1585, 1520, 1460,

780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 371.5 (68,300), 322 (60,600), 243 (45,500).

Elemental analysis: Found, C,81.38; H,7.88% $C_{82}H_{94}O_4Cu$ requires C,81.64; H,7.79%.

Bis[1-(4-n-dodecylbiphenyl)-3-(4‴-n-propylbiphenyl)propane-1,3-dionato]copper(II), (4.d.2)

Yield 45.5%; m.p. 234.0°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1585, 1520, 1420, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 370.5 (68,000), 321 (62,000), 244 (46,000).

Elemental analysis: Found, C,82.17; H,8.13% $C_{84}H_{98}O_4Cu$ requires C,81.71; H,7.94%.

Bis[1-(4-n-dodecylbiphenyl)-3-(4‴-n-butylbiphenyl)propane-1,3-dionato]copper(II), (4.d.3)

Yield 47.5%; m.p. 241.5°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1585, 1520, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 371.0 (68,900), 321.5 (59,500), 242.5 (46,100).

Elemental analysis: Found, C,82.13; H,8.26% $C_{86}H_{102}O_4Cu$ requires C,81.80; H,8.08%.

Bis[1-(4-n-dodecylbiphenyl)-3-(4‴-n-bromobiphenyl)propane-1,3-dionato]copper(II), (4.d.4)

This complex was prepared from [1-(4-n-dodecylbiphenyl)-3-(4‴-bromobiphenyl) propane-1,3-dione] (0.2 g, 0.032 mmol), cupric chloride dihydrate (0.027 g, 0.016 mmol), potassium hydroxide (0.018 g, 0.032 mmol) and ethyl alcohol (16 ml) by following a procedure described for the synthesis of compound 4.c.2.

Yield (0.08 g, 38%); m.p. 166.0°C; IR ν_{max}^{nujol} 2920, 2850, 1600, 1590, 1540, 1485, 1430, 1400, 1300, 1012, 730 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 363.5 (83,800), 318 (60,400), 242 (44,600).

Elemental analysis: Found, C,71.61; H,6.49% $C_{80}H_{84}O_4Br_2Cu$ requires C,71.61; H,6.42%.

Bis[1-(4-n-dodecylbiphenyl)-3-(4‴-n-ethoxybiphenyl)propane-1,3-dionato]copper(II), (4.d.5)

This complex was prepared from [1-(4-n-dodecylbiphenyl)-3-(4‴-ethoxybiphenyl) propane]1,3-dione (0.2 g, 0.034 mmol), cupric chloride dihydrate (0.03 g, 0.017 mmol), potassium hydroxide (0.019 g, 0.034 mmol) and ethyl alcohol (20 ml) by following a procedure described for the synthesis of compound 4.c.2.

Yield (0.08 g, 40%); m.p. 241.0°C; IR ν_{max}^{nujol} 2915, 2850, 1610, 1585, 1520, 1460, 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 374.5 (89,200))327.5 (56,400)) 242.5 (49,700).

Elemental analysis: Found, C,79.11; H,7.65% $C_{82}H_{92}O_6Cu$ requires C,79.50; H,7.59%.

Bis[1-(4-n-undecylbiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato]palladium(II), (4.e.2)

A mixture of [1-(4-n-undecylbiphenyl)-3-(4‴-methoxybiphenyl) propane]-1,3-dione (0.25 g, 0.45 mrnol), palladium chloride (0.044 g, 0.24 mrnol), dry acetonitrile (50 ml) and anhydrous potassium carbonate (0.094 g, 0.68 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 (100 ml) and washed with water (3 × 50 ml) and dried (Na_2SO_4). Removal of solvent afforded a yellow product which was crystallised from butan-2-one, several times until the melting point was constant.

Yield (0.10 g, 38%); m.p. 227.6°C; IR ν_{max}^{nujol} 2900, 2850, 1610, 1580, 1520, 1460, 825, 785 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.2-2.1 [m, 36H, (9×C$\underline{H}_2$)$_2$], 2.66 (t, 4H, 2×ArC$\underline{H}_2$), 3.8 (s, 6H, 2× -OC$\underline{H}_3$), 6.9 [s, 2H, (-C=C$\underline{H}$)$_2$], 7-8.2 (m, 32H, Ar$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 384 (55,100), 336 (81,800), 246 (69,500).

Elemental analysis: Found, C,76.45; H,7.11% $C_{78}H_{86}O_6Pd$ requires C,76.44; H,7.02%.

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

Bis[1-(4-n-decylbiphenyl)-3-(4‴-methoxybiphenyl)**propane-1,3-**dionato] **palladium(II),** (4.e.l)

Yield 50%; m.p. 236.8°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1570, 1520, 1460, 825, 780 cm^{-1}; NMR δ 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.2-2.1 [m, 32H, (8×C$\underline{H}_2$)$_2$], 2.66 (t, 4H, 2×ArC$\underline{H}_2$), 3.8 (s, 611, 2× -OC$\underline{H}_3$), 6.9 [s, 211, (-C=C$\underline{H}$)$_2$], 7-8.2 (rn, 32H, Arfl); UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 384 (54,500))336 (80,800))245.5 (69,000).

Elemental analysis: Found, C,76.24; H,6.90% $C_{76}H_{80}O_6Pd$ requires C,76.22; H,6.85%.

Bis[1-(4-n-dodecylbiphenyl)-3-(4‴-methoxybiphenyl)propane-1,3-dionato] **palladium(II), (4.e.3)**

Yield 38%; m.p. 227.2°C; IR ν_{max}^{nujol} 2920, 2850, 1610, 1582, 1520, 1460, 825, 780 cm^{-1}; NMR 6 0.88 (t, 6H, 2×-C$\underline{H}_3$), 1.2-1.8 [m, 40H, (10×C$\underline{H}_2$)$_2$], 2.66 (t, 4H, 2×ArC$\underline{H}_2$), 3.8 (s, 6H, 2× -OC$\underline{H}_3$), 6.8 [s, 2H, (-C=C$\underline{H}$)$_2$], 7.1-8.2 (m, 32H, Ar$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 384 (55,000), 336 (80,500), 247 (70,000).

Elemental analysis: Found, C,76.38; H,7.18% $C_{80}H_{90}O_6Pd$ requires C,76.65; H,7.18%.

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