

Chapter 4

Synthesis and mesomorphic properties of

- (i) 1-(4''-n-Dodecylbiphenyl)-3-(4-n-alkylphenyl)propane-1,3-diones**

- (ii) 1-(4''-n-Dodecylbiphenyl)-3-(4-n-alkyloxyphenyl)propane-1,3-diones**

4.1 Survey of the mesomorphic properties of aryl β -diketones and their metal complexes

Many aryl β -diketones which are easily synthesised, are useful liquid crystalline derivatives.¹⁻⁷ Further, these compounds have a great ability to complex with various metal ions and many of these chelates are mesogenic.^{8,9} Amongst the most widely studied coordination compounds are the complexes of β -diketones, which appear to have been investigated with virtually every metal and metalloid in the periodic table.

A brief description of the chemistry of β -diketone ligands is given below:

β -Diketones are capable of exhibiting keto-enol tautomerism (figure 4.1). The hydrogen atom of the central methylene group is activated by the adjacent C=O groups and a conjugate system can arise by a prototropic shift. These tautomers exist in equilibrium with each other and structurally they possess a cis configuration and a *syn (cisoid)* conformation. Under appropriate conditions the enolic hydrogen atom of the ligand can be replaced by a metal cation to produce a six-membered chelate ring (figure 4.1), thereby shifting the keto-enol equilibrium in favour of the enol form.

The liquid crystalline properties of compounds having a β -diketone group have been investigated only recently. The first report of such a compound was on 1,3-di(*p*-n-decylphenyl)propane-1,3-dione, by Giroud and Billard.² Later, they reported a few more similar β -diketones and concluded that only those compounds having more than eighteen carbon atoms in the side chains exhibit a mesophase. Through optical and miscibility studies they also tentatively identified the mesophase exhibited by the above compounds as smectic E.²

Ohta *et al.*^{3,4} have investigated a number of β -diketones including some of the

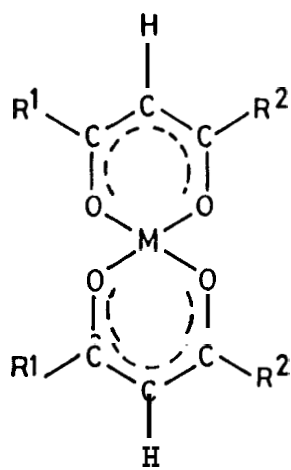
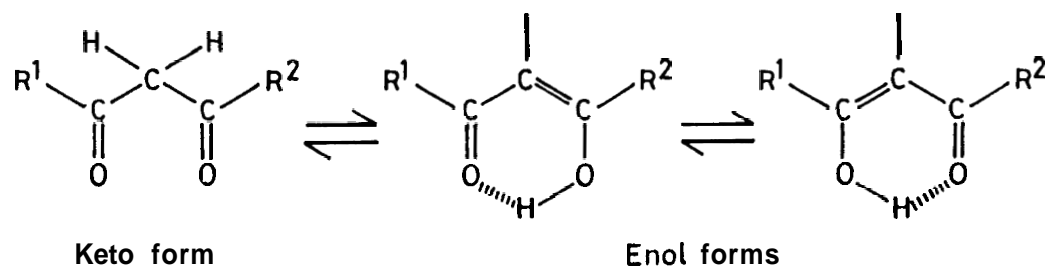


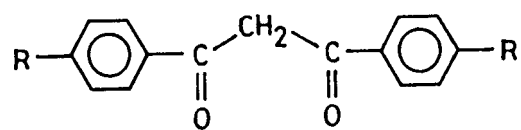
Figure 4.1

compounds reported² earlier. They were 1,3-di(p-n-alkylphenyl)propane-1,3-diones, 4.a. The texture exhibited by these compounds has not been conclusively identified by them, though they state that it is similar to that reported by Giroud and Billard.² A similar series of diketones with unsymmetrical substituents, synthesised by the author⁷ has already been discussed in chapter 2.

In all the above mentioned cases, the β -diketone group is linked to phenyl rings. On replacement of the phenyl rings by either a biphenyl moiety or normal alkyl chains, the nature of the mesophase completely changes. For example, Sadashiva *et al.*⁶ have investigated a series of 1-(p-n-alkylbiphenyl)-3-(phenyl)propane-1,3-diones, 4.b. The first four homologues in the series exhibit the classical nematic phase and a smectic phase. By optical, miscibility and X-ray studies they found that the smectic phase is of the **A** type. This is the first example of a β -diketone exhibiting a nematic as well as a smectic **A** phase. They have also studied the effect of different terminal substituents on the mesomorphic properties of these β -diketones.

Ohta *et al.*¹⁰ have reported some 1-(p-n-alkyloxybiphenyl)-3-n-alkylpropane-1,3-diones. They show a focal conic texture which has been characterised as smectic **A** mesophase. They have established the nature of the mesophase by detailed X-ray studies on these compounds. Later, they reported¹¹ a series of 1-(4-n-alkyloxybiphenyl)-3-(methyl)propane-1,3-diones. These exhibit enantiotropic smectic **E** and smectic **A** phases. In addition to mesomorphism, they exhibit polymorphism as well.

Sadashiva *et al.*¹² have reported a series of β -diketones exhibiting smectic **A** and smectic **E** phases. Sadashiva *et al.*¹³ also examined some 1-(p-n-dodecylbiphenyl)-3-(p-substituted biphenyl)propane-1,3-diones. Some of them have been found to be mesomorphic. Later, they investigated¹⁴ a homologous series of 1-(p-n-alkylbiphenyl)-3-(p-chlorophenyl)propane-1,3-diones. Here, the lower homologues exhibit an

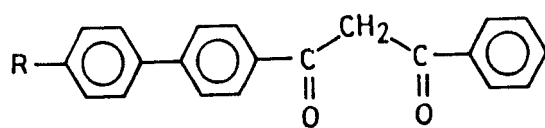


$\text{R} = \text{C}_n\text{H}_{2n+1}$

or

$\text{OC}_n\text{H}_{2n+1}$

4.a



4.b

enantiotropic smectic **A** phase, while the higher ones exhibit smectic **E** phase in addition to smectic **A** phase. Thompson *et al.*^{15,16} have investigated a number of mesogenic β -diketones, particularly the effect of polar terminal substituents *viz.*, Br, CF₃, CN on the nature of the mesophase.

The detailed survey of mesogenic metallo β -diketonates has already been made in chapters 2 and 3 and only relevant references to these will be made at appropriate places here.

4.2 Results and discussion

Chandrasekhar *et al.*¹⁷ have investigated a few nematogenic bis[1-(*p*-*n*-decylbiphenyl)-3-(substituted phenyl)propane-1,3-dionato]copper(II) complexes, with either short alkyl or alkyloxy chains on the phenyl ring. Sadashiva *et al.*⁶ have examined the effect of para substituents on the nature of the mesophase of many β -diketones.

In order to study the effect of different *p*-substituents on the mesomorphic properties in such systems, the following two homologous series of β -diketones and a few of their copper(II) complexes were prepared.

- (i) 1-(4''-*n*-Dodecylbiphenyl)-3-(4-*n*-alkylphenyl)propane-1,3-diones, **4.c** and
- (ii) 1-(4''-*n*-Dodecylbiphenyl)-3-(4-*n*-alkyloxyphenyl)propane-1,3-diones, **4.d**.

Most, of the β -diketones in the above two series were found to be mesogenic. They exhibit a smectic **A** phase. Among the copper(II) complexes synthesised, only methyloxy derivative was found to be mesogenic, exhibiting a monotropic nematic phase. Since the β -diketones were mesogenic, the same were investigated in detail.

1-(4''-*n*-Dodecylbiphenyl)-3-(4-*n*-alkylphenyl)propane-1,3-diones (**4.c**), were prepared starting from 4-*n*-dodecyl-4'-acetylbiphenyl and **ethyl-4-*n*-alkylbenzoates**. 1-

(4''-n-Dodecylbiphenyl)-3-(4-n-alkyloxyphenyl)propane-1,3-diones (4.d), were prepared starting from 4-n-dodecyl-4'-acetylbiphenyl and ethyl-4-n-alkyloxybenzoates. These reactions are schematically shown in figure 4.2. The corresponding copper(II) complexes of 4.c and 4.d were prepared following the scheme shown in figure 4.3. Thus, on treating 4.c and 4.d with cupric chloride dihydrate in ethyl alcohol using potassium hydroxide as a base, afforded the required copper(II) complexes, 4.e.

The transition temperatures and enthalpies of transitions for 1-(4''-n-dodecylbiphenyl)-3-(⁴⁻ⁿ⁻alkylphenyl)propane-1,3-diones (4.c), are given in table 4.1 . All the homologues except the compound 4.c.12 are mesogenic. They exhibit focal-conic texture, characteristic of smectic A phase. As can be seen from the table, compounds 4.c.1 to 4.c.9 are enantiotropic and compounds 4.c.10 and 4.c.11 are monotropic. Compound 4.c.12 is non-mesomorphic. A few of the copper complexes synthesised using these ligands were found to be non-mesomorphic. These results are in complete contrast to those observed,¹⁷ for a similar series of compounds. It was found that the ligand β -diketones did not exhibit any liquid crystalline property whereas the corresponding copper chelates exhibited a monotropic nematic phase.¹⁷

A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for 4.c, is shown in figure 4.4. It is seen that there is an alternation in the $S_A \rightarrow I$ transition temperatures. Further, the melting point of compound with $n=10$ increases suddenly and hence this exhibits a monotropic mesophase. Since compound 4.c.12 has a high melting point, it does not exhibit any liquid crystalline property.

The transition temperatures and enthalpies of transitions for 1-(4''-n-dodecylbiphenyl) -3- (4-n-alkyloxyphenyl)propane-1,3-diones (4.d), are given in table 4.2 . Most of the homologues are mesogenic. They exhibit a focal-conic texture, char-

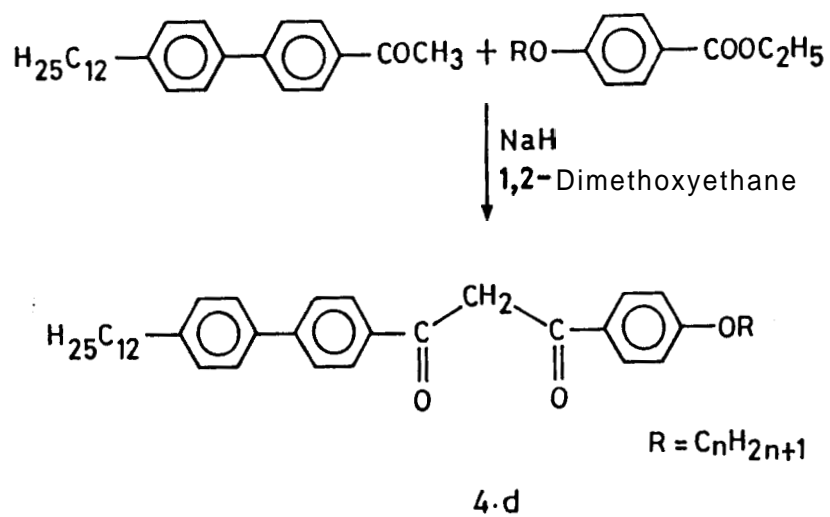
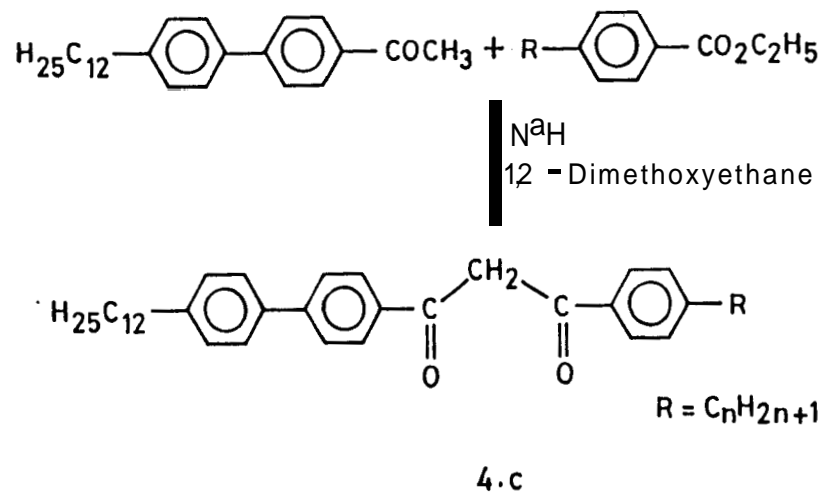


Figure 4.2

Table 4.1
 Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kcal/mol) for
1-(4''-n-Dodecylbiphenyl)-3-(4-n-alkylphenyl)propane-1,3-diones,
4.c

Compound number	n	C	S _A	I
4.c.1	1	. 100.5 4.95	. 108.0 0.99	.
4.c.2	2	. 79.0 7.43	. 99.0 1.02	.
4.c.3	3	. 83.5 5.40	. 101.5 1.06	.
4.c.4	4	. 82.0 5.21	. 99.5 1.20	.
4.c.5	5	. 81.5 4.92	. 101.5 1.23	.
4.c.6	6	. 83.5 5.06	. 100.0 1.25	.
4.c.7	7	. 85.0 5.12	. 103.5 1.30	.
4.c.8	8	. 86.0 4.20	. 101.0 1.11	.
4.c.9	9	. 91.5 7.71	. 103.5 1.40	.
4.c.10	10	. 103.5 9.97	(. 102.5) 1.41	.
4.c.11	11	. 104.0 8.29	(. 101.5) 1.51	.
4.c.12	12	. 108.5 10.28	-	.

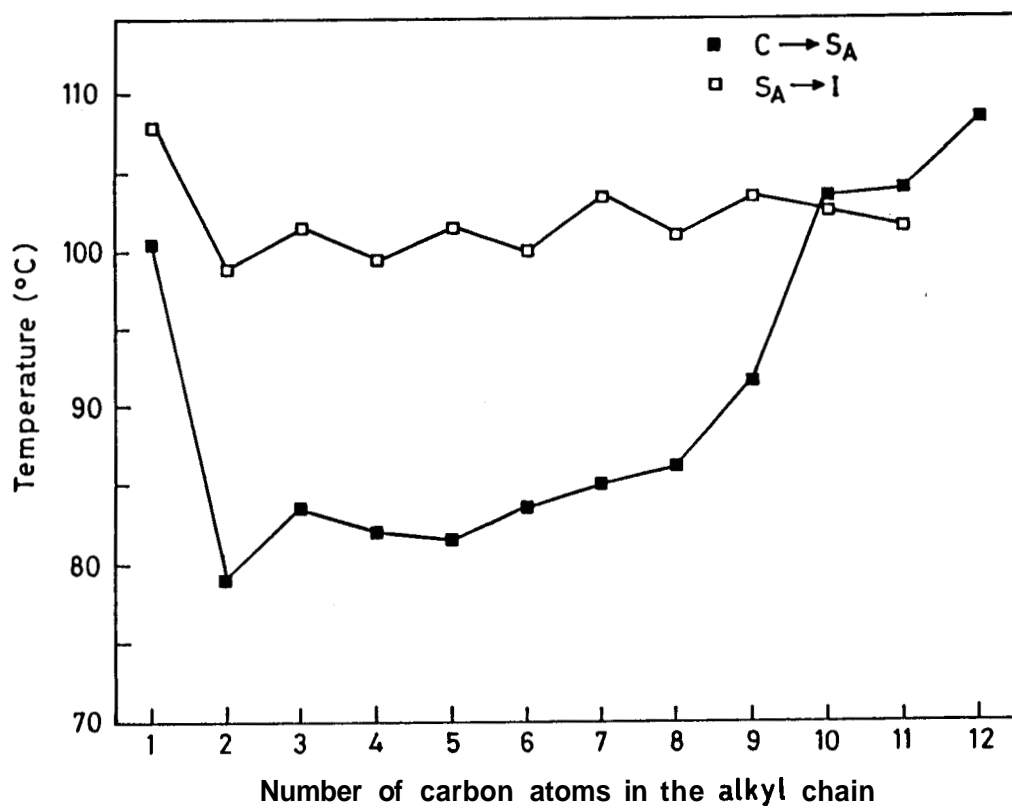


Figure 4.4: A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for series 4.c.

Table 4.2

Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kcal/mol) for
1-(4''-n-Dodecylbiphenyl)-3-(4-n-alkyloxyphenyl)propane-1,3-diones,
 4.d

Compound number	n	C_1	C	S_A	I
4.d.1	1	. 105.5 2.70	. 109.5 3.24	-	
4.d.2	2	. 99.5 8.58	. 105.0 0.95	(. 100.0)'	.
4.d.3	3	. 96.5 9.73	. 107.5 2.24	(. 95.0)'	.
4.d.4	4	. 90.0 3.10	. 100.5 5.98	(. 99.5)'	.
4.d.5	5		. 88.0 4.43	. 97.0 0.86	.
4.d.6	6		. 82.0 6.63	. 98.5 0.82	.
4.d.7	7	. 81.5 6.30	. 90.0 0.51	. 98.0 0.52	.
4.d.8	8	. 77.0 6.20	. 104.0 1.37	. 108.0 1.19	.
4.d.9	9	. 79.5 8.99	. 109.0 3.85	(. 108.5)'	.
4.d.10	10	. 76.5 8.67	. 110.5 3.87	(. 109.5)'	.
4.d.11	11	. 79.5 1.16	. 112.5 3.46	-	
4.d.12	12	. 74.0 7.10	. 113.0 4.52	-	

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

acteristic of smectic A phase. Compound 4.d.1 is non-mesogenic, compounds 4.d.2 to 4.d.4 are monotropic and compounds 4.d.5 to 4.d.8 are enantiotropic. Again, the compounds 4.d.9 and 4.d.10 are monotropic while the compounds 4.d.11 and 4.d.12 are non-mesomorphic. Among it few copper chelates synthesised using these β -diketones, only the methyloxy derivative is mesomorphic [C 180.0 N (168.5) I]. The dsc thermogram for compound 4.d.10 is shown in figure 4.5.

A graphical representation of transition temperatures versus the number of carbon atoms in the alkyloxy chain for 4.d, is shown in figure 4.6. As can be seen from the graph, there is alternation in $S_A \rightarrow I$ temperature upto $n=7$, but from $n=8$ onwards there is an increase in $S_A \rightarrow I$ transition temperature. This kind of behaviour is rather unusual. There is a sudden increase in melting points of compounds from $n=7$ onwards. Once again as in the case of 4.c.12, due to their high melting points, compounds 4.d.11 and 4.d.12 are non-mesomorphic.

In conclusion, all the β -diketones reported so far, exhibit either a nematic or a smectic mesophase. In some cases they exhibited both the phases. The smectic mesophase exhibited by these generally belong to either smectic A or smectic E modification. The smectic phase exhibited by the above discussed β -diketones (4.c and 4.d) belong to A modification only. All the homologues, except the last one in the series 4.c, are mesomorphic. In the case of series 4.d, only middle homologues are mesomorphic. Except for the methyloxy derivative, none of the other copper(II) chelates substituted by alkyl or alkyloxy chains in the para position of the phenyl ring showed any mesophase.

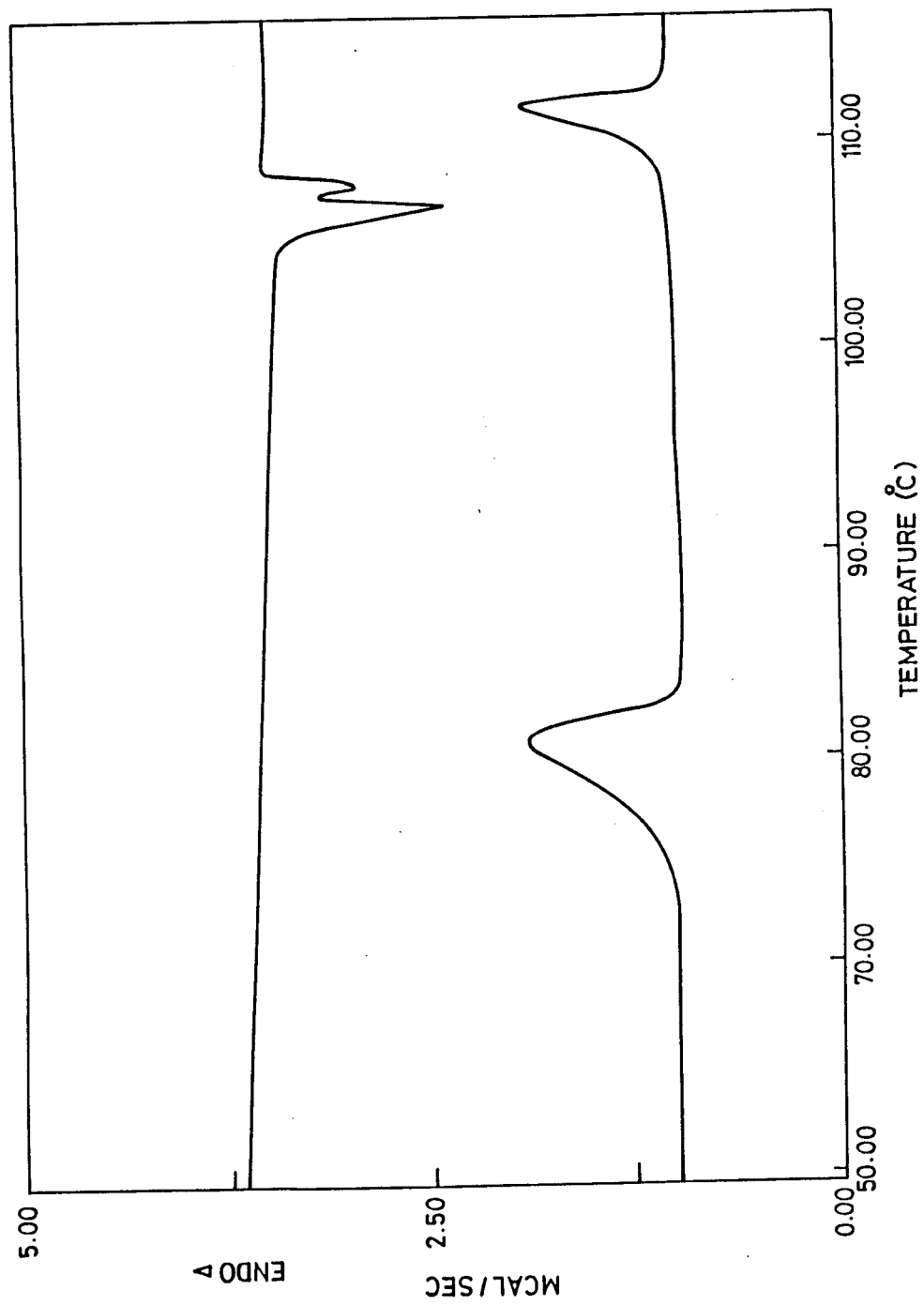


Figure4.5: The dsc thermogram for compound 4.d.10.

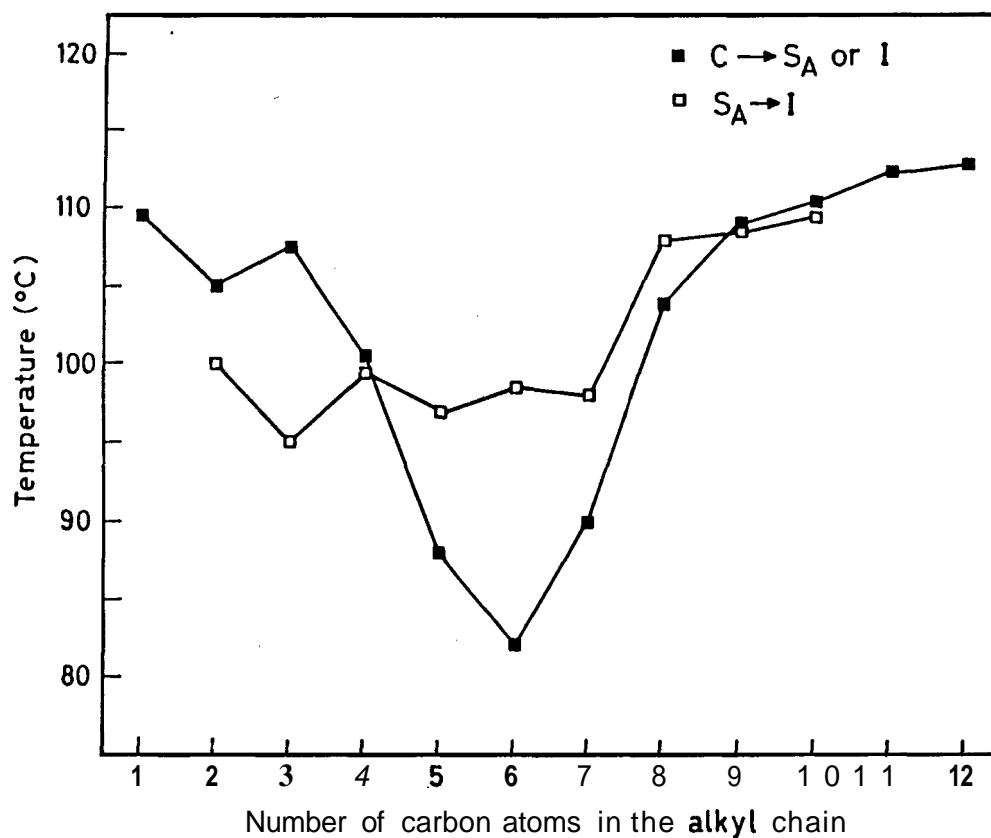


Figure 4.6: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 4.d.

4.3 Experimental

4-n-Dodecyl-4'-acetylbiphenyl was prepared as described in chapter 3. 4-n-Alkylbenzoic acids were prepared following the procedure of Johnson, Gutsche and Offenbauer.¹⁸ The ethyl esters of these acids were prepared following a standard procedure given below for the hexyl derivative.

Ethyl-4-n-hexylbenzoate:

A mixture of 4-n-hexylbenzoic acid (19.6 g), ethyl alcohol (200 ml) and concentrated sulphuric acid (2 ml) was refluxed for sixteen hours. The excess ethyl alcohol present in the reaction mixture was distilled off, the residue was poured onto ice (400 g) and extracted with ether (2×100 ml). The combined ethereal solution was washed with water (2×100 ml), 5% sodium bicarbonate solution (2×100 ml), water (3×100 ml) and dried (Na_2SO_4). Removal of solvent and fractional distillation of the residue gave pure ethyl-4-n-hexylbenzoate. Yield, 18.0 g, (81%); b.p. 155-158°C/1mm.

In a similar way the other required ethyl-4-n-alkylbenzoates were also prepared and their physical constants are given in table 4.3.

1-(4''-n-Dodecylbiphenyl)-3-(4-n-hexylphenyl)propane-1,3-dione:

In a 250 ml two-necked round bottom flask fitted with a reflux condenser and a nitrogen inlet tube was placed a mixture of 4-n-dodecyl-4'-acetylbiphenyl (3.64 g, 0.01 mol) and ethyl-4-n-hexylbenzoate (2.34 g, 0.01 mol) in dry 1,2-dimethoxyethane (80 ml). This was stirred magnetically, sodium hydride (0.8 g, 0.02 mol, 60% in paraffin oil) was added and the mixture refluxed for four hours. Then it was cooled, ice cold dilute hydrochloric acid (30 ml) was added and the mixture extracted with chloroform (3×50 ml). The combined chloroform solution was washed with water (4×100 ml) and dried (Na_2SO_4). Removal of solvent and chromatography of the

Table 4.3

**Physical constants for ethyl-4-n-alkylbenzoates,
 $C_nH_{2n+1} \cdot C_6H_4 \cdot COOC_2H_5$**

n	Boiling point(°C)/mm
1	60-61/0.5
2	76/2
3	88/12.5
4	120-123/1
5	150-152/1
7	160-162/2
8	183-185/2
9	190-192/2
10	197-199/2
11	205-208/2
12	210-213/2

residue gave a pale yellow product which was crystallised using propan-2-ol.

Yield, 1.7 g, (31%); m.p. 83.5°C; IR ν_{max} : 2930, 2850, 1608, 1590, 1470, 1380, 1300, 1180 and 775 cm^{-1} ; NMR δ : 0.9 (t, (ill, 2 \times -CH₃), 1.0–2.0 (m, 28H, 14 \times -CH₂), 2.65 (s, 4H, 2 \times arCH₂), 6.9 (s, 1H, -C=C(H)), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, =C-OH).

Anal. calcd. for C₃₉H₅₂O₂,

C, 84.78 ; H, 9.42 %

Found: C, 84.92 ; H, 9.58 % .

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

1-(4''-n-Dodecylbiphenyl)-3-(4-methylphenyl)propane-1,3-dione:

Yield, 35%; m.p. 100.5°C; IR ν_{max} : 2920, 2860, 1608, 1588, 1470, 1380, 1310, 1190 and 780 cm^{-1} ; NMR δ : 0.9 (t, 3H, -CH₃), 1.1–2.0 (m, 20H, 10 \times -CH₂), 2.45 (s, 3H, arCH₃), 2.7 (t, 2H, arCH₂), 6.85 (s, 1H, -C=C(H)), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, =C-OH).

Anal. calcd. for C₃₄H₄₂O₂,

C, 84.64 ; H, 8.71 %

1 C, 84.47 ; H, 9.21 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-ethylphenyl)propane-1,3-dione:

Yield, 32%; m.p. 79.0°C; IR ν_{max} : 2930, 2860, 1608, 1588, 1470, 1380, 1310, 1190 and 780 cm^{-1} ; NMR δ : 0.9 (t, (ill, 2 \times -CH₃), 1.1–2.0 (m, 20H, 10 \times -CH₂), 2.7 (t, 4H, 2 \times arCH₂), 6.85 (s, 1H, -C=C(H)), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, =C-OH).

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Anal. calcd. for $C_{35}H_{44}O_2$,

C, 84.67 ; H, 8.87 %

Found: C, 84.63 ; H, 9.02 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-propylphenyl)propane-1,3-dione:

Yield, 211%; m.p. 83.5°C; IR ν_{max} : 2930, 2860, 1610, 1590, 1470, 1380, 1300, 1185 and 775 cm^{-1} ; NMR. δ : 0.95 (t, 6H, 2 \times -CH₃), 1.1–2.0 (m, 22H, 11 \times -CH₂), 2.7 (t, 4H, 2 \times arCH₂), 6.85 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, =C-OH).

Anal. calcd. for $C_{36}H_{46}O_2$,

C, 84.70 ; H, 9.02 %

Found: C, 84.98 ; H, 9.26 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-butylphenyl)propane-1,3-dione:

Yield, 35%; m.p. 82.0°C; IR ν_{max} : 2930, 2850, 1608, 1590, 1470, 1380, 1300, 1180 and 775 cm^{-1} ; NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 24H, 12 \times -CH₂), 2.65 (t, 4H, 2 \times arCH₂), 6.9 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

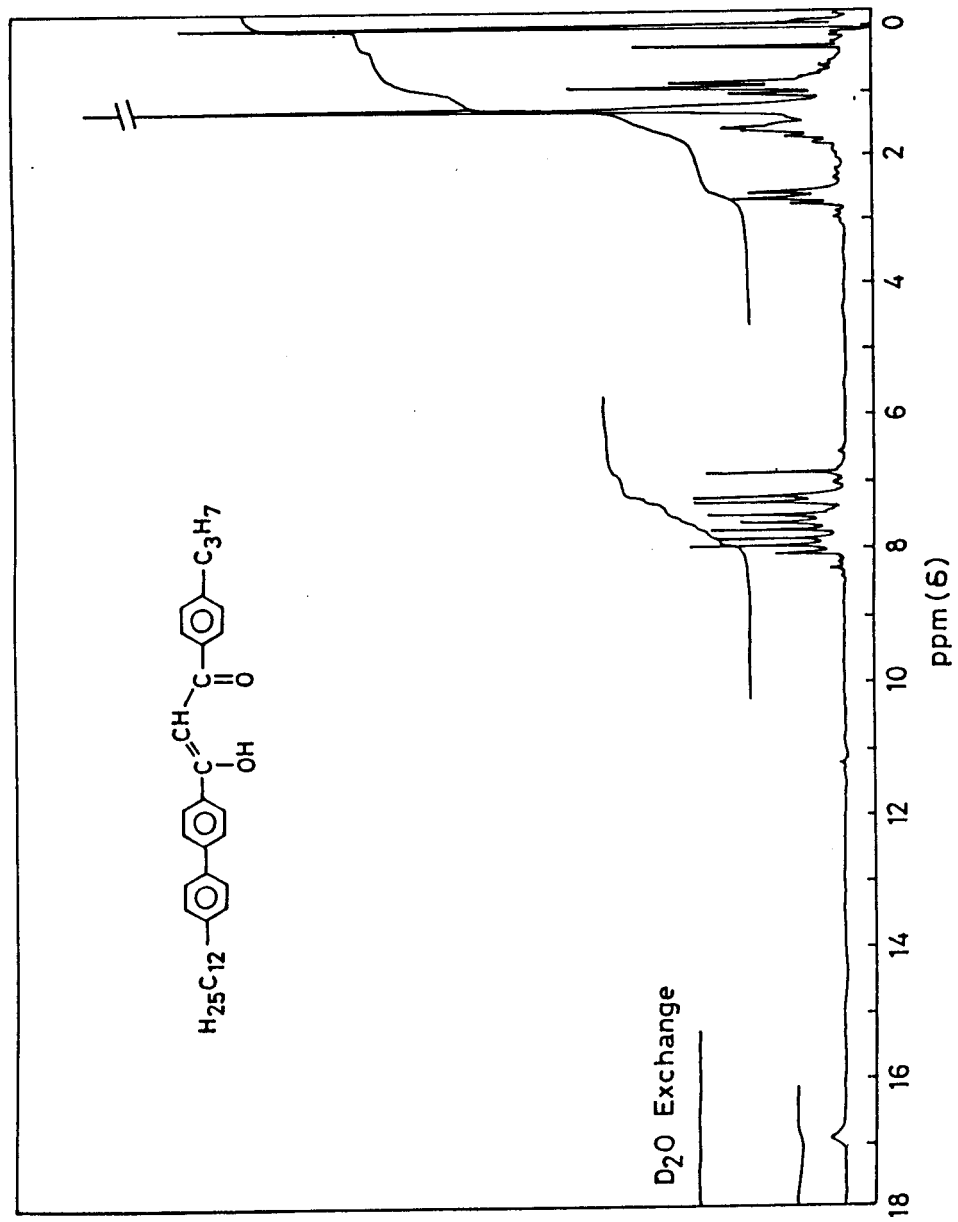
Anal. calcd. for $C_{37}H_{48}O_2$,

C, 84.73 ; H, 9.16 %

Found: C, 84.55 ; H, 9.41 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-pentylphenyl)propane-1,3-dione:

Yield, 33%; m.p. 81.5°C; IR ν_{max} : 2920, 2850, 1608, 1590, 1470, 1380, 1300, 1180 and 775 cm^{-1} ; NMR δ : 0.9 (t, (ill), 2 \times -CH₃), 1.0–2.0 (m, 26H, 13 \times -CH₂), 2.7 (t, 4H, 2 \times arCH₂), 6.85 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).



¹H NMR spectrum for compound 4.c.3.

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Anal. calcd. for $C_{38}H_{50}O_2$,

C, 84.75 ; H, 9.29 %

Found: C, 84.76 ; H, 9.53 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-heptylphenyl)propane-1,3-dione:

Yield, 28%; m.p. 85.0°C; IR ν_{max} : 2940, 2850, 1610, 1590, 1465, 1380, 1300, 1180 and 775 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times -CH_3$), 1.0–2.0 (m, 30H, $15 \times -CH_2$), 2.65 (t, 4H, $2 \times arCH_2$), 6.85 (s, 1H, $-C=CH$), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{40}H_{54}O_2$,

C, 84.80 ; H, 9.54%

Found: C, 84.64 ; H, 9.78 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-octylphenyl)propane-1,3-dione:

Yield, 34%; m.p. 86.0°C; IR ν_{max} : 2940, 2860, 1610, 1590, 1465, 1380, 1300, 1190 and 775 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times -CH_3$), 1.0–2.0 (m, 32H, $16 \times -CH_2$), 2.65 (t, 4H, $2 \times arCH_2$), 6.85 (s, 1H, $-C=CH$), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, $=C-Off$).

Anal. calcd. for $C_{41}H_{56}O_2$,

C, 84.82 ; H, 9.65 %

Found: C, 85.15 ; H, 9.77 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-nonylphenyl)propane-1,3-dione:

Yield, 31%; m.p. 91.5°C; IR ν_{max} : 2940, 2870, 1610, 1590, 1470, 1380, 1300, 1190 and 775 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times -CH_3$), 1.0–2.0 (m, 34H, $17 \times -CH_2$),

2.65 (t, 4H, 2×arCH₂), 6.85 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₄₂H₅₈O₂,

C, 84.84 ; H, 9.76 %

Found: C, 85.06 ; H, 9.55 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-decylphenyl)propane-1,3-dione:

Yield, 34%; m.p. 103.5°C; IR ν_{max} : 2930, 2850, 1610, 1590, 1470, 1380, 1190 and 775 cm⁻¹; NMR δ : 0.9 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 36H, 18×-CH₂), 2.65 (t, 4H, 2×arCH₂), 6.85 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, =C-OH).

Anal. calcd. for C₄₃H₆₀O₂,

C, 84.86 ; H, 9.86 %

Found: C, 84.58 ; H, 10.17 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-undecylphenyl)propane-1,3-dione:

Yield, 33%; m.p. 104.0°C; IR ν_{max} : 2930, 2860, 1612, 1595, 1475, 1385, 1300, 1200 and 780 cm⁻¹; NMR δ : 0.95 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 38H, 19×-CH₂), 2.65 (t, 4H, 2×arCH₂), 6.85 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, =C-OH).

Anal. calcd. for C₄₄H₆₂O₂,

C, 84.88 ; H, 9.96 %

Found: C, 84.41 ; H, 10.28 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-dodecylphenyl)propane-1,3-dione:

Yield, 30%; m.p. 108.5°C; IR ν_{max} : 2930, 2850, 1610, 1590, 1480, 1380, 1300, 1190 and 775 cm^{-1} ; NMR δ : 0.95 (t, 6H, 2 \times -CH₃), 1.1–2.0 (m, 40H, 20 \times -CH₂), 2.65 (t, 4H, 2 \times arCH₂), 6.85 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, =C-OH).

Anal. calcd. for C₄₅H₆₄O₂,

C, 84.90 ; H, 10.06 %

Found: C, 84.69 ; H, 10.28 % .

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

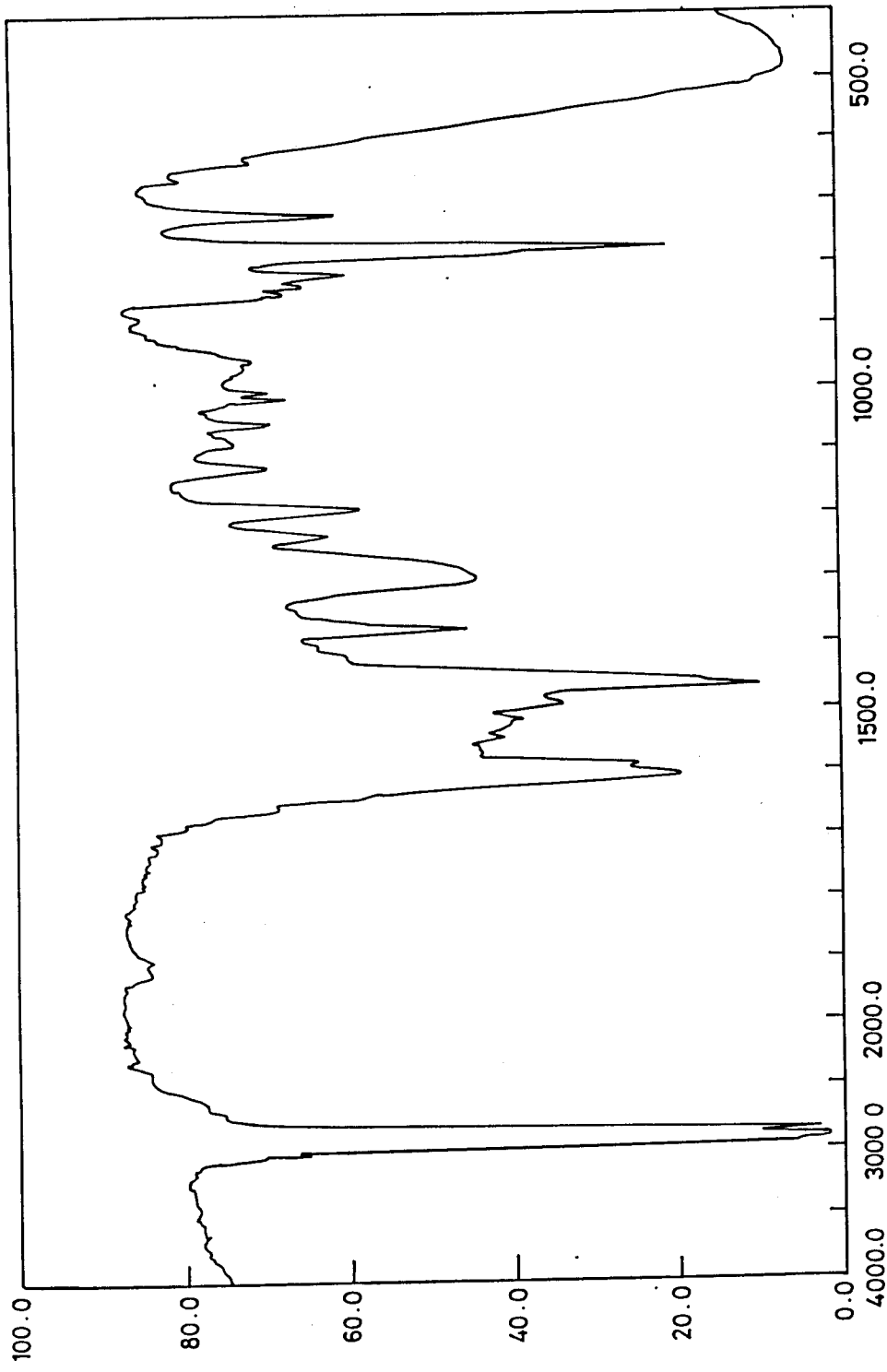
A mixture of 1-(4''-n-dodecylbiphenyl)-3-(4-methylphenyl)propane-1,3-dione (0.241 g, 0.5 mmol) in tetrahydrofuran (5 ml), cupric chloride dihydrate (0.042 g, 0.25 mmol) in ethyl alcohol (5 ml) and potassium hydroxide (0.028 g, 0.5 mmol) in ethyl alcohol (20 ml) was stirred for about four hours at room temperature. The green precipitate obtained was then filtered, washed with ethyl alcohol and dissolved in chloroform (100 ml). The chloroform solution was washed with water (3 \times 100 ml) and dried (Na₂SO₄). Removal of solvent and crystallisation of the residue using butan-2-one afforded green crystals of the complex.

Yield, 0.11 g, 43%; m.p. 208.0°C; IR ν_{max} : 2920, 2850, 1585, 1460, 1375, 1180 and 770 cm^{-1} ; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 362 (80,900), 311 (50,864).

Anal. calcd. for C₆₈H₈₂O₄Cu,

C, 79.57 ; H, 7.99 %

Found: C, 79.48 ; H, 8.12 % .



IR spectrum for compound 4.c.12.

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

Yield, 45%; m.p. 160.0°C; IR ν_{max} : 2920, 2850, 1585, 1460, 1375, 1195 and 775 cm^{-1} ; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 362 (79,200), 311 (49,546).

Anal. calcd. for $\text{C}_{86}\text{H}_{118}\text{O}_4\text{Cu}$,

C, 80.78 ; H, 9.32 %

Found: C, 80.70 ; H, 9.39 % .

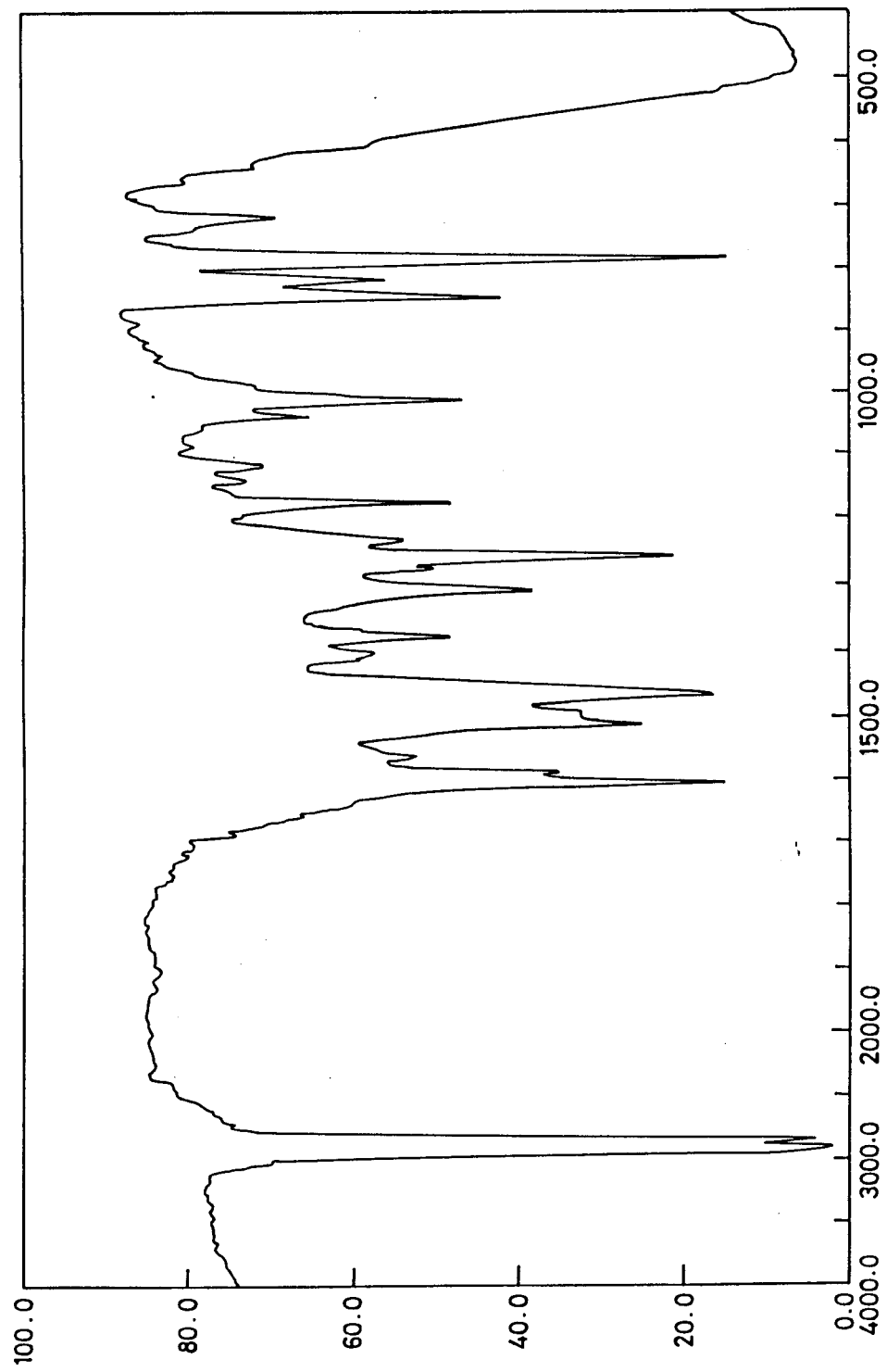
Ethyl-4-n-alkyloxybenzoates:

These were prepared as described in chapter 2.

1-(4''-n-Dodecylbiphenyl)-3-(4-n-heptyloxyphenyl)propane-1,3-dione:

A mixture of 4-n-dodecyl-4'-acetylbiphenyl (3.64 g, 0.01 mol) and ethyl-4-n-heptyloxybenzoate (2.64 g, 0.01 mol) in dry 1,2-dimethoxyethane (80 ml) was taken in a 250 ml two-necked round bottom flask fitted with a reflux condenser and a nitrogen inlet tube. The reaction mixture was stirred magnetically, sodium hydride (0.8 g, 0.02 mol, 60% in paraffin oil) was added and refluxed for four hours. Then it was cooled, ice cold dilute hydrochloric acid (30 ml) was added and the mixture extracted with chloroform (3x50 ml). The combined chloroform solution was washed with water (4x100 ml) and dried (Na_2SO_4). Removal of solvent and chromatography of the residue gave a pale yellow product. This was crystallised from acetonitrile. ,

Yield, 1.1 g, 19%; m.p. 90.0°C; IR ν_{max} : 2930, 2860, 1608, 1590, 1470, 1380, 1260, 1015 and 780 cm^{-1} ; NMR δ : 0.95 (t, 6H, 2x -CH₃), 1.1-2.0 (m, 30H, 15x-CH₂), 2.65 (t, 2H, arCH₂), 4.05 (t, 2H, arOCH₂), 6.85-8.2 (m, 13H, arH and -C=CH), 17.0 (s, 1H, =C-OH).



IR spectrum for compound 4.d.7.

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Anal. calcd. for $C_{40}H_{54}O_3$,

C, 82.47 ; H, 9.27 %

Found: C, 82.02 ; H, 9.46 % .

The physical constants of the other 1-(4''-n-dodecylbiphenyl)-3-(4-n-alkyloxyphenyl)propane-1,3-diones are given below:

1-(4''-n-Dodecylbiphenyl)-3-(4-methoxyphenyl)propane-1,3-dione:

Yield, 21%; m.p. 109.5°C; IR ν_{max} : 2930, 2860, 1608, 1590, 1470, 1380, 1260, 1030 and 785 cm^{-1} ; NMR δ : 0.9 (t, 3H, $-CH_3$), 1.1–2.0 (m, 20H, $10 \times -CH_2$), 2.7 (t, 2H, $arCH_2$), 3.9 (s, 3H, $arOCH_3$), 6.8–8.2 (m, 13H, $12 \times arH$ and $-C=CH$), 17.0 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{34}H_{42}O_3$,

C, 81.92 ; H, 8.44 %

Found: C, 81.40 ; H, 8.64 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-ethoxyphenyl)propane-1,3-dione:

Yield, 18%; m.p. 105.0°C; IR ν_{max} : 2930, 2860, 1608, 1590, 1470, 1380, 1260, 1050 and 785 cm^{-1} ; NMR δ : 0.96 (t, 6H, $2 \times -CH_3$), 1.2–1.8 (m, 20H, $10 \times -CH_2$), 2.65 (t, 2H, $arCH_2$), 4.1 (q, 2H, $arOCH_2$), 6.85–8.2 (m, 13H, $12 \times arH$ and $-C=CH$), 17.0 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{35}H_{44}O_3$,

C, 82.03 ; H, 8.59 %

Found: C, 82.40 ; H, 8.87 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-propyloxyphenyl)propane-1,3-dione:

Yield, 27%; m.p. 107.5°C; IR ν_{max} : 2920, 2850, 1608, 1588, 1470, 1375, 1260, 980 and 780 cm^{-1} ; NMR δ : 0.96 (t, 6H, 2× -CH₃), 1.2–1.9 (m, 22H, 11×-CH₂), 2.65 (t, 2H, arCH₂), 4.1 (t, 2H, arOCH₂), 6.85–8.2 (m, 13H, arH and -C=CH), 17.0 (s, 1H, =C-OH).

Anal. calcd. for C₃₆H₄₆O₃,

C, 82.13 ; H, 8.74 %

Found: C, 81.80 ; H, 8.98 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-butyloxyphenyl)propane-1,3-dione:

Yield, 16%; m.p. 100.5°C; IR ν_{max} : 2920, 2850, 1605, 1590, 1465, 1375, 1255, 1180 and 780 cm^{-1} ; NMR δ : 0.96 (t, 6H, 2× -CH₃), 1.2–1.8 (m, 24H, 12×-CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.85–8.2 (m, 13H, 12×arH and -C=CH), 17.0 (s, 1H, =C-OH).

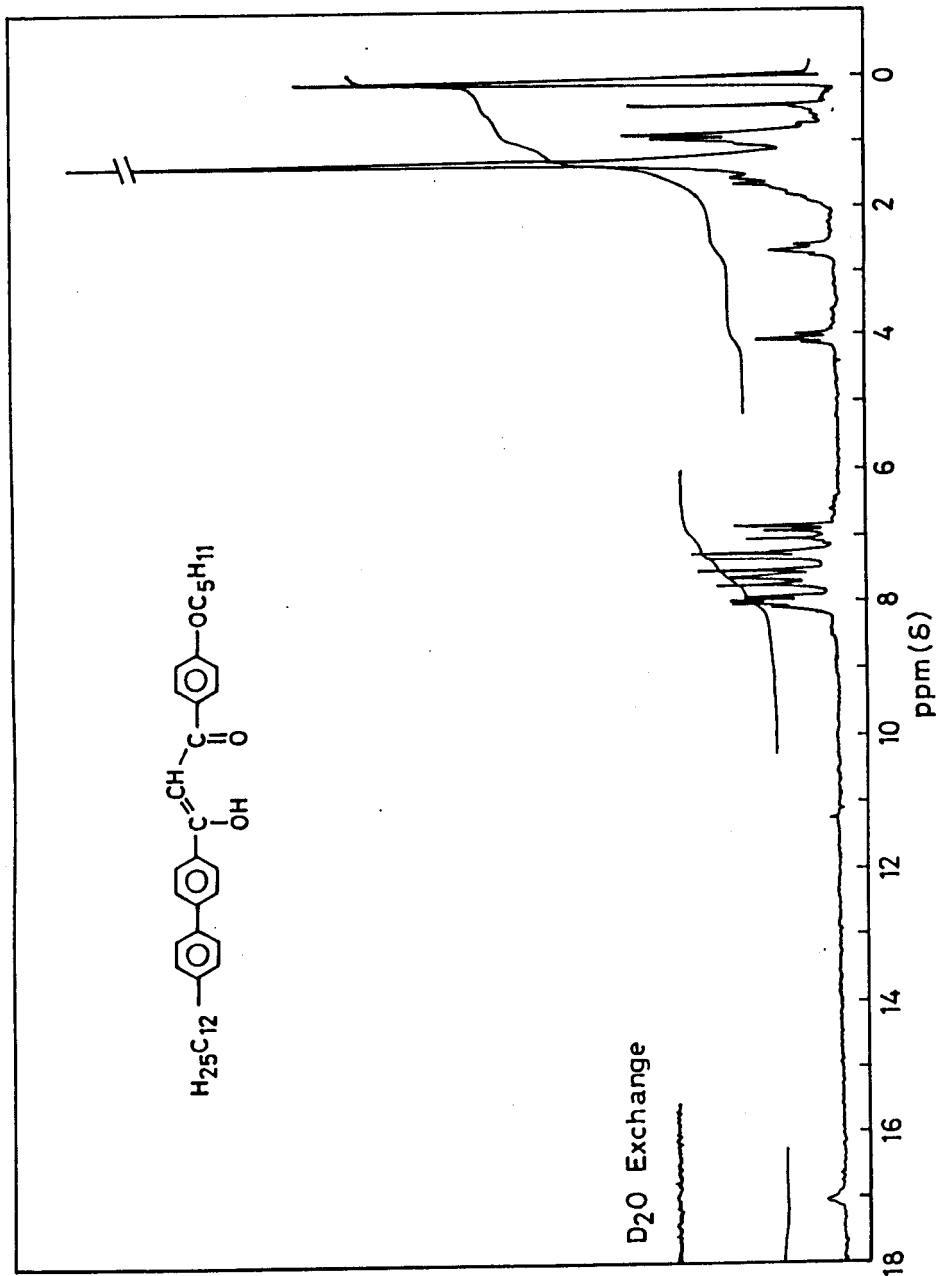
Anal. calcd. for C₃₇H₄₈O₃,

C, 82.22 ; H, 8.88 %

Found: C, 81.95 ; H, 9.13 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-pentyloxyphenyl)propane-1,3-dione:

Yield, 18%; m.p. 88.0°C; IR ν_{max} : 2910, 2850, 1608, 1590, 1465, 1475, 1360, 1260, 1180 and 780 cm^{-1} ; NMR δ : 0.96 (t, 6H, 2×-CH₃), 1.1–1.9 (m, 26H, 13×-CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.85–8.2 (m, 13H, 12×arH and -C=CH), 17.0 (s, 1H, =C-OH).



¹H NMR spectrum for compound 4.d.5.

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Anal. calcd. for $C_{38}H_{50}O_3$,

C, 82.31 ; H, 9.02 %

Found: C, 82.75 ; H, 9.36 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-hexyloxyphenyl)propane-1,3-dione:

Yield, 15%; m.p. 82.0°C; IR ν_{max} : 2920, 2850, 1608, 1590, 1465, 1360, 1260, 1175 and 780 cm^{-1} ; NMR δ : 0.96 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 28H, 14×-CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.85–8.2 (m, 13H, 12×arH and -C=CH), 17.0 (s, 1H, =C-OH).

Anal. calcd. for $C_{39}H_{52}O_3$,

C, 82.40 ; H, 9.15 %

Found: C, 82.80 ; H, 9.45 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-octyloxyphenyl)propane-1,3-dione:

Yield, 23%; m.p. 104.0°C; IR ν_{max} : 2920, 2850, 1608, 1590, 1470, 1360, 1260, 1180 and 780 cm^{-1} ; NMR δ : 0.96 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 32H, 16×-CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.85–8.2 (m, 13H, 12×arH and -C=CH), 17.0 (s, 1H, =C-OH).

Anal. calcd. for $C_{41}H_{56}O_3$,

C, 82.55 ; H, 9.39 %

Found: C, 82.36 ; H, 9.57 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-nonyloxyphenyl)propane-1,3-dione:

Yield, 31%; m.p. 109.0°C; IR ν_{max} : 2920, 2850, 1608, 1590, 1470, 1365, 1260, 1180 and 780 cm^{-1} ; NMR δ : 0.96 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 34H, 17×-CH₂),

2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.85–8.2 (m, 13H, 12×arH and -C=CH), 17.0 (s, 1H, =C-OH).

Anal. calcd. for C₄₂H₅₈O₃,

C, 82.62 ; H, 9.50 %

Found: C, 82.70 ; H, 9.72 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-decyloxyphenyl)propane-1,3-dione:

Yield, 20%; m.p. 110.0°C; IR ν_{max} : 2920, 2860, 1608, 1590, 1470, 1365, 1260, 1180 and 780 cm⁻¹; NMR δ : 0.96 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 36H, 18×-CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.85–8.2 (m, 13H, 12×arH and -C=CH), 16.95 (s, 1H, =C-OH).

Anal. calcd. for C₄₃H₆₀O₃,

C, 82.69 ; H, 9.61 %

Found: C, 82.78 ; H, 9.81 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-undecyloxyphenyl)propane-1,3-dione:

Yield, 23%; m.p. 112.5°C; IR ν_{max} : 2920, 2860, 1608, 1595, 1470, 1365, 1260, 1180 and 780 cm⁻¹; NMR δ : 0.92 (t, 6H, 2× -CH₃), 1.0–2.0 (m, 38H, 19×-CH₂), 2.5 (t, 2H, arCH₂), 3.95 (t, 2H, arOCH₂), 6.80–8.0 (m, 13H, 12×arH and -C=CH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₄₄H₆₂O₃,

C, 82.75 ; H, 9.71 %

Found: C, 82.95 ; H, 9.99 % .

1-(4''-n-Dodecylbiphenyl)-3-(4-n-dodecyloxyphenyl)propane-1,3- dione:

Yield, 25%; m.p. 113.0°C; IR ν_{max} : 2920, 2860, 1608, 1595, 1470, 1365, 1260, 1180 and 780 cm^{-1} ; NMR δ : 0.92 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 40H, 20 \times -CH₂), 2.5 (t, 2H, arCH₂), 3.95 (t, 2H, arOCH₂), 6.80–8.0 (m, 13H, 12 \times arH and -C=CH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₄₅H₆₄O₃,

C, 82.82 ; H, 9.81 %

Found: C, 83.28 ; H, 9.84 % .

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

A mixture of 1-(4''-n-dodecylbiphenyl)-3-(4-methoxyphenyl)propane-1,3-dione (0.249 g, 0.5 mmol) in tetrahydrofuran (5 ml), powdered potassium hydroxide (0.028 g, 0.5 mmol) in ethyl alcohol (5 ml) and cupric chloride dihydrate (0.042 g, 0.25 mmol) in ethyl alcohol (20 ml) was stirred for about four hours at room temperature. The complex formed in the form of green precipitate was then filtered, washed with ethyl alcohol and dissolved in chloroform (100 ml). The chloroform solution was washed with water (3 \times 100 ml) and dried (Na₂SO₄). Removal of solvent and crystallisation of the residue using butan-2-one gave green crystals of the complex.

Yield, 0.08 g, 30%; m.p. 180.0°C; IR ν_{max} : 2930, 2860, 1590, 1485, 1380, 1260, 1175 and 780 cm^{-1} ; UV-Vis $\lambda_{max}^{CHCl_3 (E)}$: 365 (97,800), 315 (65,300).

Anal. calcd. for C₆₈H₈₂O₆Cu,

C, 77.16 ; H, 7.75 %

Found: C, 77.25 ; H, 7.90 % .

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

Yield, 41%; m.p. 194.0°C; IR ν_{max} : 2920, 2850, 1585, 1480, 1380, 1270, 1000 and 780 cm^{-1} ; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ): 366 (98,300), 316 (67,000).

Anal. calcd. for $\text{C}_{82}\text{H}_{110}\text{O}_6\text{Cu}$,

C, 78.50 ; H, 8.77 %

Found: C, 79.0 ; H, 8.98 % .

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