

Chapter 5

Synthesis and mesomorphic properties of

- (i) 1-(4''-n-Dodecylbiphenyl)-3-(2-n-alkyloxyphenyl)propane-1,3-diones**
- (ii) 1-(4''-n-Dodecylbiphenyl)-3-(3-n-alkyloxyphenyl)propane-1,3-diones**
- (iii) 1-(4''-n-Alkanoyloxybiphenyl)-3-(n-alkanoyloxy)-3-(phenyl)-2-propene-1-ones**

5.1 A brief account of the mesomorphic properties of compounds with lateral long-chain substituents

Relationship between the molecular structure and mesomorphic behaviour is a subject of fundamental importance in the field of liquid crystals. One of the pioneers of the chemistry of liquid crystals, Vorlander, derived a rule defining the rod-like shape of molecules of thermotropic liquid crystals - a rule, which has been confirmed by thousands of examples.¹ In proving this rule, the influence of lateral substituents on the liquid crystalline properties was frequently studied.^{2,3} The results seemed to indicate that only small lateral substituents could be accommodated without drastic changes in the liquid crystalline properties.

It was only in 1983 that, Weissflog and Demus⁴ discovered a new molecular structure concept for thermotropic liquid crystals, by investigating compounds with lateral long-chain substituents. The compounds investigated were 1,4-bis[4-n-octyloxybenzoyloxy]-2-n-alkylbenzenes, 5.a. All of them were nematogenic. They found that on substitution of the aromatic ring in 2-position by methyl, ethyl and propyl groups the clearing points decreased dramatically. As the lateral alkyl group was lengthened, the trend in the depression of the clearing points became less pronounced and reached a saturation value at n=12. They also investigated⁴ many additional series of compounds with terminal alkyl, alkyloxy, alkanoyloxy and alkyloxycarbonyloxy groups; the lateral substitution was either alkanoyl or other groups. In all these series of compounds liquid crystalline property was proved. They proposed⁴ a molecular model for these compounds (shown in figure 5.1), wherein "the lateral alkyl chain exhibit minimal angle with the central group of the molecule". They predicted this on the basis of molecular statistical theories of the Van der Waals type.^{5,6}

Later, Weissflog and Demus⁷ synthesised nearly a hundred compounds of the

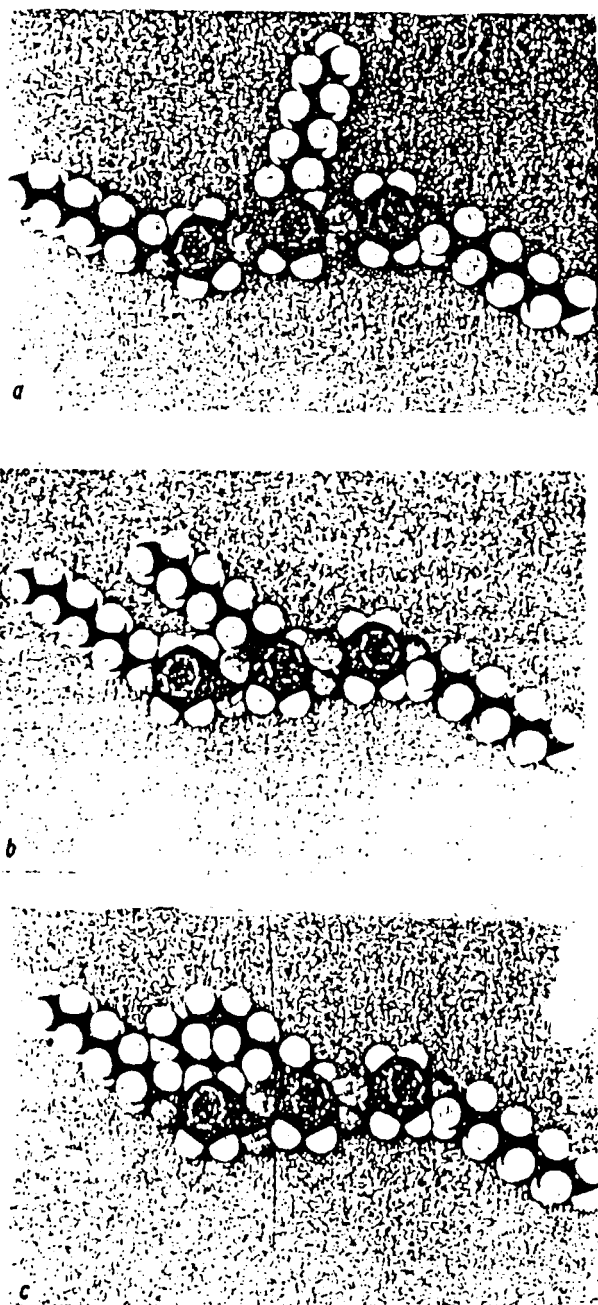


Figure 5.1: Molecular model of 1,4-bis[4-n-octyloxybenzoyloxy]-2-n-heptylbenzene in three different conformations (after Weissflog and Demus⁴).

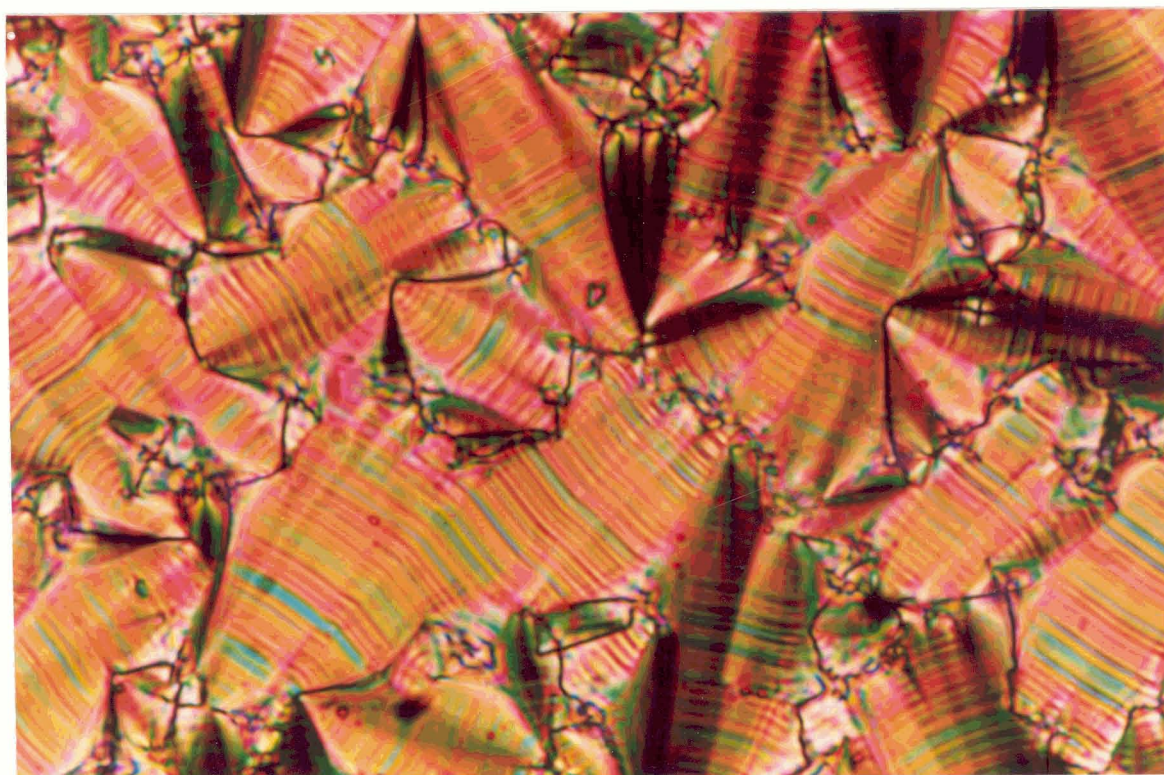


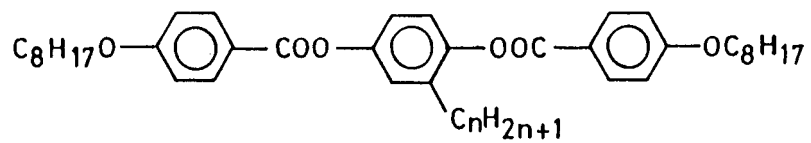
Plate 5.1: The focal-conic texture with concentric arcs of the smectic E phase of compound 5.j.6 at 95°C.

general formula 5.b, with R = alkyl, alkyloxy, alkanoyloxy and alkyloxycarbonyloxy and n=0 to 16. All these compounds were found to be nematogenic. They observed a pronounced alternation in the clearing points for the homologous series with a constant lateral substituent and lengthening terminal chains. They opined that this effect was due to an alternating change in the molecular anisotropy as a result of elongation of the alkyl chains. However, for the homologous series with constant terminal group and increasing the length of the lateral substituent they did not observe any alternation in the clearing points.

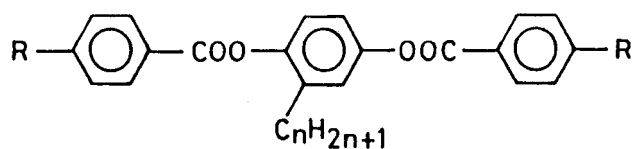
All the above compounds with long-chain lateral substituents exhibited only nematic phase. Usually, the strong attractive interactions between the central aromatic parts of the molecules are assumed to be responsible for the stabilisation of the smectic layers.⁸ It seems that on introduction of lateral substituents the distances between the aromatic parts of the molecules are enhanced to such an extent that the attractions responsible for smectic properties are decreased dramatically and these disappear. Further, the measurements of packing density in 1,4-bis[4-n-octyloxybenzoyloxy]-2-n-alkylbenzenes showed a decreasing packing density with elongation of the lateral alkyl chain.⁷

Weissflog and Demus⁹ have reported a number of compounds of the general formula 5.c, in which R² was a lateral normal or branched chain of considerable length. These compounds exhibited a nematic phase. On the basis of molecular statistical theories^{10,11} and other arguments, they proposed a molecular model for these compounds in which the lateral substituents lie more or less parallel to the long molecular axis.

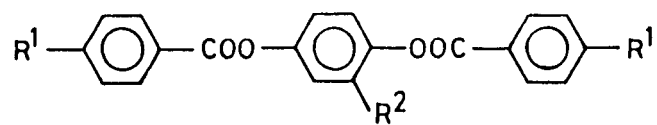
Weissflog et al.¹² have investigated the synthesis and liquid crystalline properties of four series of compounds, having the general formulae 5.d and 5.o. All these



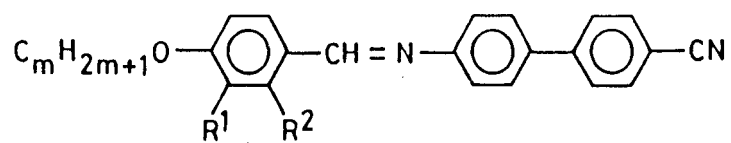
5.a



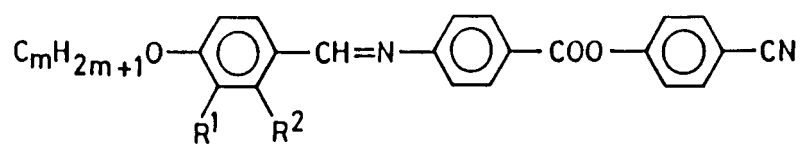
5.b



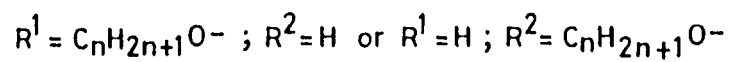
5.c



5.d



5.e

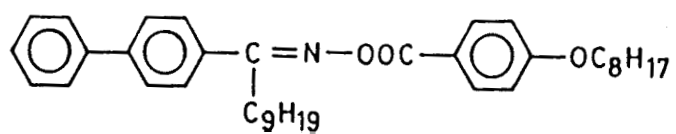


compounds exhibited nematic and some of them exhibited even smectic A phases as well. In all the earlier mentioned examples, the lateral substitution was on the middle phenyl ring. But, in compounds 5.d and 5.e, the lateral long alkyloxy chain was substituted on the terminal phenyl ring. Even in these cases also, they found that the transition temperatures decrease as the chain was lengthened. The 2-alkyloxy compounds were only nematogenic, thus confirming the rule that lateral substituents suppress smectic properties.⁷ The 3-alkyloxy compounds exhibited a smectic phase in addition to a nematic phase. This behaviour may be compared with the strong smectogenic properties of the swallow tailed compounds.¹³

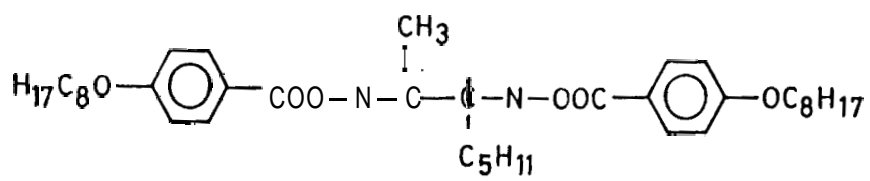
Weissflog and Demus¹⁴ have reported 2-substituted hydroquinone-bisbenzoates in which the 2-substituents contained bulky aromatic and other ring systems. Surprisingly, these compounds were also found to exhibit nematic and smectic phases. Weissflog et al.¹⁵ have reported some compounds (5.f and 5.g), wherein the lateral chain has been attached to the central bridging group. These compounds were found to be nematogenic. There are many other examples of compounds with lateral long-chain substituents, exhibiting liquid crystalline properties.^{16,17,18}

5.2 Results and discussion

In all the compounds discussed in the previous chapter, the long alkyl chain was substituted at para position of the terminal phenyl ring. Very few examples are known in the literature wherein the long-chain substituent is attached laterally to the terminal phenyl ring. All the compounds with lateral long-chain substituents reported so far, have either an *ester* or an *imino* group as a linkage unit. With a view to investigate the liquid crystalline properties of laterally substituted β -diketones the following two series of the same and some of their copper(II) complexes were



5.f



5.g

prepared.

(i) 1-(4''-n-Dodecylbiphenyl)-3-(2-n-alkyloxyphenyl)propane-1,3-diones (5.h) and

(ii) 1-(4''-n-dodecylbiphenyl)-3-(3-n-alkyloxyphenyl)propane-1,3-diones (5.i).

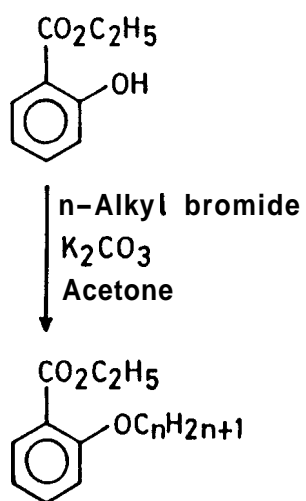
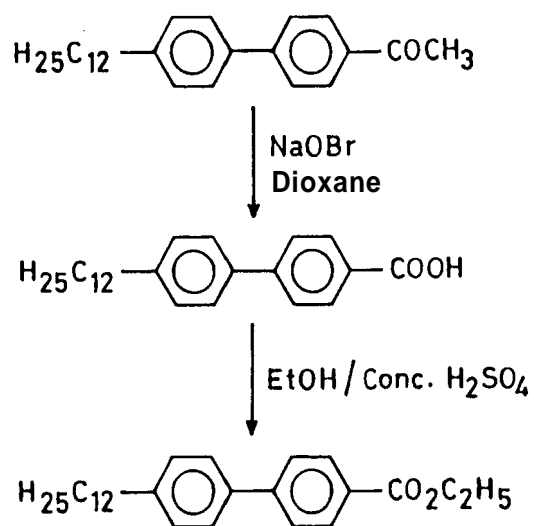
As already mentioned in chapter 3, when an attempt was made to synthesise the monoacylated compounds of 1-(4''-hydroxybiphenyl)-3-(phenyl)propane-1,3-dione, in addition to the phenolic -OH the enolic -OH group also got acylated. Thus, the products obtained were 1-(4''-n-alkanoyloxybiphenyl)-3-(n-alkanoyloxy)-3-(phenyl)-2-propene-1-ones (5.j).

All the compounds 5.h and 5.i and 5.j were found to be liquid crystalline. However, the copper(II) complexes of 5.h and 5.i were found to be non-mesogenic. The mesogenic β -diketones 5.h and 5.i as well as the acylated compounds of series 5.j were investigated in detail.

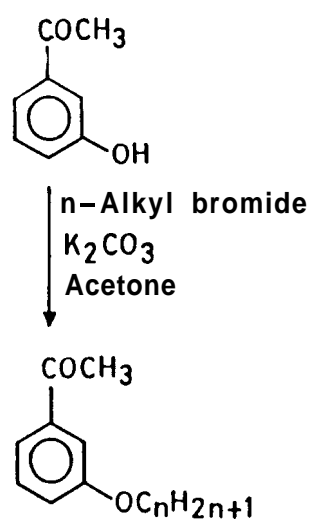
4-n-Dodecyl-4'-acetylbiphenyl was prepared as described in chapter 3. Ethyl-4-n-dodecylbiphenyl-4'-carboxylate was prepared starting from 4-n-dodecyl-4'-acetylbiphenyl. Ethyl-2-n-alkyloxybenzoates (5.k) and 3-n-alkyloxyacetophenones (5.l) were prepared by treating ethyl salicylate and 3-hydroxyacetophenone respectively, with appropriate n-alkyl bromides. These reactions are schematically shown in figure 5.2.

4-n-Dodecyl-4'-acetylbiphenyl was condensed with ethyl-2-n-alkyloxybenzoates in 1,2-dimethoxyethane, using sodium hydride as a base, to obtain the β -diketones, 5.h. In a similar way, ethyl-4-n-dodecylbiphenyl-4'-carboxylate was condensed with 3-n-alkyloxyacetophenones, to obtain the β -diketones, 5.i. The corresponding copper(II) complexes of 5.h and 5.i were prepared by treating them with cupric chloride dihydrate in ethyl alcohol using potassium hydroxide as a base. All these reactions are schematically shown in figures 5.3 and 5.4 respectively.

The transition temperatures and enthalpies of transitions for 1-(4''-n-dodecylbi-

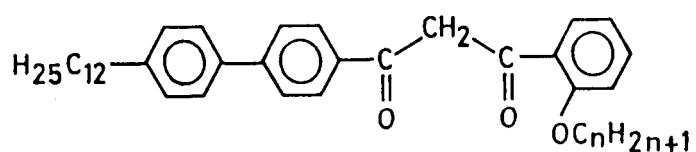
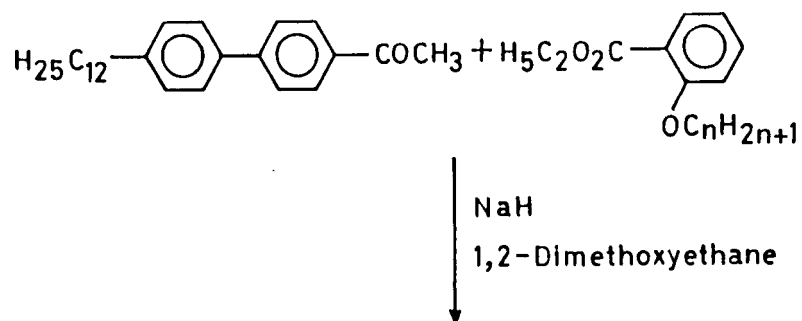


5.k

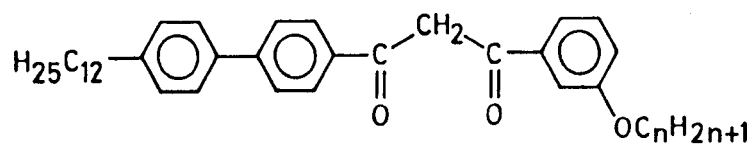
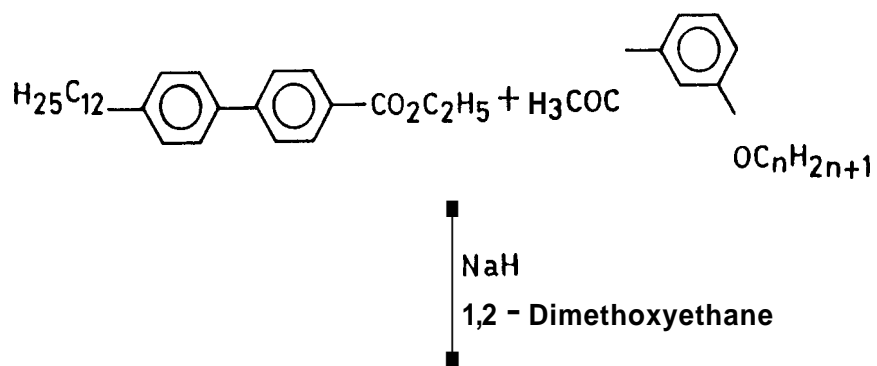


5.l

Figure 5.2



5.h



5.i

Figure 5.3

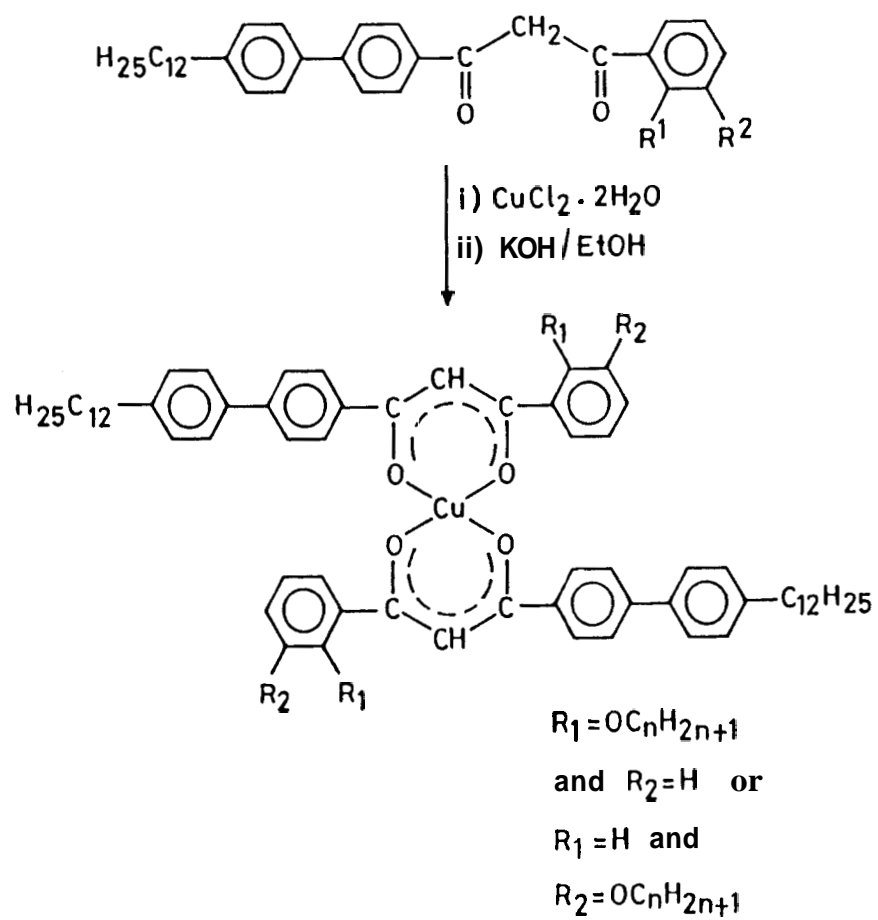


Figure 5.4

phenyl)-3-(2-n-alkyloxyphenyl)propane-1,3-diones, (5.11) are given in table 5.1. As can be seen from the table all the compounds are enantiotropic mesomorphic. They exhibit a nematic phase. Compound 5.h.12 exhibits a monotropic smectic A in addition to a nematic phase. The enthalpy value for $N \rightarrow I$ transition is about 0.1 kcal/mol in most of the cases.

A plot of the transition temperatures versus the number of carbon atoms in the alkyloxy chain for 5.h, is shown in figure 5.5. As can be seen from the graph, all the compounds have fairly low melting points (below 80°C) as well as low clearing points (below 94°C). There is an alternation in the $N \rightarrow I$ transition points. This result is in contrast to what has been observed by Weissflog and Demus.⁷

Table 5.2 gives the transition temperatures and enthalpies of transitions for 1-(4''-n-dodecylbiphenyl)-3-(3-n-alkyloxyphenyl)propane-1,3-diones, 5.i. All these compounds are found to be mesogenic. Except the compound 5.i.1 which exhibits a monotropic nematic phase, all the other homologues exhibit a smectic A phase. Compounds 5.i.2 and 5.i.3 are monotropic whereas the remaining higher homologues are enantiotropic. They show a focal-conic texture for smectic A phase. Apart from mesomorphism, some of them exhibit polymorphism as well. The dsc thermogram for compound 5.i.5 is shown in figure 5.6.

A plot of transition temperatures versus the number of carbon atoms in the alkyloxy chain for the above series 5.i is shown in figure 5.7. As can be seen from the graph, all the compounds have fairly low melting as well as clearing points (below 101°C). As usual, $S_A \rightarrow I$ transition points fall on a smooth curve.

X-ray studies in the mesophase of one of the homologues, *viz.*, 5.i.12, as a function of temperature gave a value of 43.3 Å for the layer spacing at 76°C. This value is in reasonable agreement with the measured molecular length (45.0 Å, CPK molecular

Table 5.1
 Transition temperatures (°C) and enthalpies (kcal/mol) for
 1-(4''-n-Dodecylbiphenyl)-3-(2-n-alkyloxyphenyl)propane-1,3-diones,
 5.h

Compound number	n	C	SA	N	I
5.h.1	1	79.5 <i>5.19</i>	-	89.0 <i>0.16</i>	.
5.h.2	2	70.5 <i>6.46</i>	-	93.5 <i>0.08</i>	.
5.h.3	3	60.0 <i>10.56</i>	-	66.0 <i>0.09</i>	.
5.h.4	4 ⁺	47.5 <i>6.64</i>	-	70.5 <i>0.12</i>	.
5.h.5	5	53.5 <i>9.70</i>	-	65.0 <i>0.10</i>	.
5.h.6	6	51.5 <i>10.28</i>	-	67.5 <i>0.10</i>	.
5.h.7	7	48.5 <i>12.05</i>	-	66.0 <i>0.08</i>	.
5.h.8	8	60.5 <i>8.55</i>	-	71.0 <i>0.10</i>	.
5.h.9	9	66.5 <i>9.27</i>	-	70.5 <i>0.09</i>	.
5.h.10	10	67.0 <i>8.78</i>	-	76.5 <i>0.09</i>	.
5.h.11	11	63.0 <i>8.89</i>	-	77.5 <i>0.11</i>	.
5.h.12	12	63.5 <i>7.78</i>	(. 49.5)*	81.5 <i>0.11</i>	.

⁺Compound 5.h.4 has a crystal → crystal transition at 42.0°C (3.05 kcal/mol).

*Enthalpy could not be measured.

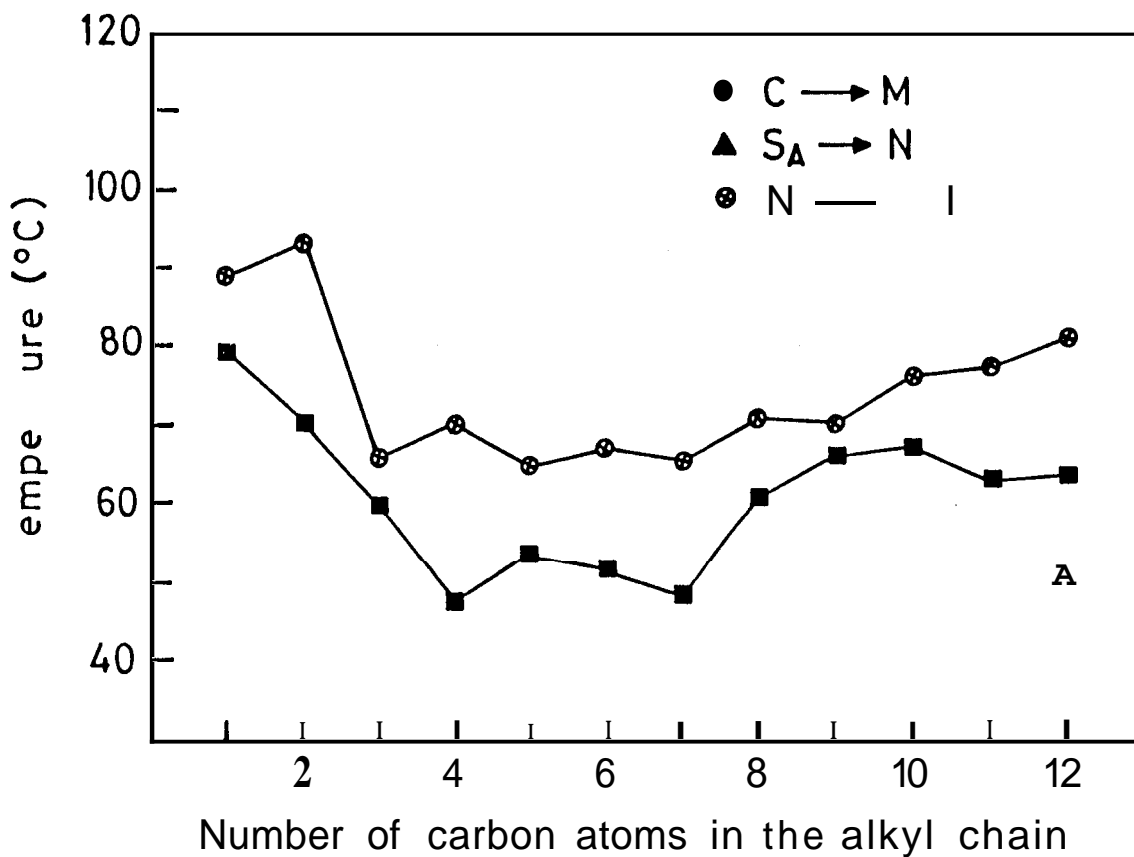


Figure 5.5: A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for series 5.h.

Table 5.2
 Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kcal/mol) for
1-(4''-n-Dodecylbiphenyl)-3-(3-n-alkyloxyphenyl)propane-1,3-diones,
5.i

Compound number	n	C_1	C	S_A	N	Δ
5.i.1	1		100.0 <i>13.6</i>	-	(. 97.5)	. <i>0.13</i>
5.i.2	2		100.0 <i>12.10</i>	(. 96.0)	-	
5.i.3	3	. 84.0 <i>4.05</i>	. 95.5 <i>9.32</i>	(. 95.0)	-	
5.i.4	4	. 79.5 <i>4.61</i>	. 93.0 <i>7.10</i>	. 98.5	-	
5.i.5	5	. 78.0 <i>4.85</i>	. 90.0 <i>7.26</i>	. 99.0	-	
5.i.6	6	. 79.0 <i>4.71</i>	. 85.5 <i>5.86</i>	. 99.5	-	
5.i.7	7		. 78.0 <i>11.78</i>	. 99.0	-	
5.i.8	8		. 76.5 <i>11.49</i>	. 99.5	-	
5.i.9	9	. 60.5 <i>2.14</i>	. 74.5 <i>11.18</i>	. 98.5	-	
5.i.10	10	. 54.5 <i>2.49</i>	. 73.5 <i>11.23</i>	. 98.0	-	. <i>2.16</i>
5.i.11	11	-	. 75.0 <i>15.46</i>	. 97.5	-	. <i>2.28</i>
5.i.12	12		. 73.5 <i>14.89</i>	. 97.5	-	. <i>2.18</i>

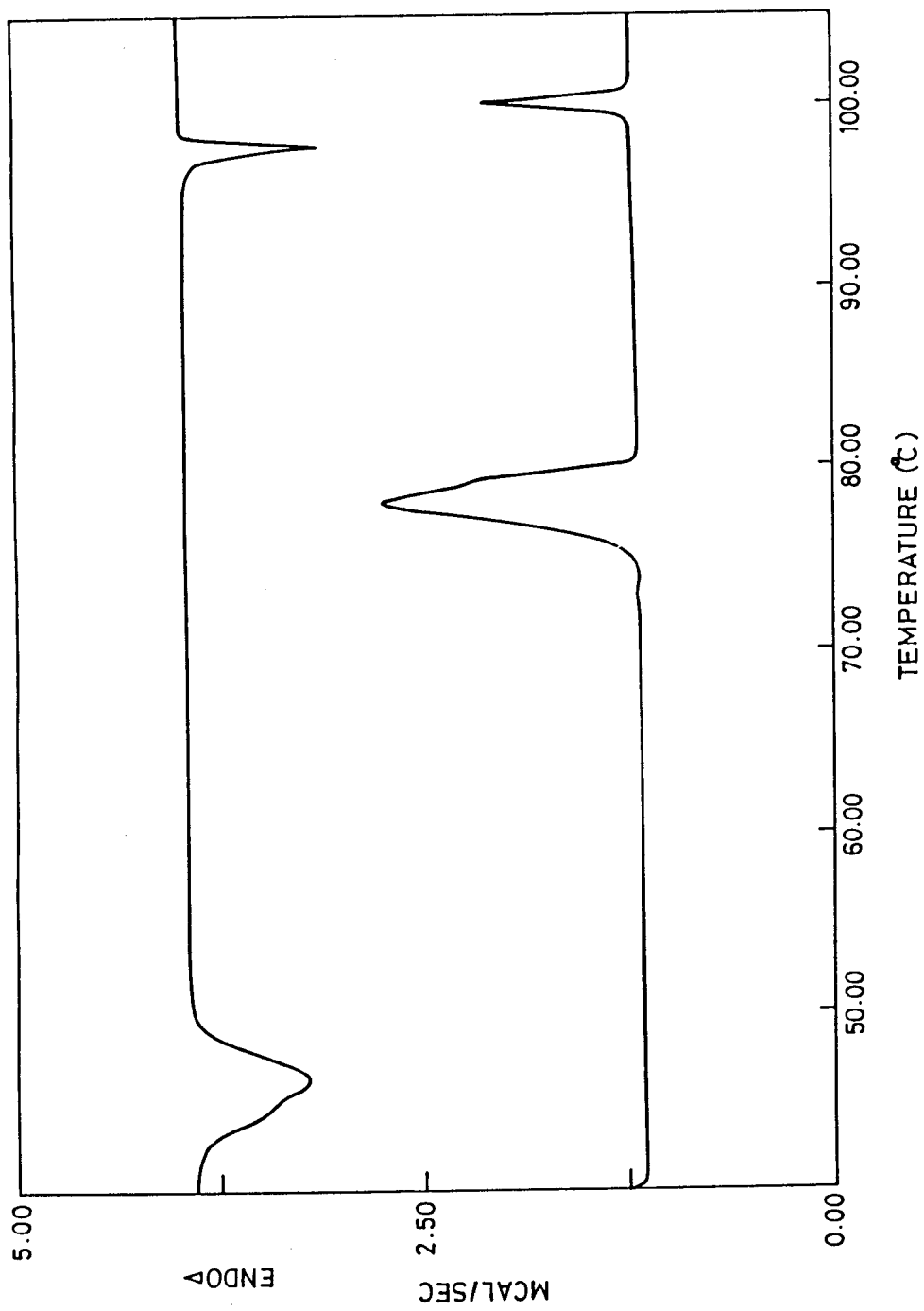


Figure 5.6: The dsc thermogram for compound 5.i.5.

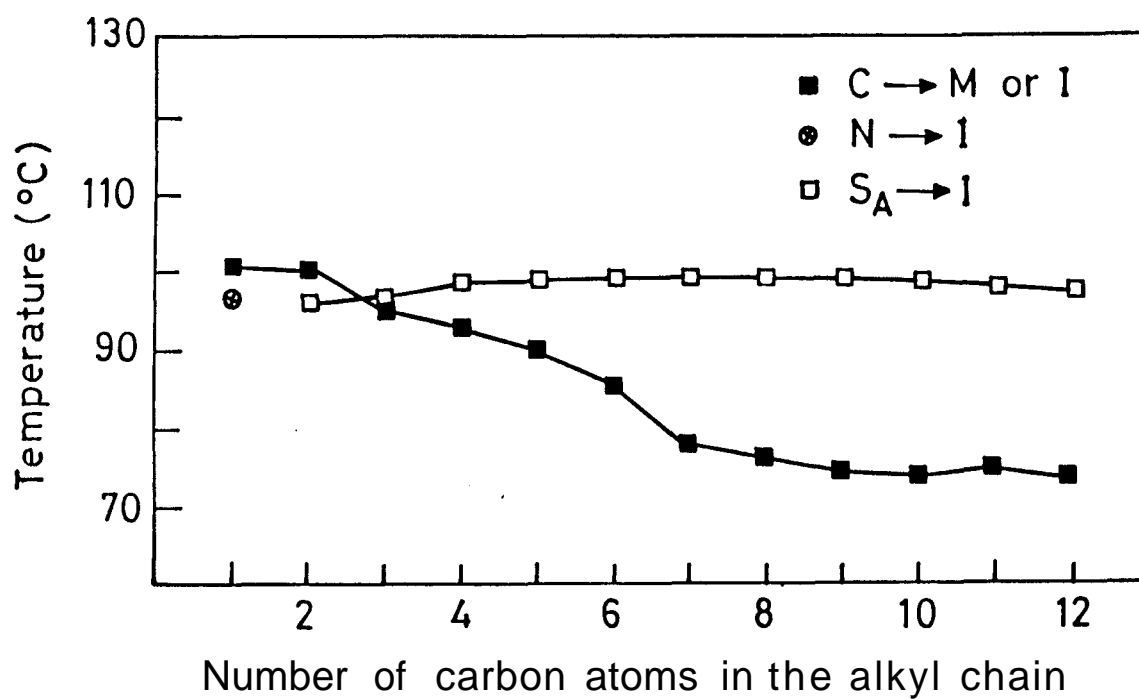
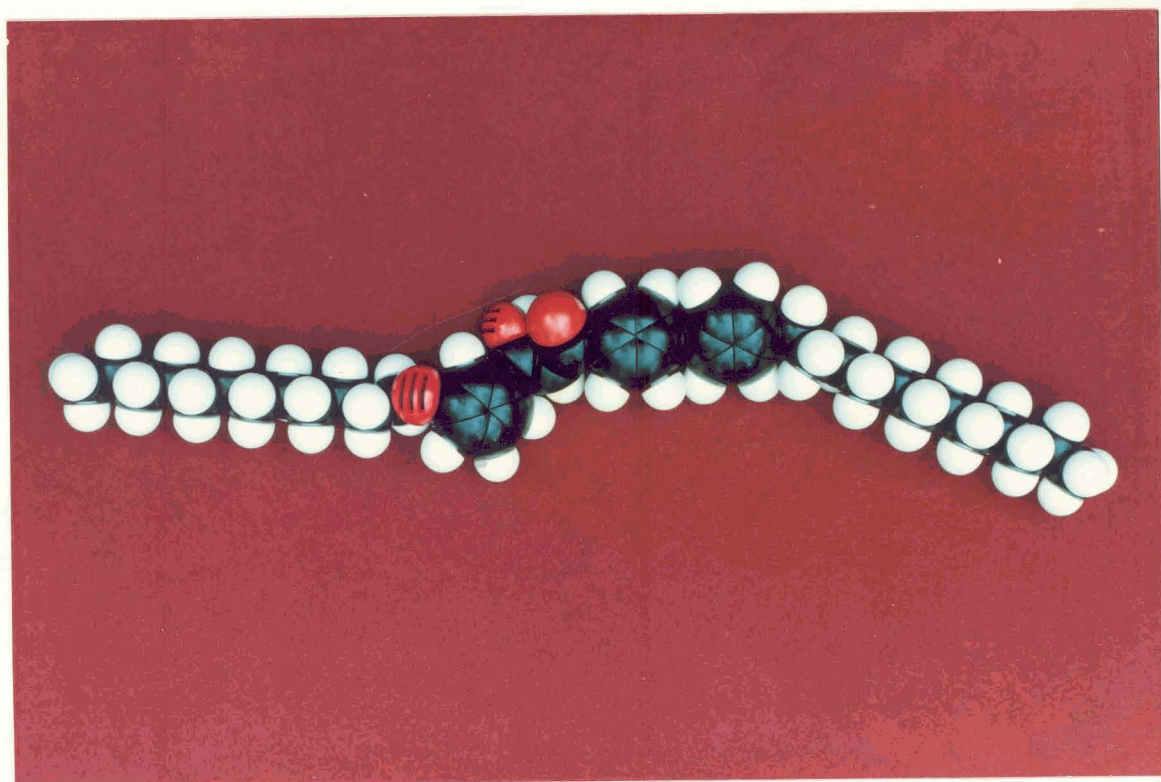


Figure 5.7: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 5.i.

Figure 5.8: Molecular model of 1-(4''-n-dodecylbiphenyl)-3-(3-n-dodecyloxyphenyl)propane-1,3-dione in its fully extended conformation.



molecular model) of the compound in its fully extended conformation, which is shown in figure 5.8.

All the 1-(4''-n-alkanoyloxybiphenyl)-3-(n-alkanoyloxy)-3-(phenyl)-2-propene-1-ones (5.j), were prepared following the scheme shown in figure 5.9. Thus, 4-methoxy-4'-acetylbiphenyl on condensation with methyl benzoate in the presence of sodium hydride gave 1-(4''-methoxybiphenyl)-3-(phenyl)propane-1,3-dione. This on demethylation using 48% hydrobromic acid and acetic acid afforded the corresponding phenolic compound. Acylation was carried out on this hydroxy compound using freshly distilled n-alkanoyl chlorides and dry pyridine to get the required 1-(4''-n-alkanoyloxybiphenyl)-3-(n-alkanoyloxy)-3-(phenyl)-2-propene-1-ones (5.j).

The transition temperatures and the associated enthalpies for the compounds of series 5.j, are given in table 5.3. Except the first homologue 5.j.1, all others are mesomorphic. They exhibit an enantiotropic smectic A phase. The middle homologues starting from 5.j.3 to 5.j.10 exhibit a monotropic smectic E phase as well. They show focal-conic and focal-conic with concentric arcs textures for smectic A and smectic E (shown in plate 5.1), respectively. All these compounds have fairly low melting as well as clearing points. The dsc thermogram for compound 5.j.5 is shown in figure 5.10.

The compounds reported by Weissflog *et al.*¹⁵, have their lateral chain attached to the central bridging group (5.f and 5.g) and these were found to be nematogenic. The compounds 5.j, are also having their lateral chain attached to the central bridging group; but, all these compounds are found to be smectogenic.

A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for the series 5.j, is shown in figure 5.11. It can be seen from the graph that $S_A \rightarrow I$ temperature falls initially, and from $n=5$ onwards it raises gradually

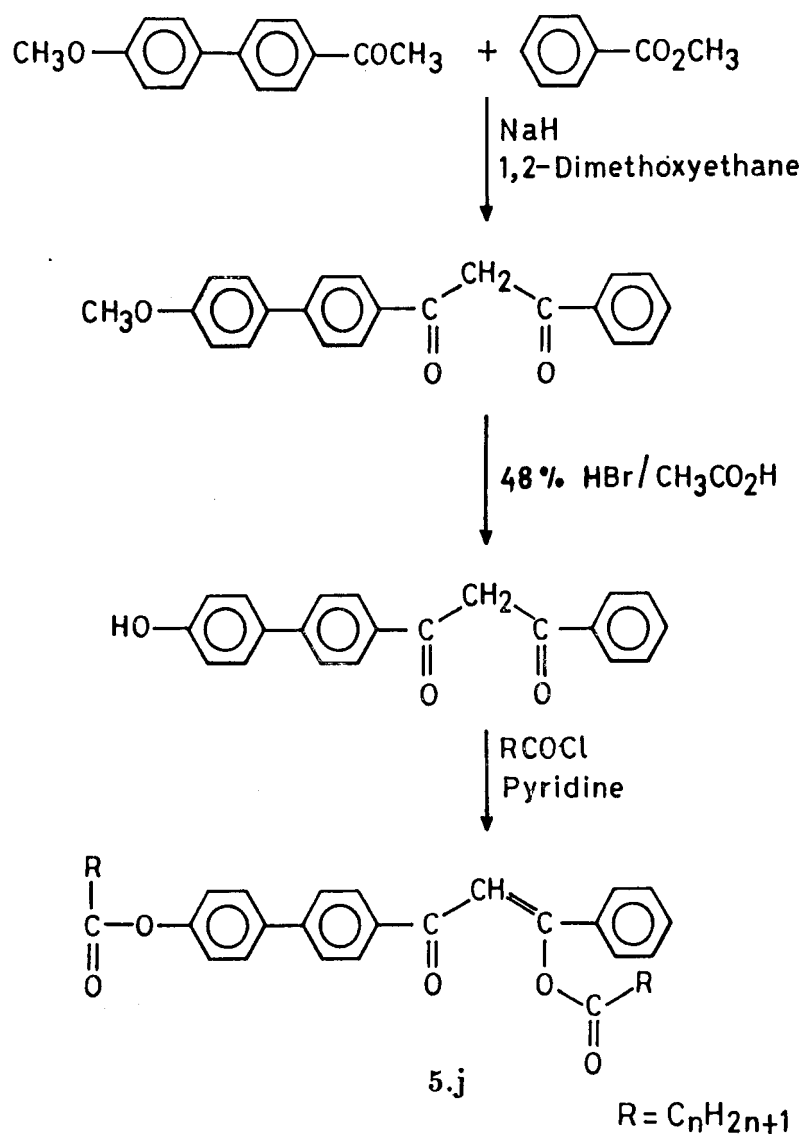


Figure 5.9

Table 5.3

Transition temperatures ($^{\circ}\text{C}$) and enthalpies of transitions (kcal/mol) for 1-(4"-n-alkanoyloxybiphenyl)-3-(n-alkanoyloxy)-3-(phenyl)-2-propene-1-one, 5.j

Compound number	n	C	S_E	S_A	I
5.j.1	3	. 102.5 5.17	-		
5.j.2	4 ⁺	. 109.5 2.0	-	. 112.0 2.58	.
5.j.3	5	. 99.5 8.33	(. 96.5) 0.71	. 110.0 2.24	.
5.j.4	6	. 99.5 8.92	(. 98.5) 0.71	. 111.5 2.47	.
5.j.5	7	. 101.0 9.79	(. 98.0) 0.70	. 113.5 2.51	.
5.j.6	8	. 98.5 9.76	(. 98.0) 0.67	. 115.0 2.62	.
5.j.7	9	. 103.5 11.21	(. 98.0) 0.66	. 117.5 2.43	.
5.j.8	10	. 102.5 9.47	(. 98.0) 0.74	. 118.0 2.23	.
5.j.9	11	. 104.0 12.55	-	. 117.5 2.31	.

⁺Compound 5.j.2 has a crystal \rightarrow crystal transition at 76.5°C (8.2 kcal/mol).

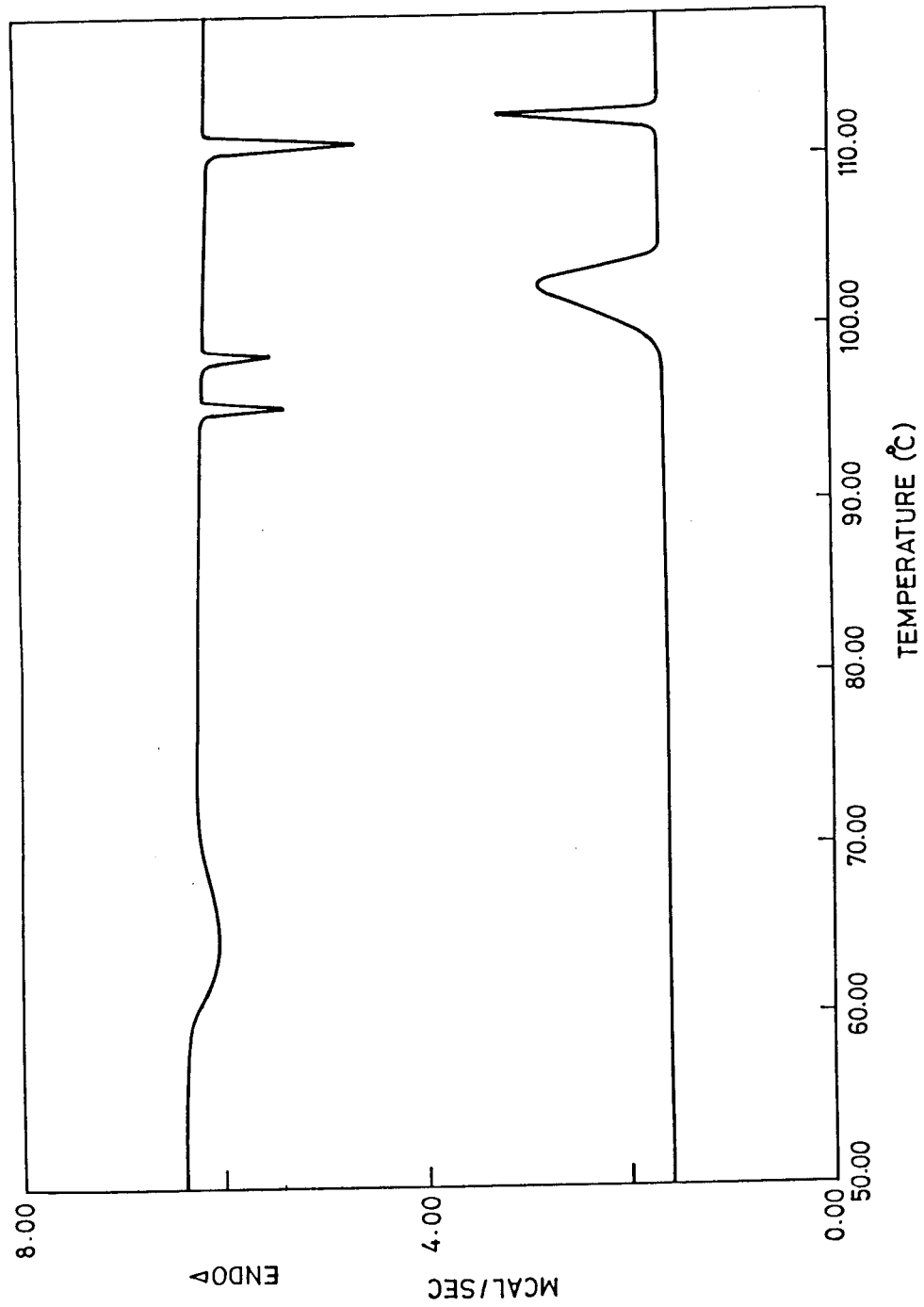


Figure 5.10: The dsc thermogram for compound 5.j.4.

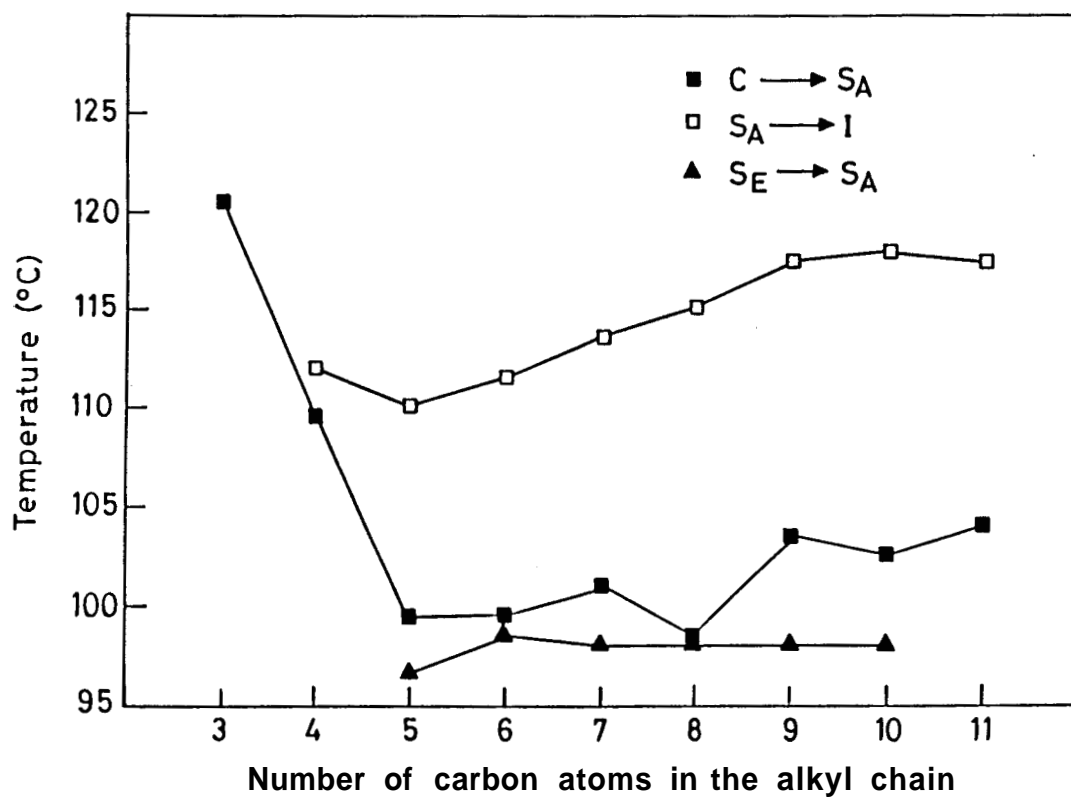


Figure 5.11: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 5.j.

and reaches a maximum at $n=10$, from where it decreases again. This is a normal trend that is seen for such transitions.

Compounds 5.j can have three different possible conformations 5.A, 5.B or 5.C. In order to determine the probable conformation, X-ray diffraction study was undertaken for two of the compounds *viz.*, 5.j.6 and 5.j.9. The layer spacing (d) determined in the mesophase as a function of temperature, for these two compounds are given below.

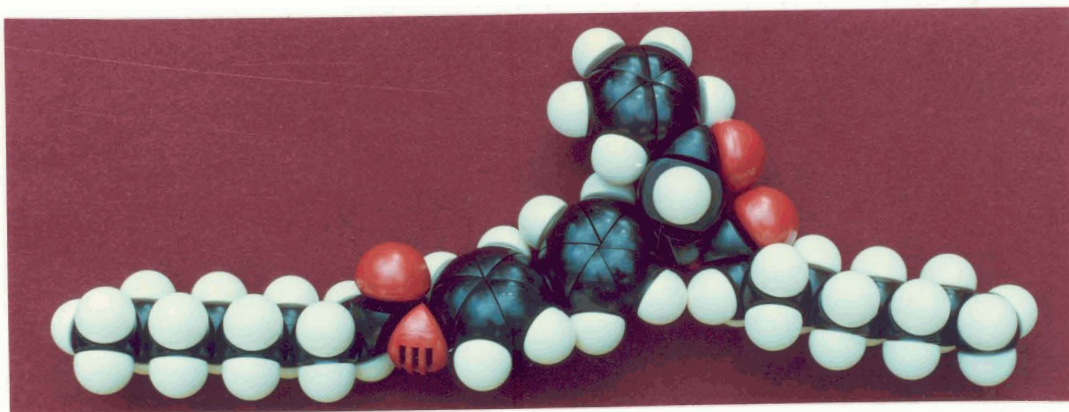
For compound 5.j.6,

Temperature ($^{\circ}\text{C}$)	Layer spacing, d (\AA)
114.1	25.0 (\pm 0.3)
107.3	24.9 (\pm 0.3)
100.5	24.7 (\pm 0.3)

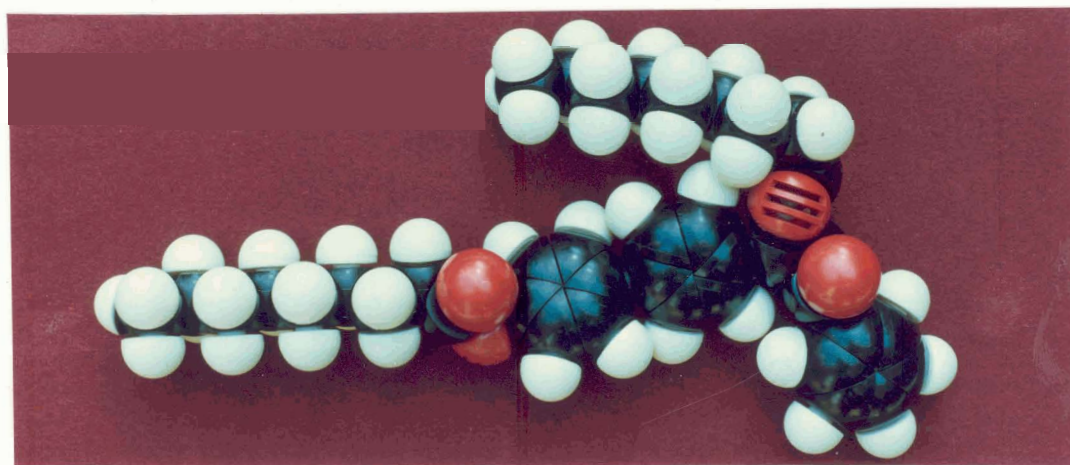
For compound 5.j.9,

Temperature ($^{\circ}\text{C}$)	Layer spacing, d (\AA)
115.2	31.2 (\pm 0.3)
112.3	31.2 (\pm 0.3)
106.6	31.1 (\pm 0.3)

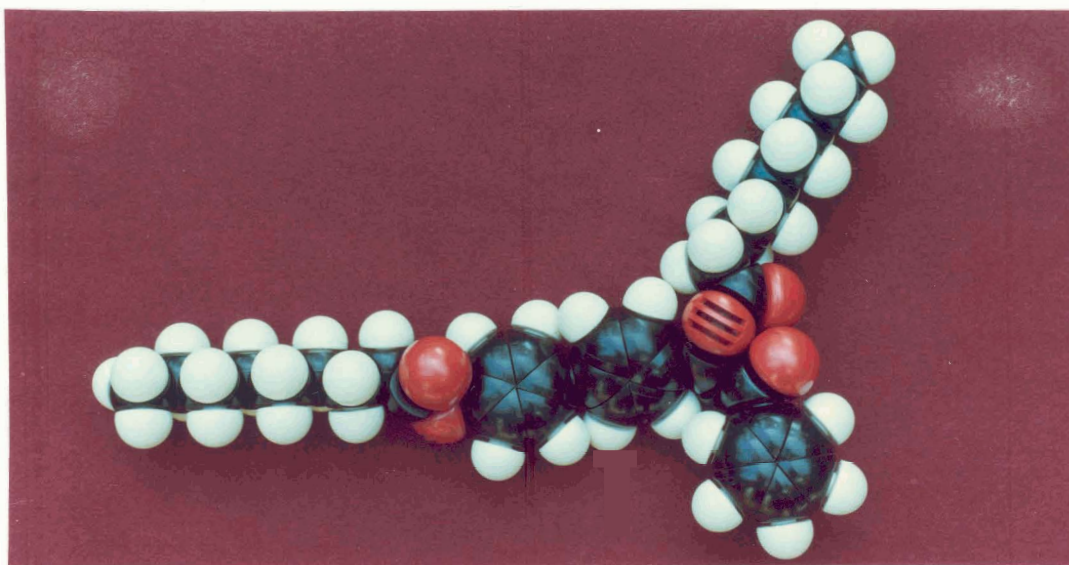
The values obtained for the layer spacing, d , is in agreement with the molecular length measured for the conformation 5.B (24 \AA for 5.j.6 and 31 \AA for 5.j.9 using CPK molecular models). Thus, it was confirmed that the lateral long-chain in the case of compounds 5.j, is not extending along the long molecular axis but bends inwards.



5.A



5.B



5.C

Molecular model of 1-(4''-n-nonanoyloxybiphenyl)-3-(n-nonanoyloxy)-3-(phenyl)-
2-propene-1-one in three different conformations.

That is to say, the molecules of these conipourids exist as shown in conformation 5.B.

To summarise, in the previous chapter, the mesogenic properties of two series of β -diketones, viz., 1-(4''-n-dodecylbiphenyl)-3-(4-n-alkylphenyl)propane-1,3-diones (4.c) and 1-(4''-n-dodecylbiphenyl)-3-(4-n-alkyloxyphenyl)propane-1,3-diones (4.d) have been discussed. In both the series, the long alkyl or alkyloxy chain was substituted in *para* position on the phenyl ring. Both the series of compounds 4.c and 4.d exhibited a smectic **A** phase and when there was no substitution on phenyl ring,¹⁹ they exhibited nematic as well as smectic **A** phases. But, when the long alkyloxy chain is substituted in *ortho* - position on the phenyl ring as in the case of 5.h, they exhibited mainly a nematic phase; the rule that lateral substituents suppress the smectic properties⁷ has been confirmed. However, when the long alkyloxy chain is substituted in *meta* - position on the phenyl ring as in the case of 5.i, they exhibited mainly a smectic **A** phase (lateral chain extends along the long molecular axis). In the case of compounds of series 5.j, wherein the lateral long-chain is attached to the central bridging group, the mesophase exhibited was of smectic type. This is perhaps due to the strong dipoles acting across the long molecular axis in these compounds.

5.3 Experimental

4-n-Dodecyl-4'-acetylbiphenyl was prepared following the procedure described in chapter 3. All the required ethyl-2-n-alkyloxybenzoates were prepared following the procedure given below (for ethyl-2-11-decyloxybenzoate) and these compounds have been characterised by their physical constants as well as spectral data.

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Ethyl-2-n-decyloxybenzoate:

A mixture of ethylsalicylate (12.5 g, 0.075 mol), anhydrous potassium carbonate (16.6 g, 0.12 mol), n-decylbromide (17.5 g, 0.08 mol), dry acetone (150 ml) was taken in a 500 ml round bottom flask and refluxed for fortythree hours. The reaction mixture was filtered and the acetone was removed completely. The residue was poured into a mixture of ice and hydrochloric acid and extracted with ether (2×100 ml). The combined ether solution was washed with ice cold 5% sodiuni hydroxide solution (2×50 ml), water (4×100 ml) and dried (Na_2SO_4). The solvent was removed and the residue was distilled under reduced pressure. Yield, 12.3 g, (53%); b.p. 182–84°C/0.5 mm.

The physical data of the other ethyl-2-n-alkyloxybenzoates (5.k) are given in table 5.4.

1-(4''-n-Dodecylbiphenyl)-3-(2-undecyloxyphenyl)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'-acetylbiophenyl (3.64 g, 0.01 mol) and ethyl-2-n-undecyloxybenzoate (3.20 g, 0.01 mol) in dry 1,2 - dimethoxyethane (80 ml). This was stirred magnetically, sodium liydride (0.8 g, 0.02 mol, 60% in paraffin oil) was added and the mixture refluxed for four hours and cooled. Ice cold dilute hydrochloric acid (30 ml) was added and the mixture extracted with chloroform (3x 50 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 propan-2-ol.

Yield, 1.1 g, (17%); m.p. 63.0°C; IR ν_{max} : 2920, 2860, 1608, 1470, 1240, 810 and 765 cm^{-1} ; NMR δ : 0.88 (t, 6H, 2× -CH₃), 1.0–2.0 (m, 38H, 19×-CH₂), 2.6 (t, 2H, arCH₂), 4.1 (t, 2H, arOCH₂), 7.0 (s, 1H, -C=CH), 7.2–8.2 (rn, 12H, arH), 16.9 (s,

Table 5.4
Physical constants for ethyl-2-n-alkoxybenzoates,
5.k

n	Boiling point (°C)/mm
1	103-105/2
2	115-117/1
3	98-100/0.1
4	117-120/0.1
5	128-130/0.2
6	160-163/0.5
7	168-171/0.5
8	178-180/0.5
9	189-191/0.5
11	206-208/1.5
12	200-202/1

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111, =C-O11).

Anal. calcd. for $C_{44}H_{62}O_3$,

C, 82.75 ; H, 9.71 %

Found: C, 83.04 ; H, 9.93 % .

The physical data of the other 1-(4''-n-dodecylbiphenyl)-3-(2-n- alkyloxyphenyl)-propane-1,3-diones are given below:

1-(4''-n-Dodecylbiphenyl)-3-(2-methyloxyphenyl)propane-1,3-dione:

Yield, 21%; m.p. 79.5°C; IR ν_{max} : 2930, 2860, 1608, 1490, 1270, 1020, 808 and 765 cm^{-1} ; NMR 5: 0.86 (t, 6H, 2× -CH₃), 1.0-2.0 (rn, 20H, 10×-CH₂), 2.62 (t, 2H, arCH₂), 4.0 (t, 3H, arOCH₃), 7.0 (s, 1H, -C=CH), 7.2-8.2 (rn, 12H, arH), 16.7 (s, 111, =C-O11).

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

C, 81.92 ; H, 8.44 %

Found: C, 82.24 ; H, 8.47 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-ethyloxyphenyl)propane-1,3-dione:

Yield, 19%; m.p. 70.5°C; IR ν_{max} : 2930, 2860, 1608, 1465, 1245, 1040, 805 and 760 cm^{-1} C; NMR 6: 0.85 (t, 6H, 2× -CH₃), 1.1-2.1 (rn, 20H, 10×-CH₂), 2.7 (t, 2H, arCH₂), 4.1 (q, 2H, arOCH₂), 7.0 (s, 1H, -C=CH), 7.2-8.2 (m, 12H, arH), 16.8 (s, 111, =C-O11).

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

C, 82.03 ; H, 8.59 %

Found: C, 82.00 ; H, 8.61 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-propyloxyphenyl)propane-1,3-dione:

Yield, 18%; m.p. 60.0°C; IR ν_{max} : 2930, 2860, 1608, 1465, 1245, 1010, 805 and 760 cm^{-1} ; NMR δ : 0.85 (t, 6H, $2 \times -\text{CH}_3$), 1.1–2.1 (m, 22H, $11 \times -\text{CH}_2$), 2.66 (t, 2H, ar CH_2), 4.1 (t, 2H, arO CH_2), 7.0 (s, 1H, $-\text{C}=\text{CH}$), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, $=\text{C}-\text{OH}$).

Anal. calcd. for $\text{C}_{36}\text{H}_{46}\text{O}_3$,

C, 82.12 ; H, 8.74 %

Found: C, 82.02 ; H, 8.92 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-butyloxyphenyl)propane-1,3-dione:

Yield, 13%; m.p. 47.5°C; IR ν_{max} : 2930, 2860, 1608, 1460, 1270, 810 and 765 cm^{-1} ; NMR δ : 0.86 (t, 6H, $2 \times -\text{CH}_3$), 1.1–2.0 (m, 24H, $12 \times -\text{CH}_2$), 2.6 (t, 2H, ar CH_2), 4.1 (t, 2H, arO CH_2), 7.0 (s, 1H, $-\text{C}=\text{CH}$), 7.2–8.2 (m, 12H, arH), 16.95 (s, 1H, $=\text{C}-\text{OH}$).

Anal. calcd. for $\text{C}_{37}\text{H}_{48}\text{O}_3$,

C, 82.22 ; H, 8.88 %

Found: C, 82.22 ; H, 9.18 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-pentyloxyphenyl)propane-1,3-dione:

Yield, 21%; m.p. 53.5°C; IR ν_{max} : 2930, 2860, 1608, 1460, 1380, 1275, 810 and 765 cm^{-1} ; NMR δ : 0.86 (t, 6H, $2 \times -\text{CH}_3$), 1.1–2.0 (m, 26H, $13 \times -\text{CH}_2$), 2.6 (t, 2H, ar CH_2), 4.1 (t, 2H, arO CH_2), 7.0 (s, 1H, $-\text{C}=\text{CH}$), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, $=\text{C}-\text{OH}$).

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

C, 82.31 ; H, 9.02 %

Found: C, 82.41 ; H, 9.31 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-hexyloxyphenyl)propane-1,3-dione:

Yield, 25%; m.p. 51.5°C; IR ν_{max} : 2940, 2850, 1610, 1465, 1380, 1260, 820 and 760 cm^{-1} ; NMR δ : 0.86 (t, 6H, $2 \times -CH_3$), 1.1-2.1 (m, 28H, $14 \times -CH_2$), 2.6 (t, 2H, arH_2), 4.1 (t, 2H, $arOCH_2$), 7.0 (s, 1H, $-C=CH$), 7.2-8.2 (rn, 12H, arH), 16.9 (s, 1H, $=C-OH$).

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

C, 82.39 ; H, 9.15 %

Found: C, 82.45 ; H, 9.36 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-heptyloxyphenyl)propane-1,3-dione:

Yield, 19%; m.p. 48.5°C; IR ν_{max} : 2940, 2860, 1608, 1465, 1380, 1240, 805 and 760 cm^{-1} ; NMR δ : 0.89 (t, 6H, $2 \times -CH_3$), 1.1-2.0 (m, 32H, $16 \times -CH_2$), 2.65 (t, 2H, $arCH_2$), 4.1 (t, 2H, $arOCH_2$), 7.0 (s, 1H, $-C=CH$), 7.2-8.2 (m, 12H, arH), 16.9 (s, 1H, $=C-OH$).

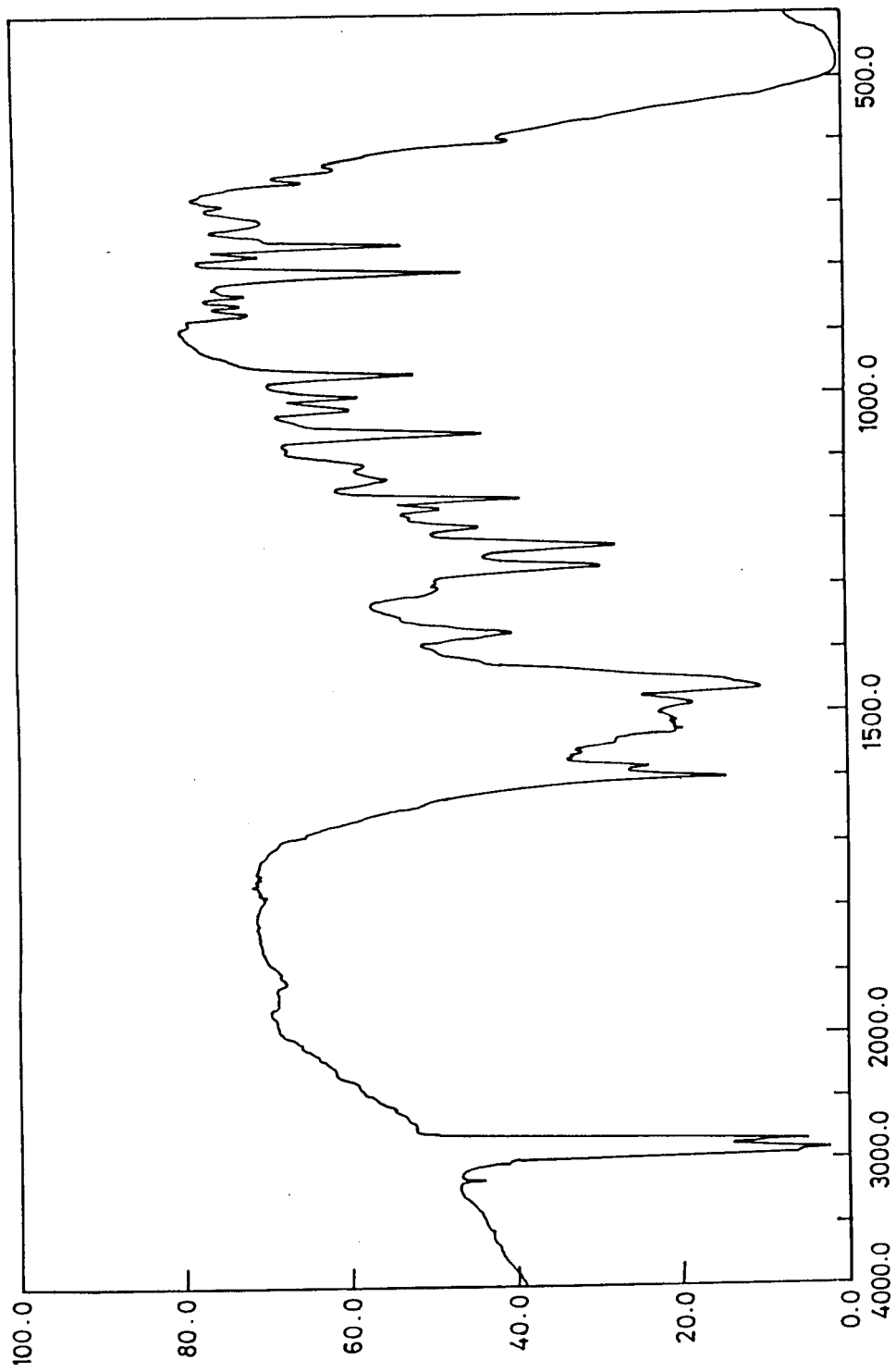
Anal. calcd. for $C_{40}H_{54}O_3$,

C, 82.47 ; H, 9.27 %

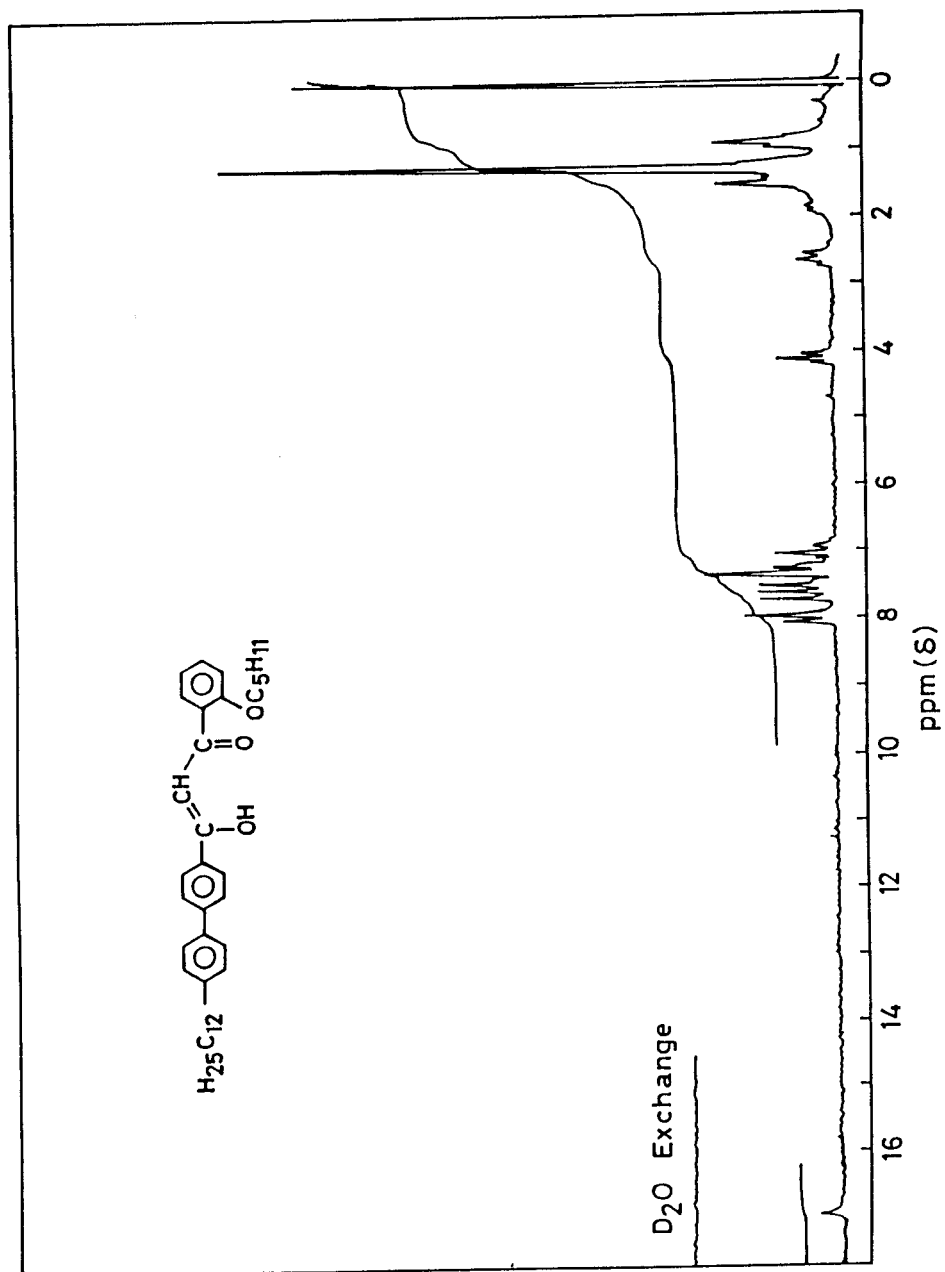
Found: C, 82.37 ; H, 9.32 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-octyloxyphenyl)propane-1,3-dione:

Yield, 25%; m.p. 60.5°C; IR ν_{max} : 2940, 2860, 1608, 1465, 1240, 800 and 760 cm^{-1} ; NMR δ : 0.89 (t, 6H, $2 \times -CH_3$), 1.1-2.0 (m, 32H, $16 \times -CH_2$), 2.65 (t, 2H,



IR spectrum for compound 5.h.4



¹H NMR spectrum for compound 5.h.5.

arCH₂), 4.1 (t, 2H, arOCH₂), 7.0 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 17.0 (s, 1H, =C-OH).

Anal. calcd. for C₄₁H₅₆O₃,

C, 82.55 ; H, 9.39 %

Found: C, 82.30 ; H, 9.55 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-nonyloxyphenyl)propane-1,3-dione:

Yield, 22%; m.p. 66.5°C; IR ν_{max} : 2920, 2870, 1608, 1470, 1240, 800 and 765 cm⁻¹; NMR δ : 0.89 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 34H, 17×-CH₂), 2.65 (t, 2H, arCH₂), 4.1 (t, 2H, arOCH₂), 7.0 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₄₂H₅₈O₃,

C, 82.62 ; H, 9.50 %

Found: C, 82.52 ; H, 9.71 % .

1-(4''-n-Dodecylbiphenyl)-3-(2-n-decyloxyphenyl)propane-1,3-dione:

Yield, 17%; m.p. 67.0°C; IR ν_{max} : 2920, 2860, 1608, 1465, 1380, 1240, 800 and 765 cm⁻¹; NMR δ : 0.9 (t, 6H, 2× -CH₃), 1.1–2.0 (m, 36H, 18×-CH₂), 2.65 (t, 2H, arCH₂), 4.1 (t, 2H, arOCH₂), 7.0 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₄₃H₆₀O₃,

C, 82.69 ; H, 9.61 %

Found: C, 82.79 ; H, 9.78 %

1-(4''-n-Dodecylbiphenyl)-3-(2-n-dodecyloxyphenyl)propane-1,3-dione:

Yield, 20%; m.p. 63.5°C; IR ν_{max} : 2920, 2860, 1608, 1465, 1380, 1240, 800 and 760 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times -\text{CH}_3$), 1.1–2.0 (m, 40H, $20 \times -\text{CH}_2$), 2.65 (t, 2H, ar CH_2), 4.1 (t, 2H, ar OCH_2), 7.0 (s, 1H, $-\text{C}=\text{CH}$), 7.2–8.2 (m, 12H, arH), 16.9 (s, 1H, $=\text{C}-\text{OH}$).

Anal. calcd. for $\text{C}_{45}\text{H}_{64}\text{O}_3$,

C, 82.82 ; H, 9.81 %

Found: C, 82.63 ; H, 9.97 % .

Bis[1-(4''-n-dodecylbiphenyl)-3-(2-n-dodecyloxyphenyl)propane -1,3-dionato]copper(II):

A mixture of 1-(4''-n-dodecylbiphenyl)-3-(2-n-dodecyloxyphenyl) propane-1,3-dione (0.326 g, 0.5 mmol), powdered potassium hydroxide (0.028 g, 0.5 mmol) and ethyl alcohol (10 ml) were warmed until the solution became clear. To this was added a solution of cupric chloride dihydrate (0.043 g, 0.25 mmol) in ethyl alcohol (5 ml). The mixture became dark green and precipitation occurred immediately. This was stirred for four hours at room temperature and filtered. The precipitate was collected, dissolved in chloroform (70 ml), washed with water (3×100 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of the residue from butan-2-one gave the desired complex.

Yield, 0.15 g, (44%); m.p. 181.0°C; IR ν_{max} : 2940, 2860, 1600, 1580, 1460, 1380, 1210, 800 and 745 cm^{-1} . UV-Vis: $\lambda_{max}^{\text{CHCl}_3}$ (ϵ): 365 (39,000), 321 (30,000).

Anal. calcd. for $\text{C}_{90}\text{H}_{126}\text{O}_6\text{Cu}$,

C, 79.09 ; H, 9.22 %

Found: C, 79.25 ; H, 9.43 % .

Bis[1-(4''-n-dodecylbiphenyl)-3-(2-n-hexyloxyphenyl)propane-1,3-dionato]copper(II):

Yield, 40%; m.p. 174.0°C; IR ν_{max} : 2920, 2860, 1600, 1580, 1460, 1380, 1220, 800 and 745 cm^{-1} . UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 365 (40,800), 321 (31,400).

Anal. calcd. for $\text{C}_{78}\text{H}_{102}\text{O}_6\text{Cu}$,

C, 78.16 ; H, 8.52 %

Found: C, 77.86 ; H, 8.99 % .

4-n-Dodecylbiphenyl-4'-carboxylic acid was prepared from 4-n-dodecyl-4'-acetyl-biphenyl, following the procedure of Byron, Gray and Wilson.²⁰

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

A mixture of 4-n-dodecylbiphenyl-4'-carboxylic acid (34.0 g), ethyl alcohol (500 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 (500 g) and extracted with ether (3×100 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 the solvent and crystallisation of the residue using ethyl alcohol gave pure ethyl-4-n-dodecylbiphenyl-4'-carboxylate.

Yield, 28.0 g, (93%); m.p. 57.0°C; IR ν_{max} : 2930, 2850, 1730, 1460, 1280, 1100 and 760 cm^{-1} .

Anal. calcd. for $\text{C}_{27}\text{H}_{38}\text{O}_2$,

C, 82.23 ; H, 9.64 %

Found: C, 82.47 ; H, 9.87 %

All the required 3-n-alkyloxyacetophenones were prepared following the procedure given below (for 3-n-decyloxyacetophenone) and these compounds have been characterised by their physical constants as well as spectral data.

3-n-Decyloxyacetophenone:

A mixture of 3-hydroxyacetophenone (13.6 g, 0.1 mol), anhydrous potassium carbonate (27.6 g, 0.2 mol), n-decylbromide (22.1 g, 0.1 mol) and dry acetone (200 ml) was refluxed for fortyeight hours. The reaction mixture was filtered and the solvent removed completely. The residue was poured into a mixture of ice and hydrochloric acid. Then, it was extracted with ether (2x100 ml), the combined ethereal extracts was washed with ice cold 5% sodium hydroxide solution (2x50 ml), water (4x100 ml) and dried (Na_2SO_4). The solvent was removed, the residue was chromatographed and the required compound distilled under reduced pressure. Yield, 17.8 g, (64%); b.p. 190-92°C/1mm.

The physical constants of the other 3-n-alkyloxyacetophenones (5.1) are given in table 5.5.

1-(4''-n-Dodecylbiphenyl)-3-(3-n-octyloxyphenyl)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 ethyl-4-n-dodecylbiphenyl-4'-carboxylate (3.24 g, 0.01 mol) and 3-n-octyloxyacetophenone (2.48 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 and cooled. Ice cold dilute hydrochloric acid (20 ml) was added and the mixture was 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

Table 5.5
Physical constants for 3-n-alkoxyacetophenones,
5.1

n	Boiling point (°C)/mm
1	87-90/1.8
2	110-112/1
3	120-122/1
4	115-117/0.2
5	142-145/0.3
6	130-132/10.2
7	145-147/10.2
8	158-160/1
9	165-167/0.2
11	165-167/10.1
12	195-200/1.5-2

butan-1-ol.

Yield, 1.8 g, (30%); m.p. 76.5°C; IR ν_{max} : 2940, 2860, 1610, 1565, 1465, 1380, 1260, 1205 and 785 cm^{-1} ; NMR δ : 0.8 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 32H, 16 \times -CH₂), 2.7 (t, 2H, arCH₂), 4.05 (t, 2H, arOCH₂), 6.85 (s, 1H, -C=CH), 7.2–8.2 (m, 12H, arH), 16.85 (s, 1H, =C-OH).

Anal. calcd. for C₄₁H₅₆O₃,

C, 82.55 ; H, 9.39 %

Found: C, 82.75 ; H, 9.57 % .

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

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

Yield, 33%; m.p. 100.0°C; IR ν_{max} : 2940, 2850, 1600, 1465, 1375, 1255, 1210, 1030 and 785 cm^{-1} ; NMR δ : 0.82 (t, 3H, -CH₃), 1.0–2.0 (m, 20H, 10 \times -CH₂), 2.67 (t, 2H, arCH₂), 3.98 (t, 2H, arOCH₃), 6.85 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₃₄H₄₂O₃,

C, 81.92 ; H, 8.44 %

Found: C, 82.16 ; H, 8.13 % .

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

Yield, 37%; m.p. 100.0°C; IR ν_{max} : 2930, 2860, 1608, 1595, 1465, 1380, 1270, 1160 and 760 cm^{-1} ; NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 20H, 10 \times -CH₂), 2.65 (t, 2H, arCH₂), 4.0 (q, 2H, arOCH₂), 6.85 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

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

C, 82.03 ; H, 8.59 %

Found: C, 82.04 ; H, 8.72 % .

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

Yield, 26%; m.p. 95.5"; IR ν_{max} : 2920, 2860, 1608, 1570, 1465, 1260, 1205 and 785 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times -CH_3$), 1.0–2.0 (m, 22H, $11 \times -CH_2$), 2.68 (t, 2H, ar CH_2), 4.0 (t, 2H, arO CH_2), 6.85 (s, 1H, $-C=CH$), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{36}H_{46}O_3$,

C, 82.12 ; H, 8.74 %

Found: C, 81.83 ; H, 8.81 % .

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

Yield, 27%; m.p. 93.0°C; IR ν_{max} : 2940, 2850, 1608, 1560, 1465, 1260 and 770 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times -CH_3$), 1.0–2.0 (m, 24H, $12 \times -CH_2$), 2.65 (t, 2H, ar CH_2), 4.0 (t, 2H, arO CH_2), 6.85 (s, 1H, $-C=CH$), 7.0–8.2 (m, 12H, arH), 16.85 (s, 1H, $=C-OH$).

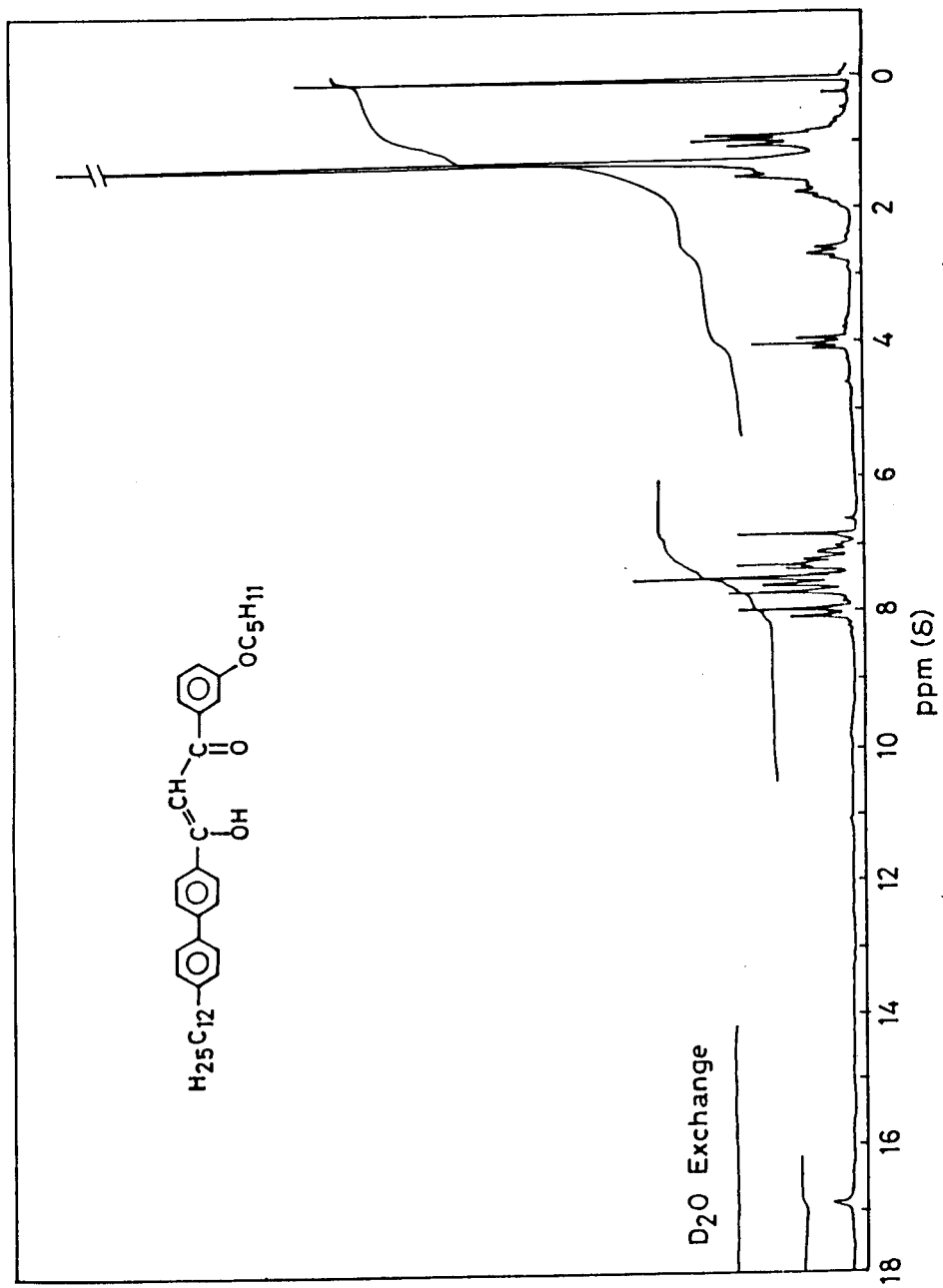
Anal. calcd. for $C_{37}H_{48}O_3$,

C, 82.22 ; H, 8.88 %

Found: C, 82.13 ; H, 8.97 % .

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

Yield, 29%; m.p. 90.0°C; IR ν_{max} : 2930, 2850, 1600, 1565, 1470, 1375, 1260 and 785 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times -CH_3$), 1.0–2.0 (m, 26H, $13 \times -CH_2$), 2.65 (t, 2H,



¹H NMR spectrum for compound 5.i.5.

arCH₂), 4.0 (t, 2H, arOCH₂), 6.85 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₃₈H₅₀O₃,

C, 82.31 ; H, 9.02 %

Found: C, 82.35 ; H, 9.07 % .

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

Yield, 21%; m.p. 85.5°C; IR ν_{max} : 2920, 2850, 1600, 1565, 1465, 1260 and 785 cm⁻¹; NMR δ : 0.95 (t, 6H, 2× -CH₃), 1.0–2.0 (m, 28H, 14× -CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.9 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₃₉H₅₂O₃,

C, 82.39 ; H, 9.15 %

Found: C, 82.73 ; H, 9.34 % .

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

Yield, 23%; m.p. 78.0°C; IR ν_{max} : 2900, 2860, 1600, 1565, 1470, 1260 and 785 cm⁻¹; NMR δ : 0.9 (t, 6H, 2× -CH₃), 1.0–2.0 (m, 30H, 15× -CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.9 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.85 (s, 1H, =C-OH).

Anal. calcd. for C₄₀H₅₄O₃,

C, 82.47 ; H, 9.27 %

Found: C, 82.30 ; H, 9.40 % .

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

Yield, 20%; m.p. 74.5°C; IR ν_{max} : 2930, 2860, 1610, 1565, 1465, 1380, 1265 and 775 cm^{-1} ; NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 34H, 17 \times -CH₂), 2.7 (t, 2H, arCH₂), 4.05 (t, 2H, arOCH₂), 6.9 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₄₂H₅₈O₃,

C, 82.62 ; H, 9.50 %

Found: C, 82.81 ; H, 9.72 % .

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

Yield, 31%; m.p. 73.5°C; IR ν_{max} : 2920, 2860, 1600, 1565, 1380, 1260, 1205 and 785 cm^{-1} ; NMR δ : 0.95 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 36H, 18 \times -CH₂), 2.7 (t, 2H, arCH₂), 4.1 (t, 2H, arOCH₂), 6.9 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

Anal. calcd. for C₄₃H₆₀O₃,

C, 82.69 ; H, 9.61 %

Found: C, 82.22 ; H, 9.68 % .

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

Yield, 25%; m.p. 75.0°C; IR ν_{max} : 2920, 2860, 1600, 1565, 1465, 1260 and 785 cm^{-1} ; NMR δ : 0.92 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 38H, 19 \times -CH₂), 2.7 (t, 2H, arCH₂), 4.05 (t, 2H, arOCH₂), 6.9 (s, 1H, -C=CH), 7.0–8.2 (m, 12H, arH), 16.9 (s, 1H, =C-OH).

chapter 5

Anal. calcd. for $C_{44}H_{62}O_3$,

C, 82.75 ; H, 9.71 %

Found: C, 82.86 ; H, 9.92 % .

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

Yield, 24%; m.p. 73.5°C; IR ν_{max} : 2930, 2870, 1600, 1570, 1470, 1380, 1260 and 785 cm^{-1} ; NMR δ : 0.95 (t, 6H, $2\times-CH_3$), 1.0-2.0 (m, 40H, $20\times-CH_2$), 2.7 (t, 2H, ar CH_2), 4.1 (t, 2H, ar OCH_2), 6.9 (s, 1H, $-C=CH$), 7.0-8.2 (m, 12H, arH), 16.95 (s, 1H, $=C-OH$).

Anal. calcd. for $C_{45}H_{64}O_3$,

C, 82.82 ; H, 9.85 %

Found: C, 83.28 ; H, 10.05 % .

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

A mixture of 1-(4''-n-dodecylbiphenyl)-3-(3-n-dodecyloxyphenyl) propane-1,3-dione (0.652 g, 1 mmol) powdered potassium hydroxide (0.056 g, 1 mmol) and ethyl alcohol (15 ml) were warmed until the solution became clear. To this was added a solution of cupric chloride dihydrate (0.085 g, 0.5 mmol) in ethyl alcohol (10 ml). Precipitation occurred instantaneously and the reaction mixture was stirred for three hours at room temperature. Then it was filtered, the precipitate collected and dissolved in chloroform (100 ml), washed with water (3x100 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of the residue using butan-2-one afforded green crystals of the complex.

Yield, 0.4 g, (59%); m.p. 200.0°C; IR ν_{max} : 2920, 2850, 1580, 1565, 1460, 1375, 1205 and 775 cm^{-1} . UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 364 (62,000), 320 (42,200).

chapter 5

Anal. calcd. for $C_{90}H_{126}O_6Cu$,

C, 79.09 ; H, 9.22 %

Found: C, 78.98 ; H, 9.50 % .

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

Yield, 66%; m.p. 220.0°C; IR ν_{max} : 2930, 2860, 1580, 1565, 1460, 1380, 1210 and 775 cm^{-1} . UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 363 (61,100), 320 (41,300).

Anal. calcd. for $C_{76}H_{98}O_6Cu$,

C, 77.98 ; H, 8.37 %

Found: C, 77.74 ; H, 8.50 % .

1-(4''-Methoxybiphenyl)-3-(phenyl)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-methoxy-4'-acetylbiphenyl (4.52 g, 0.02 mol) and methyl benzoate (2.72 g, 0.02 mol) in dry 1,2-dimethoxyethane (60 ml). This was stirred magnetically and sodium hydride (1.6 g, 0.04 mol) was added, the mixture refluxed for four hours and cooled. Ice-cold dilute hydrochloric acid (30 ml) was added and the mixture extracted with chloroform (4x50 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 yellow product. This was crystallised from butan-2-one.

Yield, 2.6 g, (39%); m.p. 176.5°C; IR ν_{max} : 2950, 2850, 1600, 1470, 1380, 1260, 1040, 840 and 780 cm^{-1} ; NMR δ : 4.0 (s, 3H, arOCH₃), 6.8–8.2 (rn, 13H, arH), 16.9 (s, 1H, =C-OH).

chapter 5

Anal. calcd. for C₂₂H₁₈O₃,

C, 80.0 ; H, 5.45 %

Found: C, 79.97 ; H, 5.50 % .

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

In a 250 ml round bottom flask was placed a mixture of 1-(4''-methoxybiphenyl)-3-(phenyl)propane-1,3-dione (8.25 g, 0.025 mol), hydrobromic acid (48% , 37.5 ml) and acetic acid (84.2 ml). This was refluxed for sixteen hours and cooled. Then it was poured into a beaker containing crushed ice (250 g), the solid material thus obtained was filtered and washed thoroughly with water until the water washings were acid free. Finally the material was dried and crystallised using acetonitrile.

Yield, 5.0 g, (65%); m.p. 210.0°C; IR ν_{max} : 3310, 2940, 2880, 1690, 1660, 1600, 1585, 1460, 1300, 1200 and 825 cm⁻¹.

1-(4''-Dodecanoyloxybiphenyl)-3-(n-dodecanoyloxy)-3-(phenyl)-2-propene-1-one:

In a 100 ml round bottom flask fitted with a calcium chloride guard tube, was placed 1-(4''-hydroxybiphenyl)-3-(phenyl)propane-1,3-dione (0.316 g, 1 mmol) to which was added dry pyridine (5 ml). To this clear solution was added n-dodecanoyl chloride (0.436 g, 2 mmol) dropwise. The mixture was stirred magnetically at room temperature for sixteen hours. Then it was poured onto a mixture of ice and hydrochloric acid and extracted with ether (2x50 ml). The combined ether solution was washed with water (4x50 ml) and dried (Na₂SO₄). The solvent was removed, the residue obtained was chromatographed and the required material was crystallised using ethyl alcohol.

Yield, 0.14 g, (35%); m.p. 104.0°C; IR ν_{max} : 2930, 2850, 1745, 1680, 1600, 1465,

1380, 1365, 1240, 815 and 720 cm^{-1} ; NMR δ : 0.9 (t, 6H, $2 \times \text{-CH}_3$), 1.1–2.0 (m, 38H, $19 \times \text{-CH}_2$), 2.7 (t, 4H, $2 \times \text{-OCOCH}_2$), 7.1–8.2 (m, 14H, $13 \times \text{arH}$, and -C=CH).

Anal. calcd. for $\text{C}_{45}\text{H}_{60}\text{O}_5$,

C, 79.41 ; H, 8.82 %

Found: C, 79.30 ; H, 8.32 % .

The physical data of the other 1-(4''-n-alkanoyloxybiphenyl)-3-(n-alkanoyloxy)-3-(phenyl)-2-propene-1-ones are given below:

1-(4''-n-Butanoyloxybiphenyl)-3-(n-butanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 37%; m.p. 102.5°C ; IR ν_{max} : 2950, 2860, 1750, 1680, 1600, 1460, 1395, 1365, 1200 and 830 cm^{-1} ; NMR δ : 1.1 (t, 6H, $2 \times \text{-CH}_3$), 1.5–2.2 (m, 4H, $2 \times \text{-CH}_2$), 2.65 (t, 4H, $2 \times \text{-OCOCH}_2$), 7.0–8.3 (m, 14H, $13 \times \text{arH}$ and -C=CH).

Anal. calcd. for $\text{C}_{29}\text{H}_{28}\text{O}_5$,

C, 76.31 ; H, 6.14 %

Found: C, 76.34 ; H, 6.46 % .

1-(4''-n-Pentanoyloxybiphenyl)-3-(n-pentanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 32%; m.p. 109.5°C ; IR ν_{max} : 2940, 2870, 1750, 1680, 1605, 1465, 1380, 1250, 1150 and 830 cm^{-1} ; NMR δ : 1.0 (t, 6H, $2 \times \text{-CH}_3$), 1.3–2.0 (m, 8H, $4 \times \text{-CH}_2$), 2.65 (t, 4H, $2 \times \text{-OCOCH}_2$), 7.1–8.3 (m, 14H, $13 \times \text{arH}$ and -C=CH).

Anal. calcd. for $\text{C}_{31}\text{H}_{32}\text{O}_5$,

C, 76.85 ; H, 6.61 %

Found: C, 76.60 ; H, 6.89 % .

1-(4''-n-Hexanoyloxybiphenyl)-3-(n-hexanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 36%; m.p. 99.5°C; IR ν_{max} : 2940, 2860, 1750, 1680, 1600, 1460, 1395, 1365, 1200, 830 and 725 cm^{-1} ; NMR δ : 1.0 (t, 6H, 2 \times -CH₃), 1.2–2.0 (m, 12H, 6 \times -CH₂), 2.65 (t, 4H, -OCOCH₂), 7.1–8.3 (m, 14H, 13 \times arH and -C=CH).

Anal. calcd. for C₃₃H₃₆O₅,

C, 77.34 ; H, 7.03 %

Found: C, 77.09 ; H, 7.23 % .

1-(4''-n-Heptanoyloxybiphenyl)-3-(n-heptanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 33%; m.p. 99.5°C; IR ν_{max} : 2920, 2850, 1745, 1680, 1600, 1460, 1395, 1365, 1200, 835 and 725 cm^{-1} ; NMR δ : 0.95 (t, 6H, 2 \times -CH₃), 1.2–2.0 (m, 16H, 8 \times -CH₂), 2.7 (t, 4H, 2 \times -OCOCH₂), 7.1–8.3 (m, 14H, 13 \times arH and -C=CH).

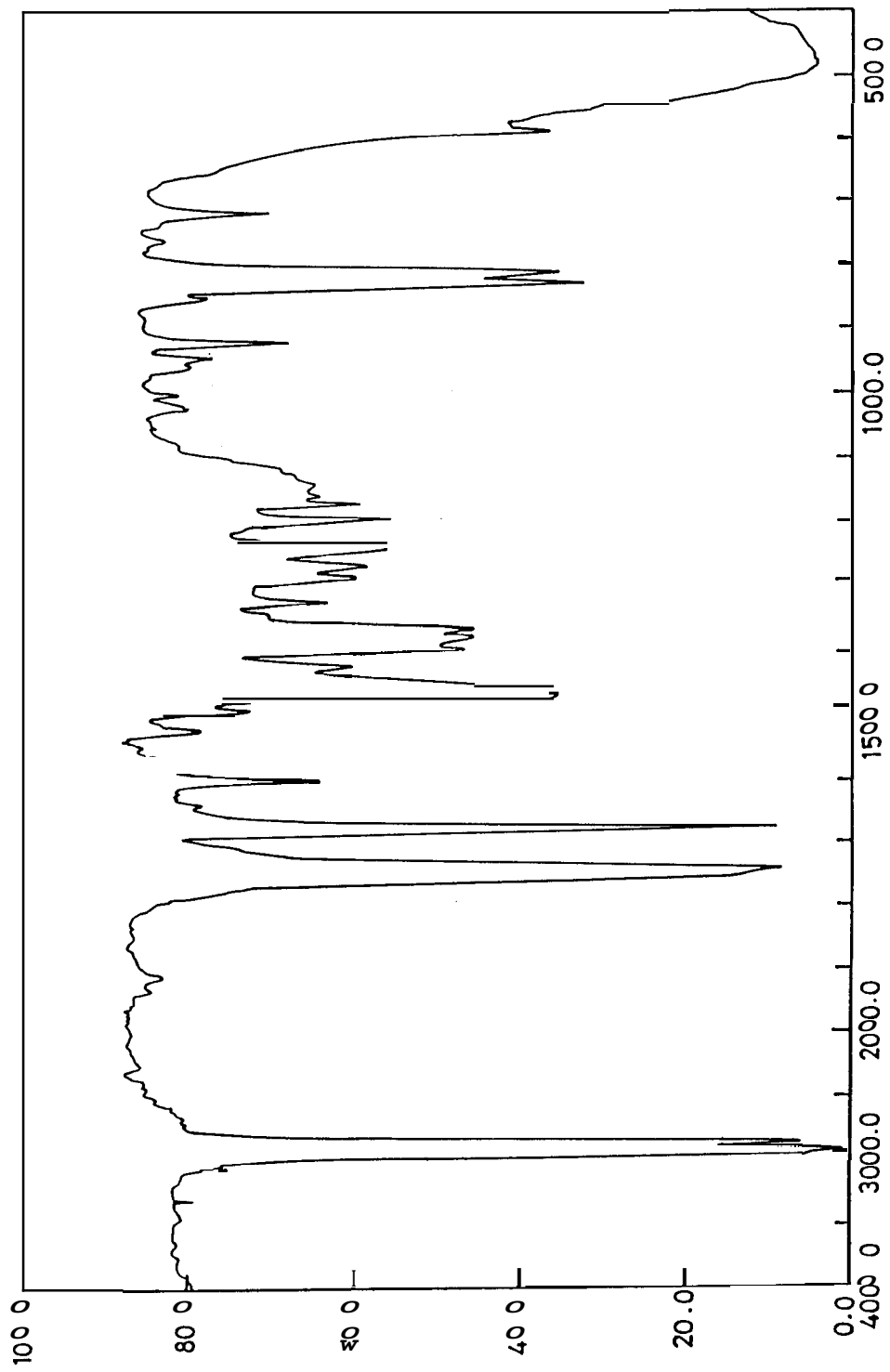
Anal. calcd. for C₃₅H₄₀O₅,

C, 77.77 ; H, 7.40 %

Found: C, 77.43 ; H, 7.90 % .

1-(4''-n-Octanoyloxybiphenyl)-3-(n-octanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 38%; m.p. 101.0°C; IR ν_{max} : 2920, 2850, 1745, 1680, 1600, 1465, 1395, 1365, 1200, 835 and 720 cm^{-1} ; NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.1–2.0 (m, 20H, 10 \times -CH₂), 2.65 (t, 4H, 2 \times -OCOCH₂), 7.1–8.2 (m, 14H, 13 \times arH and -C=CH).



IR spectrum for compound 5.j.4

Anal. calcd. for $C_{37}H_{44}O_5$,

C, 78.20 ; H, 7.74 %

Found: C, 78.61 ; H, 7.72 % .

1-(4''-n-Nonanoyloxybiphenyl)-3-(n-nonanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 31%; m.p. 98.5°C; IR ν_{max} : 2920, 2850, 1745, 1680, 1600, 1465, 1395, 1365, 1200, 835 and 720 cm^{-1} ; NMR δ : 0.85 (t, 6H, 2 \times -CH₃), 1.1–2.0 (m, 24H, 12 \times -CH₂), 2.7 (t, 4H, 2 \times -OCOCH₂), 7.1–8.2 (m, 14H, 13 \times arH and -C=CH).

Anal. calcd. for $C_{39}H_{48}O_5$,

C, 78.52 ; H, 8.05 %

Found: C, 78.17 ; H, 8.17 % .

1-(4''-n-Decanoyloxybiphenyl)-3-(n-decanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 34%; m.p. 103.5 °C; IR ν_{max} : 2920, 2850, 1745, 1680, 1600, 1465, 1395, 1365, 1200, 835 and 720 cm^{-1} ; NMR δ : 0.85 (t, 6H, 2 \times -CH₃), 1.15–2.0 (m, 28H, 14 \times -CH₂), 2.7 (t, 4H, 2 \times -OCOCH₂), 7.1–8.2 (m, 14H, 13 \times arH and -C=CH).

Anal. calcd. for $C_{41}H_{52}O_5$,

C, 78.84 ; H, 8.33 %

Found: C, 78.80 ; H, 8.55 % .

1-(4''-n-Undecanoyloxybiphenyl)-3-(n-undecanoyloxy)-3-(phenyl)-2-propene-1-one:

Yield, 37%; m.p. 102.5°C; IR ν_{max} : 2920, 2850, 1745, 1680, 1600, 1465, 1395, 1365, 1200, 835 and 720 cm^{-1} ; NMR δ : 0.85 (t, 6H, 2 \times -CH₃), 1.15–2.0 (m, 32H, 16 \times -CH₂), 2.7 (t, 4H, 2 \times -OCOCCH₂), 7.1–8.3 (m, 14H, 13 \times arH and -C=CH).

Anal. calcd. for C₄₃H₅₆O₅,

C, 79.14 ; H, 8.58 %

Found: C, 78.84 ; H, 8.64 % .

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