

# Chapter 6

**Synthesis and mesomorphic properties of**  
**1-(4''-n-dodecylbiphenyl-4-yl)-3-(2',4'-di-n-alkoxyphenyl)**  
**propane-1,3-diones**  
**and**  
**3-(4''-n-dodecylbiphenyl-4-yl)-5-(2',4'-di-n-alkoxyphenyl)**  
**isoxazoles**

## **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 liquid crystal chemistry, Vorlander derived a rule defining the rod-like shape of molecules of thermotropic liquid crystals, which has been confirmed by thousands of examples.' In proving this rule, the influence of lateral substituents on the liquid crystalline properties was vigorously studied.<sup>2,3</sup> The results seemed to indicate that only small lateral substituents could be accommodated without dramatic changes in the liquid crystalline properties.

In 1983, Weissflog and Demus<sup>4</sup> 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, 6.A. All of them show nematic phase. They established that on substitution of the aromatic ring in 2-position by methyl, ethyl and propyl groups the clearing points decreased drastically. As the lateral alkyl group was lengthened further, the trend in the depression of the clearing temperatures became less pronounced and reached a saturation value at  $n=12$ . They also investigated<sup>4</sup> many additional series of compounds with terminal alkyl, alkoxy, alkanoyloxy and alkoxy-carbonyloxy groups; the lateral substitution was either alkanoyl or other groups. In all these series of compounds liquid crystalline property was observed. They proposed<sup>4</sup> a molecular model for these compounds, wherein "the lateral alkyl chain makes a 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.<sup>5</sup>

Later, Weissflog and Demus<sup>6</sup> synthesised nearly a hundred compounds of the general formula 6.B, with R = alkyl, alkoxy, alkanoyloxy and alkoxy-carbonyloxy 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 believed 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.<sup>7</sup> It seems that on introduction of lateral substituents the distance between the aromatic parts of the molecules is 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.<sup>6</sup>

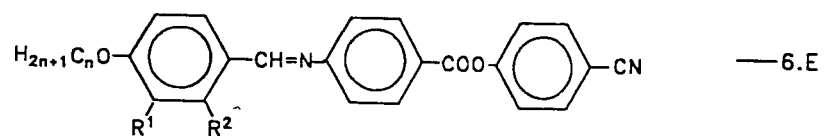
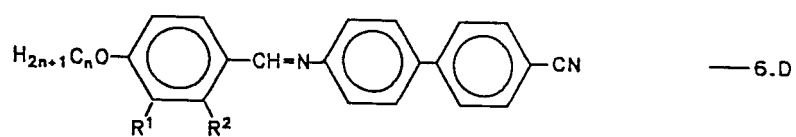
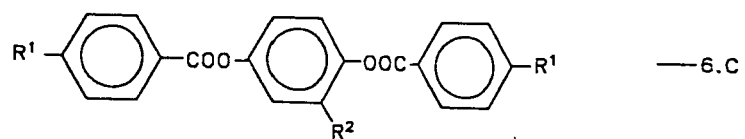
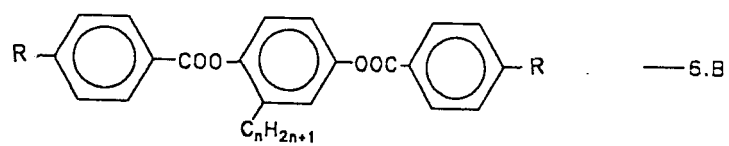
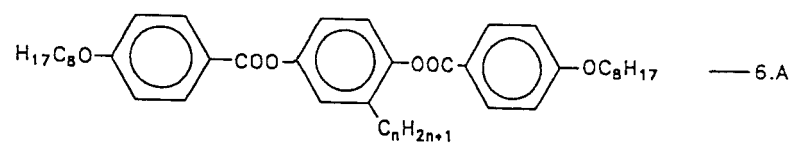
Weissflog and Demus<sup>8</sup> have reported a number of compounds of the general formula 6.C, in which R<sup>2</sup> was a normal or branched chain of considerable length. These compounds exhibited a nematic phase. On the basis of molecular statistical theories<sup>9,10</sup> and other arguments, they proposed a molecular model for these compounds in which the lateral substituents lie more or less parallel to the long molecular axis.

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Weissflog *et al.*<sup>11</sup> have investigated the synthesis and liquid crystalline properties of four series of compounds, having the general formulae 6.D and 6.E. All these 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 6.D and 6.E, the lateral long alkoxy 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-alkoxy compounds were only nematogenic, thus confirming the rule that lateral substituents suppress smectic properties.<sup>6</sup> The 3-alkoxy 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.<sup>12</sup>

Weissflog and Demus have reported 2-substituted hydroquinone-bis-benzoates 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.*<sup>14</sup> have reported some compounds (6.F and 6.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.<sup>15-17</sup>

The liquid crystalline properties of compounds containing a  $\beta$ -diketone group were investigated several years ago. The first report of such a compound was on 1,3-di-(p-n-decylphenyl)propane-1,3-dione, by Giroud and Billard.<sup>18</sup> Later, they reported a few more similar  $\beta$ -diketones and concluded that only those compounds having more than eighteen carbon atoms in the side chains exhibit a mesophase. Through optical and miscibility



$R^1 = OC_nH_{2n+1}, R^2 = H$  (or)

$R^2 = OC_nH_{2n+1}, R^1 = H$

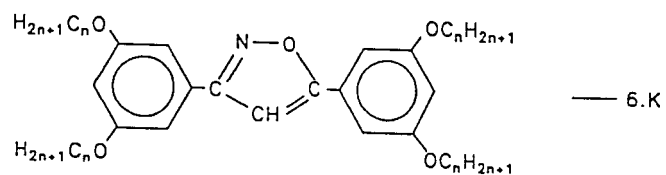
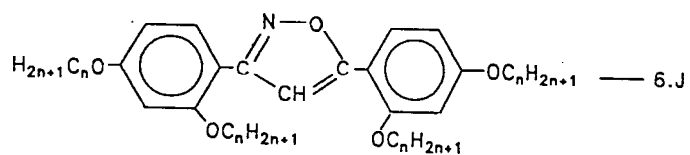
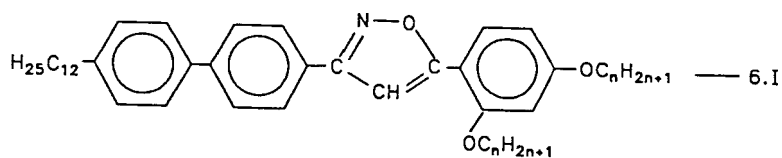
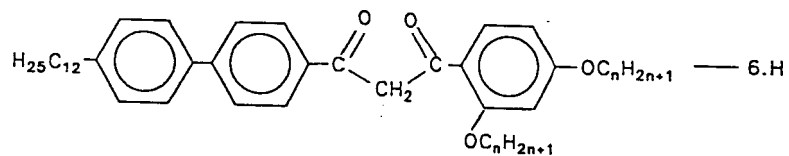
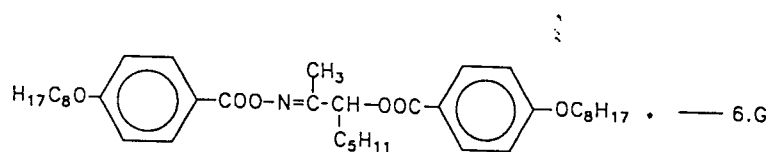
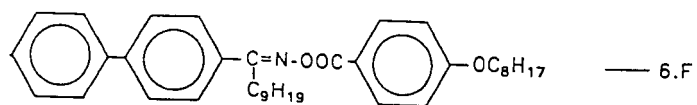
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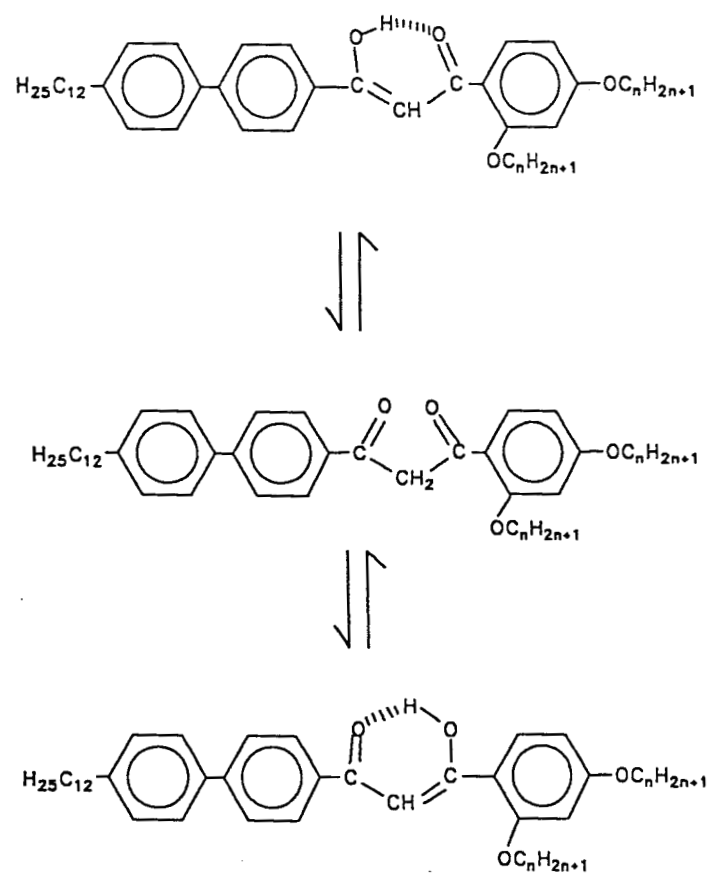
studies they also tentatively identified the mesophase exhibited by the above compounds as smectic E.<sup>18</sup>

In all the cases, the  $\beta$ -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.*<sup>19</sup> reported the first examples of a homologous series of [1-(*p*-n-alkylbiphenyl)-3-(phenyl)propane]1,3-diones which exhibited nematic as well as  $S_A$  phases. They established the nature of this smectic phase by optical textures, miscibility and X-ray studies as that of smectic  $A_1$  phase. In addition they also synthesised a number of  $\beta$ -diketones with different terminal substituents in order to examine the substituent effect on the mesomorphic properties. Later, Ohta *et al.*<sup>20</sup> also reported a number of  $\beta$ -diketones exhibiting smectic A and smectic E phases.

$\beta$ -Diketones are capable of exhibiting keto-enol tautomerism (figure 6.1). 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.

Many aryl  $\beta$ -diketones which are easily synthesised, are useful liquid crystalline derivatives.<sup>18,21-24</sup> Further, these compounds have an ability to form isoxazoles,<sup>25</sup> pyrazoles<sup>26</sup> and many of these are mesogenic.<sup>27,28</sup> The introduction of an azole ring between two phenyl rings opens the possibility of generating new mesogenic units. Besides, the hetero atoms can cause considerable changes in polarity, polarisability and geometry of the molecules and influence the type and transition temperature of the mesophase.





**Figure 6.1.** Keto-enol tautomerism of  $\beta$ -diketone (series 6.H).



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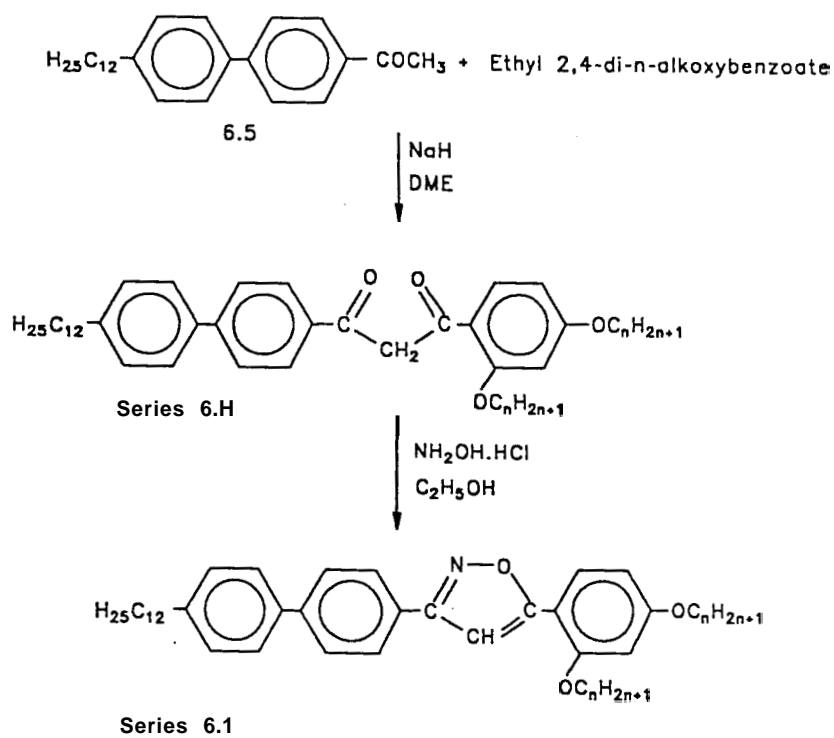
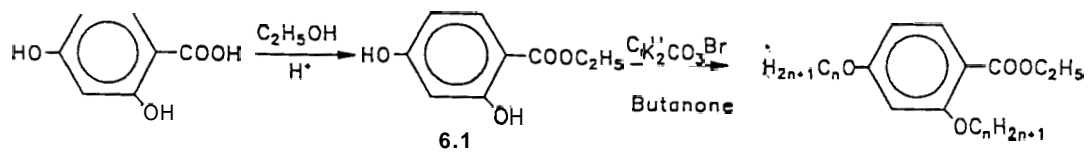
Under appropriate conditions a  $\beta$ -diketone can produce a five-membered isoxazole ring (figure 6.2), thereby shifting the keto-enol equilibrium in favour of the enol form.

### Results and discussion

As described above, a number of  $\beta$ -diketones exhibiting mesophases are known. However, the effect of two chain substituents have not been examined. In order to study the effect of 2,4-disubstituents on the mesomorphic properties of such systems, a homologous series of five  $\beta$ -diketones *viz.* 1-(4''-n-dodecylbiphenyl-4-yl)-3-(2',4'-di-n-alkoxyphenyl) propane-1,3-diones, (series 6.H) were synthesised. In addition, the corresponding isoxazoles (series 6.1) have also been prepared and their mesomorphic properties assessed. The five membered isoxazole group has aromatic character, planar conformation and high dipole moment perpendicular to the principal molecular axis. Hence it was of interest to investigate their liquid crystalline properties.

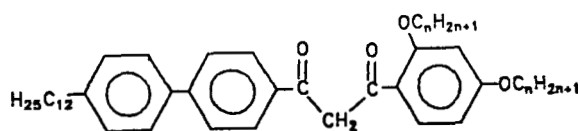
The 1-(4''-n-Dodecylbiphenyl-4-yl)-3-(2',4'-di-n-alkoxyphenyl)propane-1,3-diones, (6.H) were prepared following a procedure described by Sadashiva *et al.*<sup>19</sup> starting from 4-n-dodecyl-4'-acetylbiphenyl and ethyl-2,4-di-n-alkoxybenzoates in 1,2-dimethoxyethane using sodium hydride as a base. The transition temperatures and associated enthalpies for these compounds are summarised in table 6.1 and a plot of transition temperatures as a function of the alkyl chain length is shown in figure 6.3.

As can be seen in table 6.1, although all the  $\beta$ -diketones are mesogenic they are either metastable or show very narrow mesophase temperature ranges. This is probably due to the bent structure of the molecules of these compounds as well as lateral chain. Compounds 6.H.1 to 6.H.4 exhibit a nematic phase as evidenced by a schlieren texture.

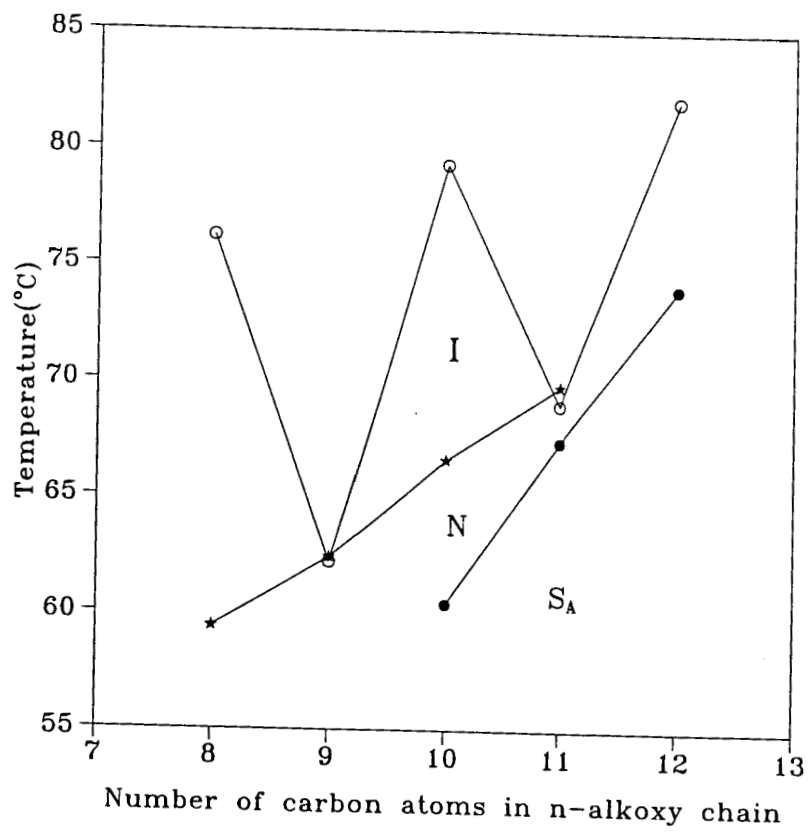


**Figure 6.2.** Synthetic scheme for the preparation of the compounds of series 6.H and 6.1.

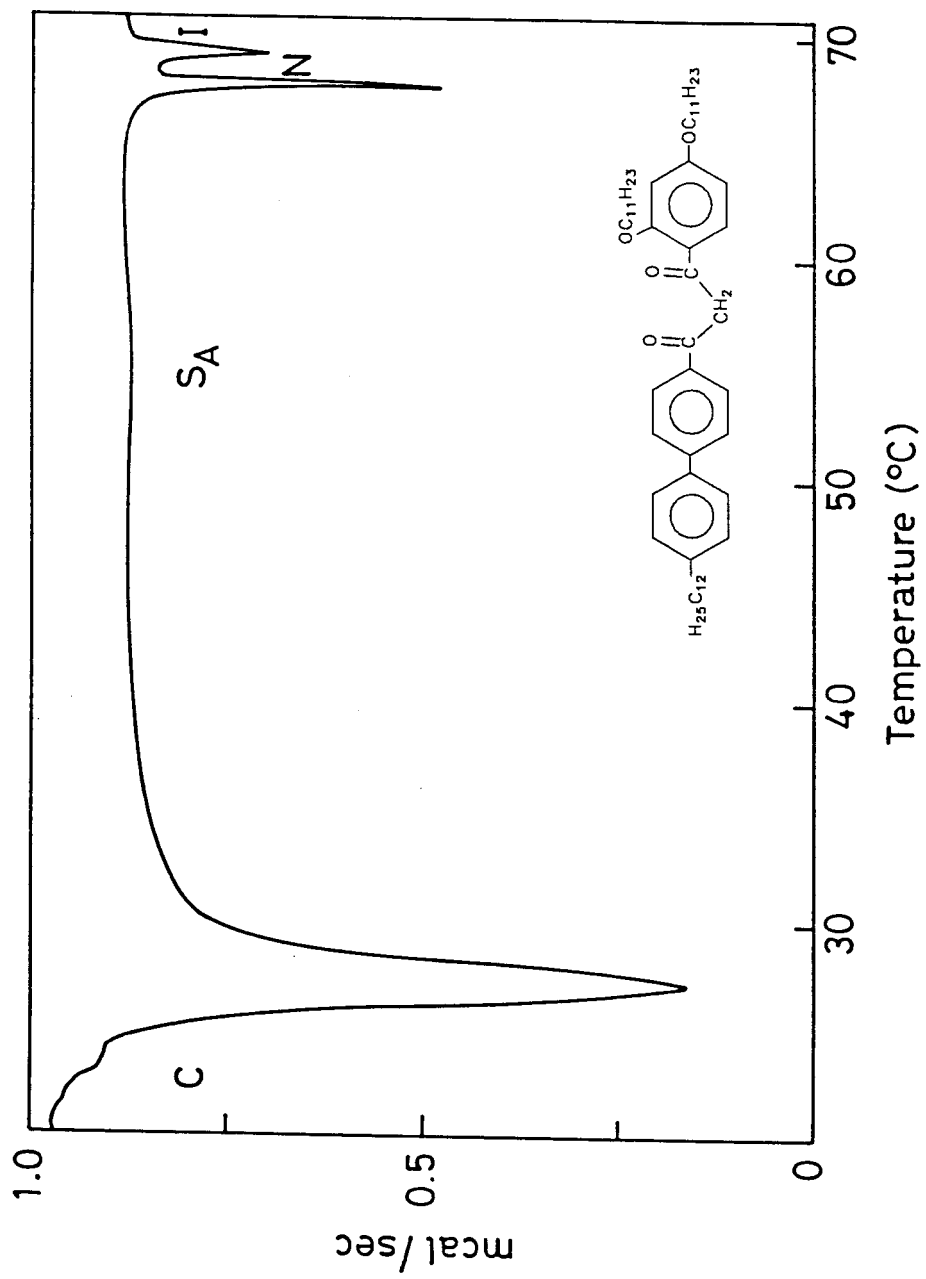
Table 6.1. Phase sequence, transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{J g}^{-1}$ ) of



Compound number	n	C	S <sub>A</sub>	N	I	
6.H.1	8	76.2 114.5	-	(.	59.4) 1.8	
6.H.2	9	62.2 108.2	-		62.4 1.0	
6.H.3	10	79.3 122.4	(.	60.4) 1.0	(.	66.6) 3.2
6.H.4	11	69.0 105.9	(.	67.4) 3.3	.	69.8 1.7
6.H.5	12	82.1 104.9	(.	74.0) 8.9	-	



**Figure 6.3.** A plot of transition temperatures as a function of n-alkoxy chain length for series 6.H.



The dsc thermogram of compound 6.H.4.

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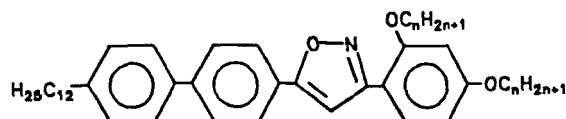
The higher homologues 6.H.3 to 6.H.5 show a monotropic smectic phase which exhibit a focal-conic texture and has been characterised as smectic A. It is interesting to know that there is strong odd-even effect in the melting points while both the  $N \rightarrow I$  and  $S_A \rightarrow N$  phase transition curves show a rising trend.

A comparison of the mesomorphic properties of the above disubstituted  $\beta$ -diketones with those of the corresponding monosubstituted derivatives clearly indicates that the *ortho* substituted chain destabilises the mesophases. Also, a nematic phase though metastable is obtained in the disubstituted derivatives in addition to lowering of the clearing temperatures.

The isoxazoles were prepared by treating the  $\beta$ -diketones (6.H) with hydroxylamine hydrochloride in ethanol. The transition temperatures and their enthalpies for 3-(4''-n-dodecylbiphenyl-4-yl)-5-(2',4'-di-n-alkoxyphenyl)isoxazoles (6.1) are given in table 6.2. As can be seen all the isoxazoles were found to be mesogenic. A plot of transition temperatures as a function of the n-alkyl chain length is shown in figure 6.4. One can clearly see an odd-even effect in the nematic - isotropic transition temperatures curve. As compared to the  $\beta$ -diketones, the isoxazole derivatives are all enantiotropic nematic. The compound 6.I.5 exhibits a monotropic smectic C phase and the transition from the nematic phase could be clearly seen under the microscope though the enthalpy could not be measured. The nematic-isotropic transition points show an odd-even effect for this series.

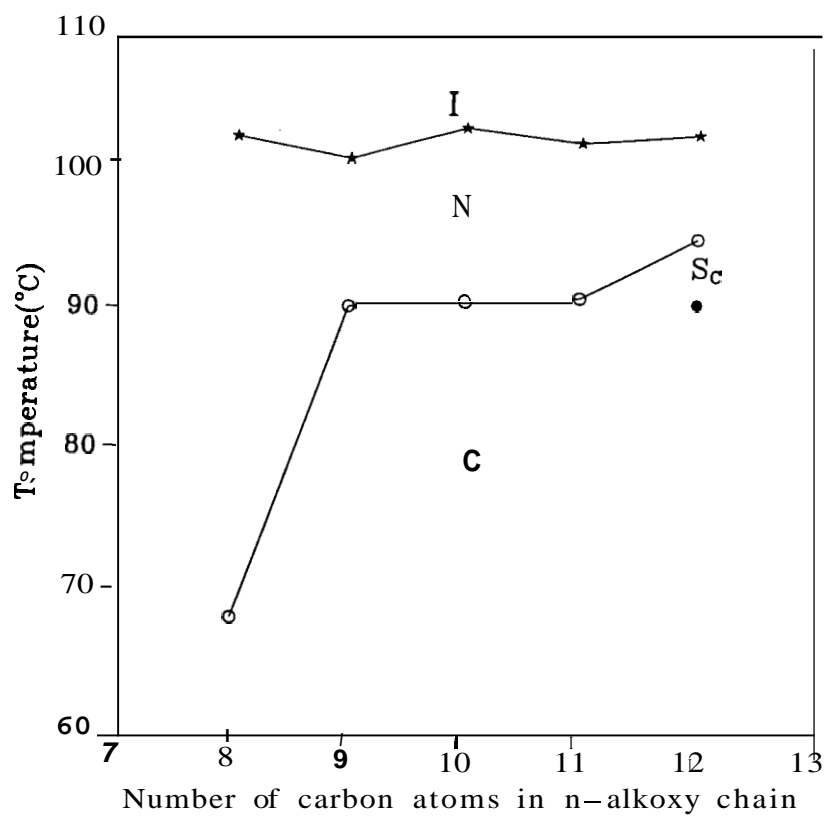
The presence of the lone pairs of electrons on the oxygen and the nitrogen atoms of the isoxazole ring enhance the polarisation of the molecules. Also, the heterocyclic ring formed enhances the molecular rigidity which perhaps is responsible for inducing stable mesophases.

Table 6.2. Phase sequence, transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{J g}^{-1}$ ) of



Compound number	n	C	$S_C$	N	I
6.I.1	8	·	68.0 76.4	-	102.5 1.0
6.I.2	9		90.5 82.3	-	101.1 1.4
6.I.3	10	·	91.1 66.8	-	103.5 1.5
6.I.4	11	·	91.5 61.4	-	98.0 1.1
6.I.5	12	·	96.0 59.9	(. 91.3) <sup>†</sup>	103.5 1.5

† : The enthalpy could not be measured



**Figure 6.4.** A plot of transition temperatures as a function of n-alkoxy chain length for series 6.1.



## Experimental

### Ethyl-2,4-dihydroxybenzoate, (6.1)

A mixture of 2,4-dihydroxybenzoic acid(50.0 g, 333 mmol), ethanol(100 ml) and concentrated sulphuric acid(6 ml) was refluxed for forty-eight hours. The excess ethanol was removed on a rotary evaporator and the residue was poured into ice-water. This was extracted with ethylacetate(2X125 ml). The combined ethylacetate solution was washed with cold 10% sodium bicarbonate solution(2X75 ml), water(2X100 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a product which was purified by crystallisation from benzene. Yield, 26.2 g, 43.7%; m.p. 70.5°C.

### Ethyl-2,4-di-n-decyloxybenzoate, (6.2)

A mixture of ethyl-2,4-dihydroxybenzoate (2.3 g, 12.8 mmol), n-decylbromide(9 g, 38.4 mmol) and anhydrous potassium carbonate (6.4g, 38.4 mmol) was stirred and refluxed in dry butan-2-one (60 ml) for twenty-four hours. The reaction mixture was cooled and poured carefully into a mixture of ice-cold water (200 ml) and hydrochloric acid (20 ml). This was extracted with diethyl ether (4X80 ml). The combined ethereal extracts was washed with water (4X80 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a product which was purified by distillation under reduced pressure. Yield . 5.9g, 95.1%; b.p. 228-232°C/0.4 mm;  $\nu$ ; 3000, 1710, 1610, 1580, 1280, 1050 $\text{cm}^{-1}$ .

Physical data of the cognate preparations of other ethyl-2, 4-di-n-alkoxybenzoates are given in table 6.3.

Table 6.3. Melting or boiling points of ethyl-2,4-di-n-alkoxybenzoates

Compound number	n	Observed b.p (°C/mm of Hg)	Observed m.p (°C)
1	8	225.0-227.0/2.2	-
2	9	135.0-138.0/11.4	-
3	11	-	58.0-58.5
4	12	-	60.0-61.0

#### 4-n-Dodecanoylbiphenyl, (6.3)

This was prepared following the procedure of Long and Henz.<sup>29</sup> Thus, to a vigorously stirred suspension of anhydrous aluminum chloride (61.6 g, 0.46 mol) in dry carbon disulphide(200 ml), contained in a one litre three-necked flask, a mixture of biphenyl(52.0 g, 0.38 mol) and n-dodecanoyl chloride(84.03 g, 0.38 mol) in dry carbon disulphide(250 ml) was added through a dropping funnel during one hour. After completion of the addition, stirring was continued for two hours and the mixture was then refluxed for a further four hours. Carbon disulphide was removed by distillation and the syrupy residue was added slowly to ice-water(500 ml) and hydrochloric acid(10 ml). The pale yellow precipitate so obtained was filtered on a buchner funnel, washed with water until the washings were acid free and air dried. This was crystallised from ethyl alcohol using activated charcoal to give colourless crystals of 4-n-dodecanoylbiphenyl, 113.0 g, 87.5%; m.p. 99.0-100.0°C (Reported <sup>30</sup> m.p. 100.0°C).

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### **4-n-Dodecylbiphenyl, (6.4)**

This was prepared by a Huang-Minlon modification<sup>31</sup> of the Wolff-Kishner reaction. Thus, a mixture of 4-n-dodecanoylbiphenyl (65.0 g, 0.19 mol), potassium hydroxide (32.5 g, 0.58 mol) and hydrazine hydrate (80%, 35.6 ml, 0.58 mol) in diethylene glycol (520 ml) was refluxed for two hours. Then the temperature was gradually raised to 200°C distilling off the volatile matter and the reaction mixture was refluxed for a further four hours. This was allowed to cool and poured into cold water. The organic material was extracted into chloroform (3X200 ml) and the combined chloroform extracts were washed with water (3X100 ml), dilute hydrochloric acid (3X50 ml) and water (3X100 ml), and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed and the crude product was recrystallised from petroleum ether to give colourless crystals. Yield, 55.0 g, 88.0%; m.p. 58.0-59.0°C, (Reported<sup>30</sup> m.p. 59.0°C).

### **4-n-Dodecyl-4'-acetylbiphenyl, (6.5)**

This was prepared following the procedure of Byron, Gray and Wilson.<sup>32</sup> Thus, to a one litre three-necked flask, fitted with a reflux condenser carrying a calcium chloride guard tube, a mechanical stirrer and a pressure equalising dropping funnel, was introduced anhydrous aluminum chloride (23.8 g, 0.17 mol), dry carbon disulphide (400 ml) and 4-n-dodecylbiphenyl (48.0 g, 0.14 mol). The reaction flask was cooled in an ice-bath. To this stirred mixture was added a solution of acetyl chloride (11.69 g, 0.14 mol) in dry carbon disulphide (50 ml) during thirty minutes. After the completion of addition it was stirred for thirty minutes and the ice-bath was removed and the stirring continued at room temperature for a further two hours. Finally, this was refluxed for three hours on a steam-bath and left overnight at room temperature. Carbon disulphide was distilled off and the

complex was decomposed by careful addition of ice-cold dilute hydrochloric acid. The pale yellow precipitate so obtained was filtered off, washed with water until the washings were acid free and dried. Crystallisation of this product from ethyl alcohol gave 4-n-dodecyl-4'-acetylbiphenyl. Yield, 40.0 g, 73.7%; m.p. 94.5°C; (Reported<sup>30</sup> m.p. 94.5°C).

**1-(4''-n-Dodecylbiphenyl-4-yl)-3-(2',4'-di-n-decyloxyphenyl)propane-1,3-dione,(6.H.3)**

This was prepared following a procedure of Sadashiva *et al.*<sup>19</sup> Thus, a mixture of 4-n-dodecyl-4'-acetylbiphenyl (3.64 g, 10 mmol) and ethyl 2,4-di-n-decyloxybenzoate (4.64 g, 10 mmol) was dissolved in dry 1,2-dimethoxyethane(80 ml) in a 250 ml two-necked flask, to which was attached a reflux condenser and a nitrogen inlet tube. This was stirred magnetically and sodium hydride (60% suspension in paraffin oil, 0.48 g, 0.02 mol) was added to it. The reaction mixture was refluxed for four hours and left at room temperature overnight. The reaction flask was cooled in ice and cold dilute hydrochloric acid (20 ml) was carefully added to it. A yellow stew was obtained and this was extracted into chloroform(3X40 ml). The combined chloroform solution was washed with water(3X40 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of solvent and chromatography of the residue gave a pale yellow material. This was crystallised from n-hexane several times until the transition temperatures were constant. Yield, 2.2 g, 45.0%. m.p. 73.9°C;  $\nu$ : 2950, 2850, 1605, 1590, 1460, 1370, 1300, 840 and 780 cm<sup>-1</sup>;  $\delta$ : 0.85(9H, t, J=9.0 Hz, 3XCH<sub>3</sub>), 1.1-2.0 (52H, m, 26XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2XArOCH<sub>2</sub>) 6.9(1H, s,C=CH), 7.2-8.25 (11H, m, ArH), 16.95(1H, s, enol-OH);

Elemental analysis: Found, C, 81.51; H, 10.5% C<sub>53</sub>H<sub>80</sub>O<sub>4</sub> requires  
C, 81.53; H, 10.25%.

Physical data of the cognate preparations of other 1-(4''-n-dodecylbiphenyl-4-yl)-3-(2',4'-di-n-alkoxyphenyl)propane-1,3-diones are given below.

**1-(4''-n-Dodecylbiphenyl-4-yl)-3-(2',4'-di-n-octyloxyphenyl)propane-1,3-dione, (6.H.1)**

M.p. 76.2°C;  $\nu_{\text{max}}$ : 2950, 2850, 1605, 1590, 1460, 1370, 1300, 840 and 780  $\text{cm}^{-1}$ ;  $\delta$ : 0.85 (9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0 (44H, m, 22XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.9(1H, s, C=CH), 7.2-8.25(11H, m, ArH), 16.95(1H, s, enol-OH);

Elemental analysis: Found, C, 81.25; H, 10.1%      C<sub>49</sub>H<sub>72</sub>O<sub>4</sub> requires  
C, 81.21; H, 9.94%.

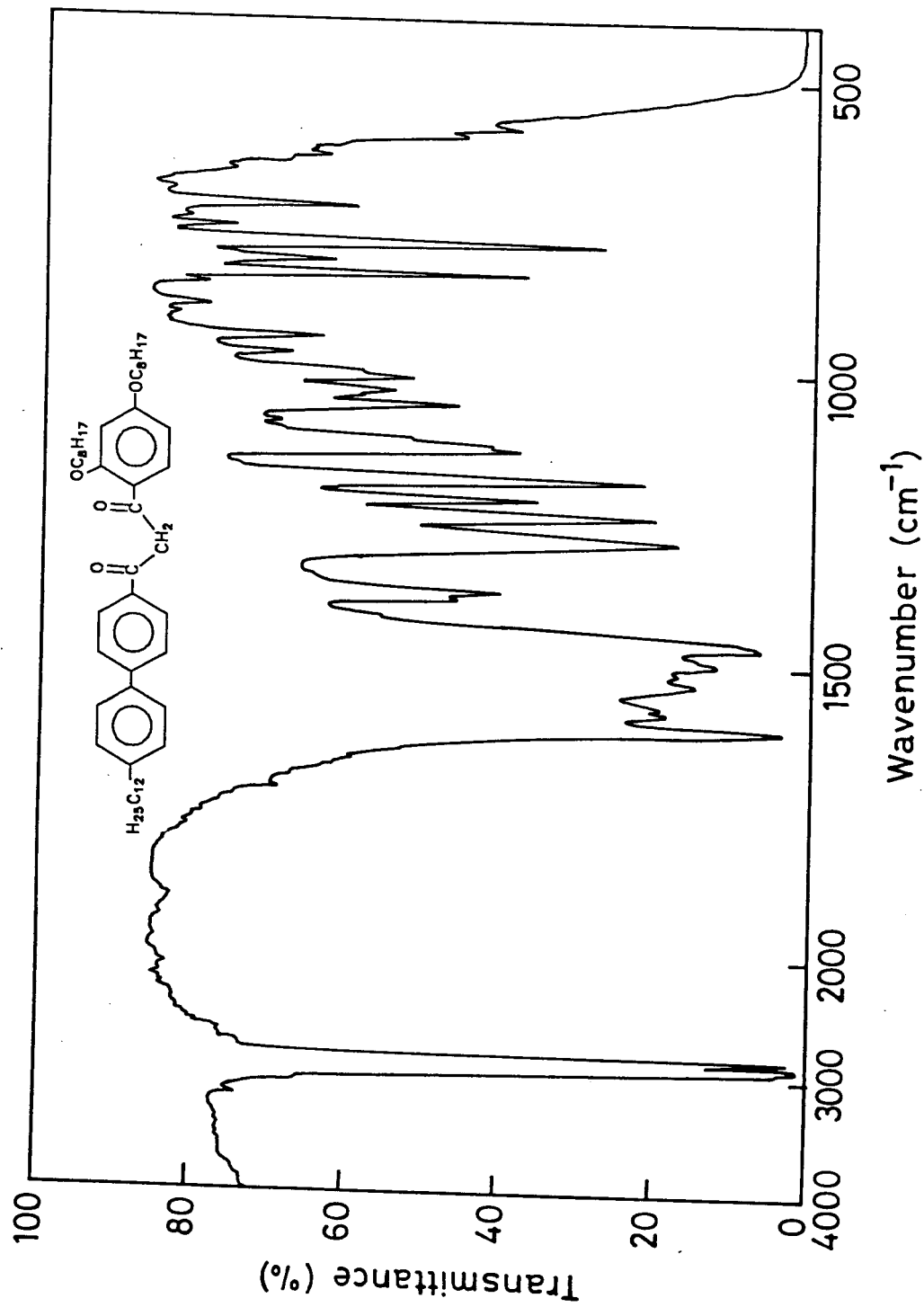
**1-(4''-n-Dodecylbiphenyl-4-yl)-3-(2',4'-di-n-nonyloxyphenyl)propane-1,3-dione, (6.H.2)**

M.p. 62.2°C;  $\nu_{\text{max}}$ : 2950, 2850, 1605, 1590, 1460, 1370, 1300, 840 and 780  $\text{cm}^{-1}$ ;  $\delta$ : 0.85 (9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0 (48H, m, 24XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.9(1H, s, C=CH), 7.2-8.25(11H, m, ArH), 16.95(1H, s, enol-OH);

Elemental analysis: Found, C, 81.74; H, 10.45%      C<sub>51</sub>H<sub>76</sub>O<sub>4</sub> requires  
C, 81.38; H, 10.10%.

**1-(4''-n-Dodecylbiphenyl-4-yl)-3-(2',4'-di-n-undecyloxyphenyl)propane-1,3-dione, (6.H.4)**

M.p. 69.0°C;  $\nu_{\text{max}}$ : 2950, 2850, 1605, 1590, 1460, 1370, 1300, 840 and 780  $\text{cm}^{-1}$ ;  $\delta$ : 0.85 (9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0 (56H, m, 28XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz,



IR spectrum for compound 6.H.1

ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.9(1H, s, C=CH), 7.2-8.25(11H, m, ArH), 16.95(1H, s, enol-OH);

Elemental analysis: Found, C, 81.59; H, 10.46% C<sub>55</sub>H<sub>84</sub>O<sub>4</sub> requires  
C, 81.68; H, 10.39%.

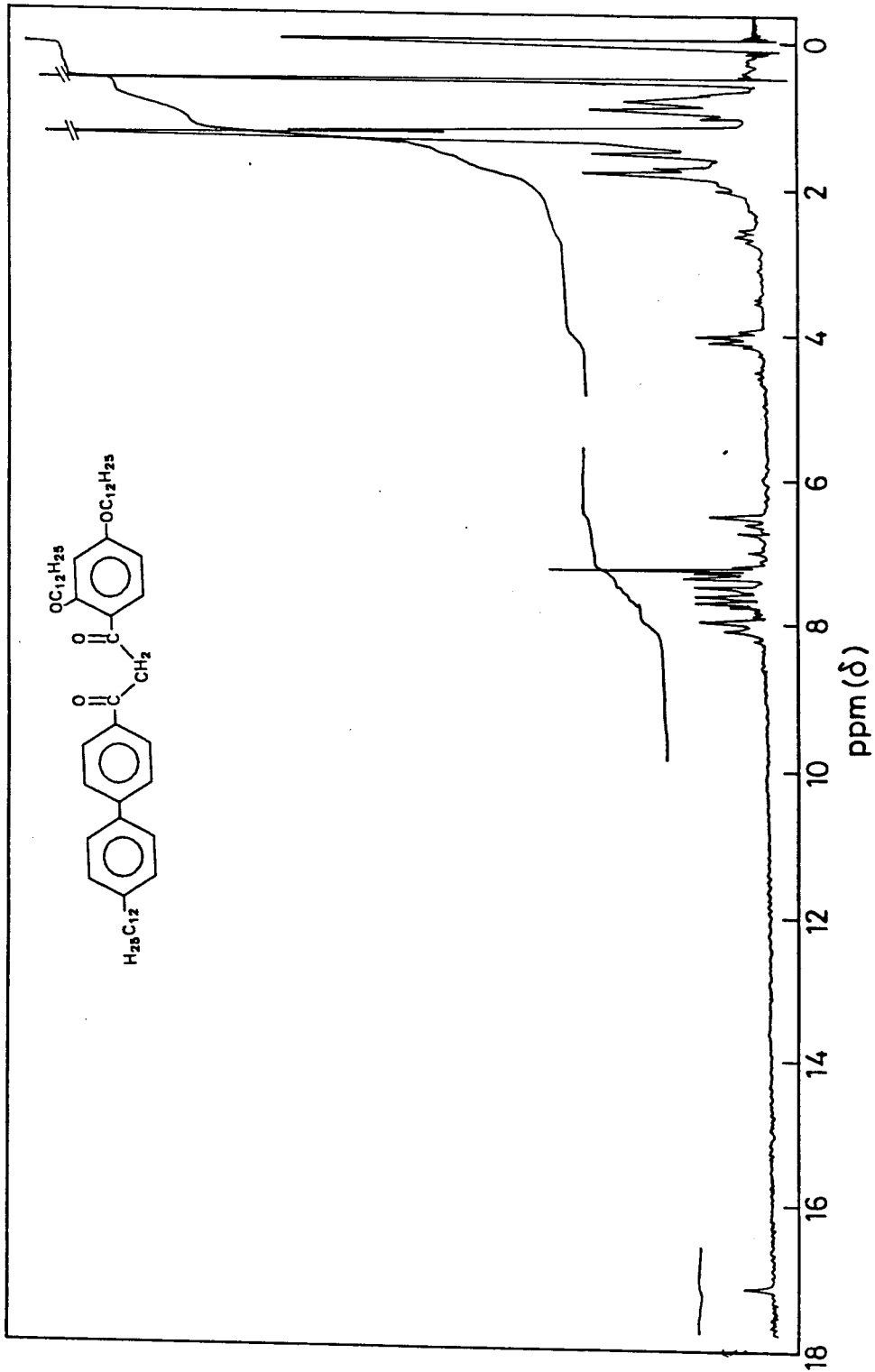
**1-(4''-n-Dodecylbiphenyl-4-yl)-3-(2',4'-di-n-dodecyloxyphenyl)propane-1,3-dione, (6.H.5)**

M.p. 82.1°C;  $\nu_{\max}$ : 2950, 2850, 1605, 1590, 1460, 1370, 1300, 840 and 780 cm<sup>-1</sup>;  $\delta$ : 0.85 (9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0 (60H, m, 30XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.9(1H, s, C=CH), 7.2-8.25(11H, m, ArH), 16.95(1H, s, enol-OH);

Elemental analysis: Found, C, 81.68; H, 10.87% C<sub>57</sub>H<sub>88</sub>O<sub>4</sub> requires  
C, 81.81; H, 10.52%.

**3-(4''-n-Dodecylbiphenyl-4-yl)-5-(2',4'-di-n-decyloxyphenyl)isoxazole, (6.I.3)**

This was prepared following a procedure of Lang *et al.*<sup>25</sup> Thus, a mixture of 1-(4''-n-dodecylbiphenyl-4-yl)-3-(2',4'-di-n-decyloxyphenyl)propane-1, 3-dione (20 mg, 0.027 mmol) and hydroxylamine hydrochloride (3.8 mg, 0.055 mmol) in ethanol (15 ml) was refluxed for ten hours with stirring. The mixture was then cooled to room temperature. The solid obtained was filtered and crystallised from ethanol; yield 13 mg (66.2%), m.p. 91.1°C,  $\nu_{\max}$ : 3120, 2950, 2850, 1620, 1570, 1460, 1370, 1300, 840 and 780 cm<sup>-1</sup>;  $\delta$ : 0.85 (9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0 (52H, m, 26XCH<sub>2</sub>), 2.65 (2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1 (4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.6 (1H, s, C=CH), 7.2-8.25 (11H, s, ArH);



<sup>1</sup>H NMR spectrum for compound 6.H.5



## Chapter 6

Elemental analysis: Found, C, 81.78; H, 10.24; N, 1.89%  $C_{53}H_{79}NO_3$  requires  
C, 81.71; H, 10.01; N, 1.86%.

Physical data of the cognate preparations of other 3-(4''-n-dodecylbiphenyl-4-yl)-5-(2':4'-di-n-alkoxyphenyl)isoxazoles are given below.

### **3-(4''-n-Dodecylbiphenyl-4-yl)-5-(2',4'-di-n-octyloxyphenyl)isoxazole, (6.I.1)**

M.p. 68.0°C;  $\nu_{\max}$ : 3120, 2950, 2850, 1620, 1570, 1460, 1370, 1300, 840 and 780  $cm^{-1}$ ;  $\delta$ : 0.85(9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0(44H, m, 22XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.6(1H, s, -C=CH-), 7.2-8.25(11H, m, ArH);

Elemental analysis: Found, C, 81.46; H, 9.86; N, 1.81%  $C_{49}H_{71}NO_3$  requires  
C, 81.55; H, 9.84; N, 1.94%.

### **3-(4''-n-Dodecylbiphenyl-4-yl)-5-(2',4'-di-n-nonyloxyphenyl)isoxazole, (6.I.2)**

M.p. 90.5°C;  $\nu_{\max}$ : 3120, 2950, 2850, 1620, 1570, 1460, 1370, 1300, 840 and 780  $cm^{-1}$ ;  $\delta$ : 0.85(9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0(48H, m, 24XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.6(1H, s, -C=CH-), 7.2-8.25(11H, m, ArH);

Elemental analysis: Found, C, 81.52; H, 10.11; N, 1.86%  $C_{51}H_{75}NO_3$  requires  
C, 81.63; H, 9.93; N, 1.90%.

**3-(4''-n-Dodecylbiphenyl-4-yl)-5-(2',4'-di-n-undecyloxyphenyl)isoxazole,**

**(6.I.4)**

M.p. 92.2°C;  $\nu_{\max}$ : 3120, 2950, 2850, 1620, 1570, 1460, 1370, 1300, 840 and 780  $\text{cm}^{-1}$ ;  $\delta$ : 0.85(9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0(56H, m, 28XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.6(1H, s, -C=CH-), 7.2-8.25(11H, m, ArH);

Elemental analysis: Found, C, 81.68; H, 9.96; N, 1.81%      C<sub>55</sub>H<sub>53</sub>NO<sub>3</sub> requires  
C, 81.78; H, 10.09; N, 1.83%.

**3-(4''-n-Dodecylbiphenyl-4-yl)-5-(2',4'-di-n-dodecyloxyphenyl)isoxazole,**

**(6.I.5)**

M.p. 96.0°C;  $\nu_{\max}$ : 3120, 2950, 2850, 1620, 1570, 1460, 1370, 1300, 840 and 780  $\text{cm}^{-1}$ ;  $\delta$ : 0.85(9H, t, J=9.0 Hz, 3X CH<sub>3</sub>), 1.1-2.0(60H, m, 30XCH<sub>2</sub>), 2.65(2H, t, J=8.0 Hz, ArCH<sub>2</sub>), 4.1(4H, t, J=6.4 Hz, 2X ArOCH<sub>2</sub>), 6.6(1H, s, -C=CH-), 7.2-8.25(11H, m, ArH);

Elemental analysis: Found, C, 81.76; H, 10.21; N, 1.76%      C<sub>57</sub>H<sub>57</sub>NO<sub>3</sub> requires  
C, 81.85; H, 10.16; N, 1.80%.

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