

## CHAPTER III

### **SYNTHESIS AND MESOMORPHIC PROPERTIES OF A HOMOLOGOUS SERIES OF 4-CYANOPHENYL-3'-METHYL-4'-(4''-n-ALKYL- BENZOYLOXY) BENZOATES**

#### **3.1 Survey of the mesomorphic properties exhibited by diesters containing three phenyl rings**

It is well known that most of the organic compounds exhibiting liquid crystalline properties contain at least two phenyl rings with substituents in the *para* positions. The thermal stability and the mesophase range in these compounds may be enhanced by the addition of a phenyl group in one of the *para* positions. Dewar and Schroeder<sup>1</sup> prepared a number of *p*-phenylene and *p,p'*-biphenylene esters and studied the effects of structural changes on phase transitions. They found very broad mesomorphic ranges and high mesophase-liquid transition temperatures in these compounds. Later, Dewar and Goldberg<sup>2</sup> concluded that the *p*-phenylene units perform a dual function, providing a rigid linearity and contributing to the polarisability of the molecule. This observation was based on comparison with compounds in which phenyl rings were replaced by cyclohexane or bicyclo (2.2.2)octane. Dewar and Goldberg<sup>3</sup> further studied the effect of central and terminal groups on nematic mesophase stability in a number of *p*-phenylene esters of hydroquinone and *para* substituted phenyl esters of terephthalic acid.

Around the same time Arora et al.<sup>4</sup> synthesised a number of 1,4-phenylene bis(4'-alkoxybenzoates) to study the effect of central carboxyl groups on the formation of smectic phases and the thermal stability of the mesophases. They also prepared a parallel series with methyl substituent at the 2-position of the 1,4-phenylene ring to investigate the effect of a lateral substituent on the mesomorphic properties of this system. It was found that many derivatives of this series had lower melting points and nematic-isotropic transition temperatures,  $T_{N-I}$ , than the corresponding unsubstituted parent compounds. All these compounds are symmetrical in the sense that they have identical wing groups. Haut et al.<sup>5</sup> explored the possibility of obtaining compounds with lower melting points by introducing dissymmetry into such a molecule. They prepared several unsymmetrical *p*-phenylene di-*p'*-*n*-alkoxybenzoates and found that, although the melting points were somewhat lowered the  $T_{N-I}$  remained relatively high.

Young and co-workers<sup>6</sup> in an effort to obtain stable, low melting nematic liquids with large mesophase ranges synthesised a series of esters derived from phenyl 4-benzoyloxybenzoates. They also prepared a few compounds with laterally placed methyl groups in this system to understand the role of lateral substituents upon mesomorphic properties. Van Meter and Klanderemann<sup>7</sup> also reported a large number of phenyl

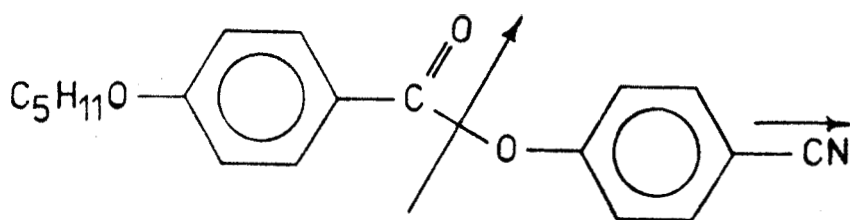
4-benzoyloxybenzoates. They chose this system because of increased dissymmetry associated with them so that there is less efficient packing in the crystal lattice which would lower the melting temperatures. From these studies it was found that (i) the melting point does not show any clear cut increasing or decreasing trend as the molecular structure is regularly varied, (ii) the  $T_{N-I}$  decreases systematically as the number of aromatic methyl group appendages increase, and (iii) since this system contains three p-phenylene groups, it can accommodate a lateral substituent without affecting the mesomorphic range drastically; the lateral substituent would also contribute to the dissymmetry of the molecule. In all the cases discussed above the terminal substituents are either alkyl or alkoxy chains. Van Meter and Klandermann<sup>7</sup> have also reported a few phenyl 4-benzoyloxybenzoates with F, Cl, Br and CN groups as terminal substituents.

In the present study we proposed to synthesise a homologous series of compounds with positive dielectric anisotropy, wide thermal ranges and preferably with low-melting points. The following factors were taken into consideration in choosing the system to be investigated. It is known that the introduction of a terminal cyano group into a molecule results in a material of high positive dielectric anisotropy, as a Ph-CN group has a moment of 4.05 D.<sup>8</sup> However, in esters which are already polar by

virtue of the -CO.O- p u p , the position of the cyano group relative to the ester linkage is also important. Klingbiel et al<sup>9</sup> have shown this for phenyl benzoate esters of structures I and II (figure 3.1). These results have been explained in terms of the dipole moments of the cyano group and the ester linkage either opposing (I) or reinforcing (II) each other. The liquid crystal transition temperatures are also affected by the relative positions of the cyano and ester groups. Coates and Gray,<sup>10</sup> based on some results have shown that the presence of the cyano group in the phenolic moiety will lead to much higher positive dielectric anisotropies, but giving slightly lower N-I transition temperatures. In a substituted benzoyloxybenzoate system, there is dissymmetry, as this can be considered to have been derived from p-hydroxybenzoic acid. This would contribute to the lowering of melting points, as compared to the more symmetrical diesters<sup>3</sup> derived from hydroquinone or terephthalic acid. Lastly, a lateral substituent either on a phenyl ring or in the  $\alpha$ -position of a central linkage generally reduces the melting as well as the clearing temperatures, the latter effect however being more marked.

### 3.2 Synthesis of 4-cyanophenyl-3'-methyl-4'-(4''-n-alkylbenzoyloxy)benzoates

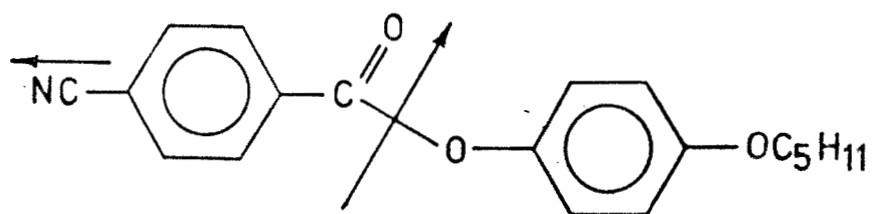
The 4-cyanophenyl-3'-methyl-4'-(4''-n-alkylbenzoyloxy) benzoates were prepared in six convenient steps by a procedure



$$\epsilon_{\parallel} = 27.8 ; \quad \epsilon_{\perp} = 11.66$$

$$\Delta\epsilon = 16.13$$

I



$$\epsilon_{\parallel} = 10.60 ; \quad \epsilon_{\perp} = 6.04$$

$$\Delta\epsilon = 4.56$$

II

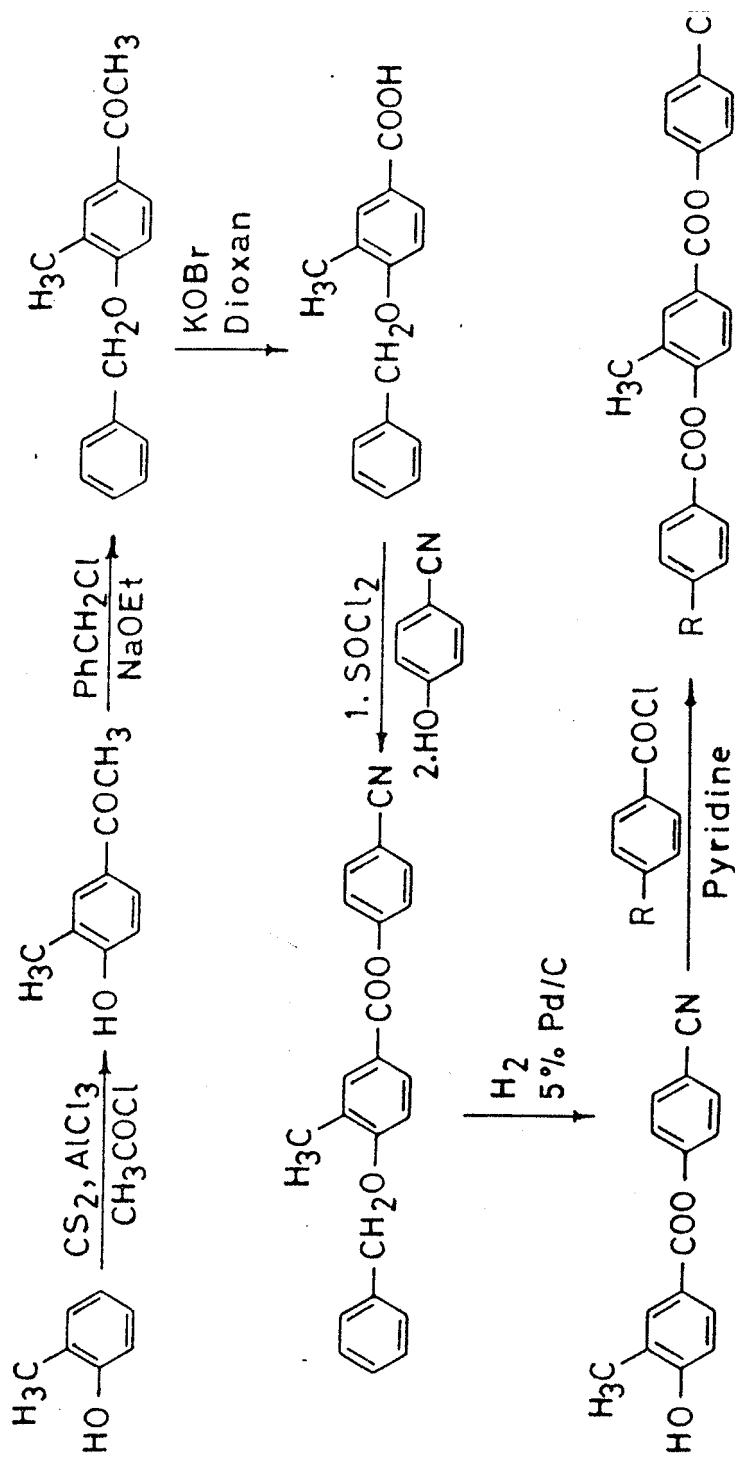
Figure 3.1

Structures of phenyl benzoate esters showing the dipole moments of the cyano group and the ester linkage either reinforcing (I) or opposing (II) each other.

similar to the one described by Young and Green<sup>11</sup> (Chart III). Van Meter and Klander<sup>7</sup> used another method involving only two steps to prepare substituted phenyl 4-benzoyloxybenzoates and in their procedure (chart IV) one of the steps involves esterification of a 4-alkyl- or 4-alkoxyphenol with 4-hydroxybenzoic acid or one of its substituted derivatives to afford a substituted 4-hydroxybenzoate. A combination of sulphuric acid and boric acid was used as a catalyst for this esterification,<sup>12</sup> as this was found to be specific for the esterification of the hydroxyl group of the 4-alkylphenol *only*. We could not use this method since the reaction of 4-hydroxybenzotrile with either 4-hydroxybenzoic acid or 3-methyl-4-hydroxybenzoic acid failed to proceed, presumably due to the presence of a deactivating para cyano group in 4-hydroxybenzotrile. However, it must be emphasized that the six step method gives excellent yields.

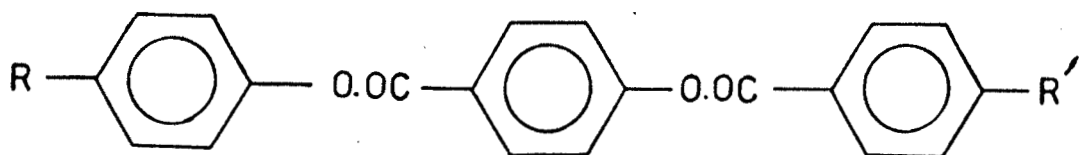
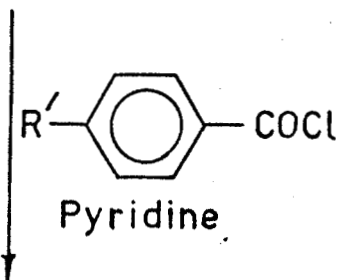
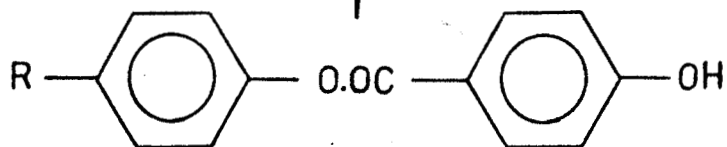
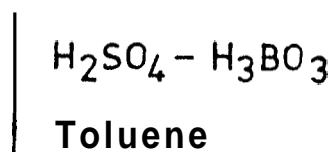
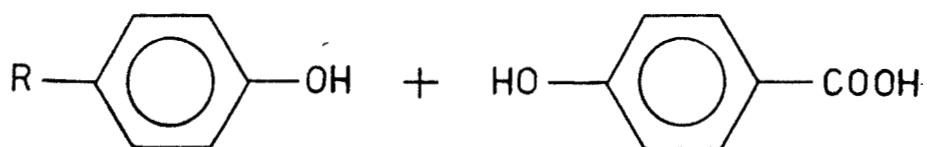
The esters prepared in this study are colourless compounds and are highly transparent in the ultraviolet region in comparison with Schiff's bases, azobenzenes, azoxybenzenes, nitrones and stilbenes.<sup>13,14,15</sup> For example ester 4, exhibited  $\lambda_{\max}$  251 nm ( $\epsilon$  4.74) and ester 5 exhibited  $\lambda_{\max}$  250 nm ( $\epsilon$  4.73). All these compounds showed intense vibrational absorption in the infrared region at 2225-2235  $\text{cm}^{-1}$  (C≡N stretching) 1738-1740  $\text{cm}^{-1}$  (carbonyl stretching) and 1603  $\text{cm}^{-1}$  (phenyl ring vibrations). In

CHART III



R = Methyl to n-Dodecyl

CHART IV



$R, R' = n$ -Alkyl or  $n$ -Alkoxy



the nmr spectra taken in deuteriochloroform, sharp singlets for the absorption of the methyl group of the central aromatic ring appeared at 2.3 ppm down field from TMS, while the methyl group on the terminal chains appeared as triplet around 0.9 ppm.

### 3.3 Mesomorphic properties of 4-cyanophenyl-3'-methyl-4''-(4''-n-alkylbenzyloxy)benzoate

The transition temperatures for this homologous series of compounds are summarised in table 3.1. As can be seen these have fairly wide mesophase thermal ranges. There is a gradual reduction of the range of the mesophase as the series is ascended. Compound 2 has the widest nematic range, viz.  $105.5^\circ$  and compound 4 the lowest melting point, viz.  $93^\circ\text{C}$ . All these compounds have large positive dielectric anisotropy, evidently because of the Ph-CN group. The dielectric constants of compound 6 at  $120^\circ\text{C}$  were experimentally found to be  $\epsilon_{\parallel} = 19.28$ ,  $\epsilon_{\perp} = 5.12$ ,  $\Delta\epsilon \approx +14$ .

Figure 3.2 shows a plot of the transition temperatures versus the number of carbon atoms in the alkyl chain. The nematic-isotropic transition temperature decreases on ascending the homologous series, the points lying on two smooth falling curves) the curve for the odd homologues lying above that for the even homologues. It is interesting to see that there is an alternation in the melting points from compound 2 to compound 7, a behaviour that has been

Table 3.1

Melting and clearing temperatures of 4-cyanophenyl-  
3'-methyl-4''-(4''-n-alkylbenzoxy)benzoate

Compound number	R = n-Alkyl	Temperature of transition to				$\Delta T$ , °C nematic range
		Re-entrant nematic °C	Smaectic °C	Nematic °C	Isotropic °C	
1	CH <sub>3</sub>	-	-	157	219.5	58.5
2	C <sub>2</sub> H <sub>5</sub>	-	-	99	204.5	105.5
3	C <sub>3</sub> H <sub>7</sub>	-	-	105.5	204	98.5
4	C <sub>4</sub> H <sub>9</sub>	-	-	92	192.5	100.5
5	C <sub>5</sub> H <sub>11</sub>	-	-	108.5	188	79.5
6	C <sub>6</sub> H <sub>13</sub>	-	-	101.5	175.5	74
7	C <sub>7</sub> H <sub>15</sub>	-	-	103.5	172	68.5
8	C <sub>8</sub> H <sub>17</sub>	-	-	106	162	56
9	C <sub>9</sub> H <sub>19</sub>	-	-	104	159	55
10	C <sub>10</sub> H <sub>21</sub>	-	-	100.5	153	52.5
11	C <sub>11</sub> H <sub>23</sub>	(78.5)	103	127	152.5	25
12	C <sub>12</sub> H <sub>25</sub>	(59.8)	102	138.5	148	9.5

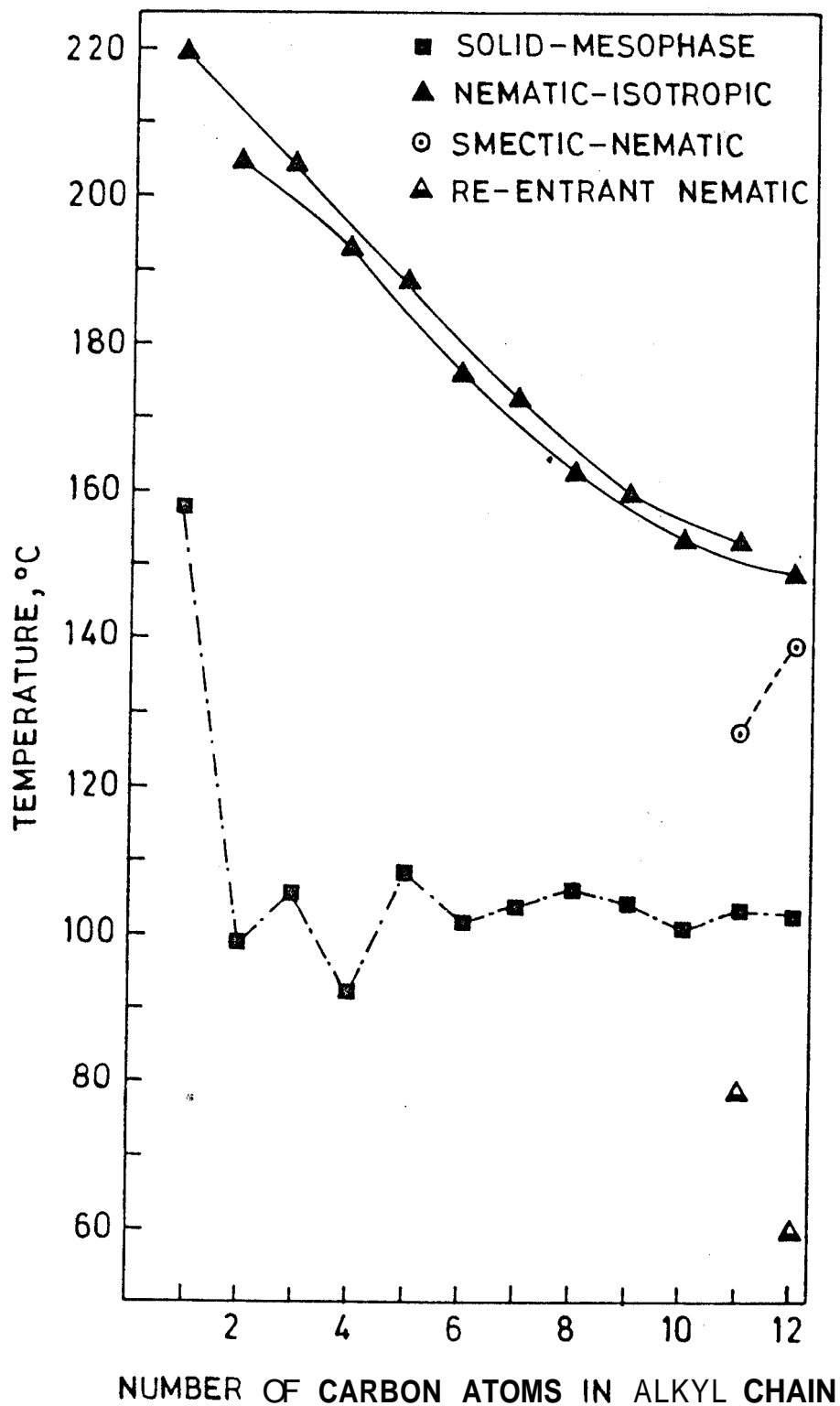
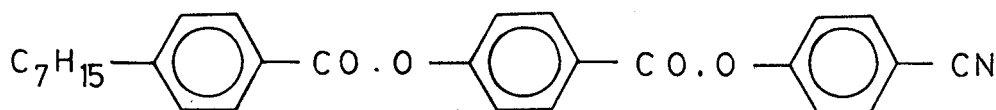


Fig. 3.2

Plot of transition temperatures against number of carbon atom in the alkyl chain for 4-cyanophenyl 3'-methyl-4'-(4"-n-alkylbenzoyloxy)benzoates.

attributed to a possible similarity in the crystal structures of these homologues. The smectic phase appears from compound 11 onwards as an enantiotropic phase. This phase exhibits a simple fan-shaped texture and is believed to be smectic A, in analogy with what is observed in many other compounds of high positive dielectric anisotropy.<sup>10,16,17</sup> Compounds 11 and 12 also show a 'Re-entrant' nematic phase which is discussed in the next section. The curve for the smectic-nematic transition in figure 3.2 shows the usual initial upward trend.

Van Meter et al<sup>18</sup> have prepared the unsubstituted parent homologue, 4-cyanophenyl-4'-(4"-n-heptylbenzoyloxy) benzoate. Comparing the transition temperatures of this compound with the corresponding methyl substituted homologue



K94S111N225I

(compound 7, table 3.1), it is seen that the lateral methyl group has lowered the nematic-isotropic transition temperature, eliminated the smectic phase and also increased the melting point. It has been generally observed<sup>19</sup> that a lateral substituent which increases the breadth of  $\delta$  molecule will affect the thermal stability of the smectic mesophase more than that of the nematic mesophase.

### 3.4 Re-entrant nematic phase in pure 4-cyanophenyl-3'-methyl-4'-(4"-n-alkylbenzoyloxy)benzoate

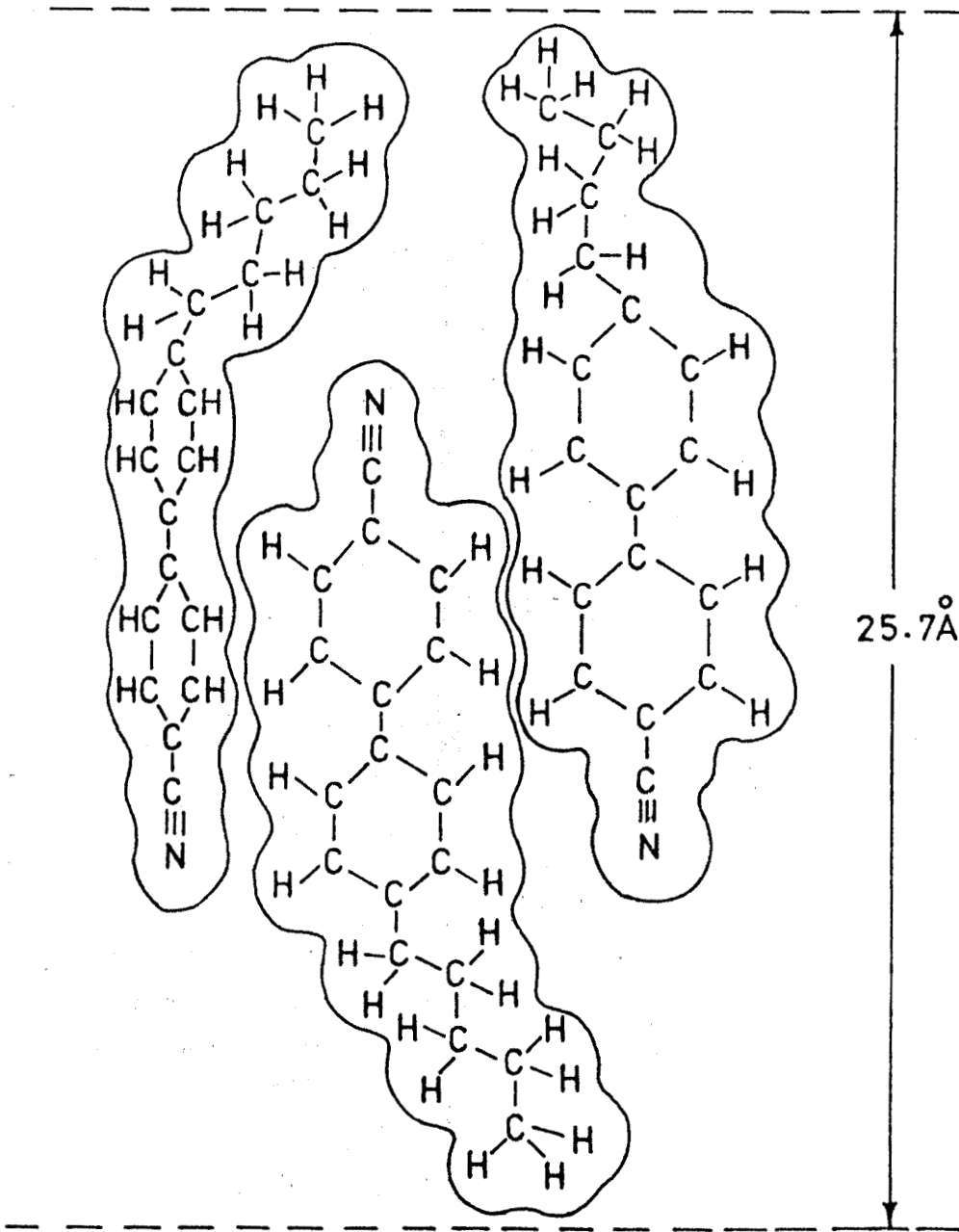
A few years ago, Cladis<sup>20</sup> found that binary mixtures of certain mesogenic compounds containing a terminal cyano group exhibit the following interesting sequence of phase transitions on cooling;

Isotropic liquid  $\longrightarrow$  Nematic  $\longrightarrow$  Smectic A  $\longrightarrow$  Nematic

The second nematic phase which occurs at a lower temperature than the smectic A phase is called the 're-entrant' nematic phase. More recently Cladis et al<sup>21</sup> also observed the re-entrant nematic phase in pure compounds having a terminal cyano group at certain elevated pressures.

All these compounds have a highly polar cyano group attached to one end of the molecule which results in strong antiparallel correlations between neighbouring molecules.<sup>22</sup>

This, in turn leads to a bilayer structure with interdigitated molecules in each bilayer,<sup>23</sup> as shown in figure 3.3 for 4-n-alkyl-4'-cyanobiphenyls.<sup>24</sup> Generally one expects that the distance between layers of smectic A liquid crystals corresponds to the molecular length. However, the layer spacing in compounds possessing a very polar terminal group, such as a cyano group, is about one and half times the molecular length. Gray and Lydon,<sup>25</sup> based on some X-ray studies, attributed this discrepancy to some kind of inter-



**Figure 3.3**

Schematic representation of antiparallel local order in 5CB. The repeat distance along the nematic axis is about 1.4 times the molecular length. (After Leadbetter, Richardson and Colling.<sup>24</sup>)

digitation of the molecules and called it a bilayer smectic A. As the temperature and pressure are varied, the molecular packing is altered slightly and the resulting subtle changes in the bilayer structure appear to be responsible for the occurrence of the re-entrant nematic phase. This phase had only been observed either in mixtures<sup>20,26</sup> or at high pressures in single component systems.<sup>21</sup>

As mentioned in chapter II, we observed the re-entrant nematic phase in *p*-cyanophenyl-*p*'-*n*-decyloxy- $\alpha$ -methylcinnamate at atmospheric pressure. This phase was also observed in two of the pure cyanophenyl 4-benzoyloxybenzoates at atmospheric pressure. These are (i) 4-cyanophenyl-3'-methyl-4'-(4''-*n*-undecylbenzoyloxy)benzoate, and (ii) 4-cyanophenyl-3'-methyl-4'-(4''-*n*-dodecylbenzoyloxy)benzoate. This together with the case mentioned in chapter II represent the first observations of re-entrant nematic behaviour in pure compounds at atmospheric pressure. [Simultaneously Hardouin *et al*<sup>27</sup> also observed enantiotropic re-entrant nematic and smectic phases in pure compounds at atmospheric pressure.] The transition temperatures of the two compounds (i) and (ii) are given in table 3.2. As can be seen in this table, the re-entrant nematic phase is formed readily and the crystallisation occurs well below the smectic A-re-entrant nematic transition point, even when the sample is cooled relatively

Table 3.2

Transition temperatures of compounds exhibiting a re-entrant nematic phase at atmospheric pressure

Compound	Heating	Cooling	Enthalpy
(I)	K → S <sub>A</sub> 103°C	I → N	152.5°C
	S <sub>A</sub> → N 127°C	N → S <sub>A</sub>	127°C
	N → I 152°C	S <sub>A</sub> → Re-entrant N	78.5°C
		Re-entrant N → K	65°C
(II)	K → S <sub>A</sub> 102°C	I → N	148°C
	S <sub>A</sub> → N 138.5°C	N → S <sub>A</sub>	138.5°C
	N → I 148°C	S <sub>A</sub> → Re-entrant N	59.8°C
		Re-entrant N → K	56°C



slowly. These transition points were determined on a Mettler hot stage (Model FP52) as well as from thermograms taken on a differential scanning calorimeter. The enthalpies were also calculated from the latter. It is interesting to note that heat is liberated at both the nematic  $\rightarrow$  smectic A and smectic A  $\rightarrow$  re-entrant nematic phase transitions and these are fairly stronger in compound (ii).

## EXPERIMENTAL

### 4-Hydroxybenzonitrile

This was prepared following the procedure of Friedman and Shecter.<sup>28</sup> A mixture of 4-bromophenol (17.3 g, 0.1mol), anhydrous cuprous cyanide (13.43 g, 0.15 mol) and anhydrous dimethyl formamide (100 ml) was refluxed for 8 hours and cooled. The reaction mixture was poured onto a stirred mixture of hydrated ferric chloride (7.5 g), concentrated hydrochloric acid (2.5 ml) and water (100 ml). This was heated to 60°C and maintained at that temperature for about 30 minutes. The cooled reaction mixture was extracted with ether (4x75 ml) and the combined ether extract was washed with water (2 x 100 ml) and dried ( $\text{Na}_2\text{CO}_3$ ). Removal of solvent afforded a white material which was recrystallised from benzene (11.0 g, 92.5%), m.p. 113°C (reported<sup>29</sup> m.p. 113°C).

### 3-Methyl-4-hydroxyacetophenone

Into a one litre three-necked flask fitted with a mercury-sealed stirrer, a reflux condenser and a pressure equalising separatory funnel was introduced dry carbon disulphide (300 ml), anhydrous aluminium trichloride (146.85 g, 1.1 mol) and o-cresol (54.0 g, 0.5 mol). The mixture was stirred and freshly distilled acetyl chloride (39.25 g, 0.5 mol) was added drop by drop during 45 minutes. The

reaction mixture was refluxed for 4 hours and left at room temperature overnight. Carbon disulphide was removed by distillation and the dark brown complex was decomposed with crushed ice and concentrated hydrochloric acid (100 ml). The mixture was extracted with ether (3x150 ml) and the ethereal solution was washed with water (2x100 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent gave a pale brown material which was distilled under reduced pressure. The colourless product was recrystallised from benzene (65.25 g, 87%), b.p. 175-180°C/1 mm, m.p. 110-112°C (reported<sup>30</sup> m.p. 104°C).

### 3-Methyl-4-benzoyloxyacetophenone

A solution of sodium ethoxide was prepared in a one litre three-necked flask, fitted with a reflux condenser and a pressure equalising separatory funnel, by dissolving sodium (6.9 g, 0.3 mol) in absolute ethyl alcohol (100 ml). To this solution was added 3-methyl-4-hydroxyacetophenone (45.0 g, 0.3 mol) in absolute ethyl alcohol (250 ml) through the separatory funnel. The mixture was stirred magnetically and refluxed for 30 minutes and to this was added freshly distilled benzyl chloride (39.21 g, 0.31 mol) drop, by drop during 45 minutes. The mixture was refluxed for a further 8 hours and alcohol (200 ml) was removed by distillation. Water (500 ml) and hydrochloric acid (100 ml) were added to the cooled reaction mixture and extracted with ether (3x300ml).

The combined ethereal extract was washed with 10% sodium hydroxide solution (2 x 100 ml) and water (2 x 150 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a pale yellow material which was crystallised from petroleum ether (b.p. 60-80°C) to yield 64.8 g (90%) of product.

3-Methyl-4-benzoyloxybenzoic acid

A solution of potassium hypobromite prepared at 0°C, by dissolving bromine (128 g, 0.8 mol) in a solution of potassium hydroxide (89.6 g, 1.6 mol) in water (800 ml) was added to a stirred solution of 3-methyl-4-benzoyloxyacetophenone (48 g, 0.2 mol) in dioxan (400 ml). The addition was carried out at 30-35°C during 30 minutes. Stirring was continued and the temperature was raised to 50°C and held there for one hour to ensure completion of the reaction. Enough aqueous sodium metabisulphite was added to destroy the excess of hypobromite. Water (1000 ml) was added and about 400 ml of the liquid was distilled. The residual clear solution was cooled and acidified with concentrated hydrochloric acid. The snow white product was filtered off, washed thoroughly with water and air dried. This was recrystallised from ethyl alcohol (42.4 g, 87.6%), m.p. 183-184°C.

4-Cyanophenyl-3'-methyl-4'-benzoyloxybenzoate

A mixture of 3-methyl-4-benzoyloxybenzoic acid (24.2 g,

0.1 mol) and freshly distilled thionyl chloride (100 ml, excess) was refluxed for 6 hours and the excess thionyl chloride was removed by distillation under reduced pressure. 4-Hydroxybenzonnitrile (11.9 g, 0.1 mol) in anhydrous pyridine (150 ml) was added to the crude acid chloride and the mixture stirred magnetically at room temperature for 20 hours and at 100°C for 2 hours and cooled. The reaction mixture was poured onto a stirred mixture of crushed ice and concentrated hydrochloric acid (200 ml) when a precipitate was obtained. It was filtered, washed with water, 10% aqueous sodium hydroxide solution, water and dried. The pale brown material was chromatographed on silica gel and eluted with benzene-petroleum ether mixture. Removal of solvent from the eluate afforded a white product which was recrystallised from absolute ethyl alcohol (29.5 g, 86%) m.p. 122-123°C;  $\nu_{\text{max}}$  2235, 1740, 1603, 1388, 1268, 1130, 1055 and 743  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 2.7 (s, 3H,  $\text{arCH}_3$ ) 5.2 (s, 2H,  $\text{arOH}_2$ ) 6.8-8.1 (m, 12H,  $\text{arH}$ ) [Found: C, 76.86; H, 4.83; N, 4.1%  $\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}$  requires C, 76.96; H, 4.95; N, 4.08%].

4-Cyanophenyl-3'-methyl-4'-hydroxybenzoate

A mixture of 4-cyanophenyl-3'-methyl-4'-benzyloxybenzoate (10.3 g, 0.03 mol), ethyl alcohol (150 ml) and

5% Pd/C (3.0 g) was stirred and heated at 50°C in an oil bath in an atmosphere of hydrogen in a hydrogenation apparatus until the theoretical quantity of hydrogen was absorbed. The reaction mixture was filtered and the alcohol was removed by distillation under reduced pressure. This afforded a white product which was recrystallised from toluene (6.6 g, 87%), m.p. 170-172°C;  $\nu_{\text{max}}$  nujol 3350, 2240, 1730, 1608, 1510, 1380, 1290, 1172, 1079, 925 and 765  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 2.26 (s, 3H,  $\text{arCH}_3$ ) 6.86-7.9 (m, 7H,  $\text{arH}$ ) 9.96 (s, 1H,  $\text{arCH}$ )

[Found: C, 71.05; H, 4.3; N, 5.46%  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$  requires C, 71.14; H, 4.54; N, 5.53%].

4-Cyanophenyl-3'-methyl-4'-(4"-n-hexylbenzoyloxy)benzoate

A mixture of 4-n-hexylbenzoic acid (2.06 g, 0.01 mol) and freshly distilled thionyl chloride (10 ml) was refluxed for 4 hours and the excess thionyl chloride was removed by distillation under reduced pressure. A solution of 4-cyanophenyl-3'-methyl-4'-hydroxybenzoate (2.53 g, 0.01 mol) in anhydrous pyridine (20ml) was added to the crude acid chloride. The mixture was stirred magnetically at room temperature for 24 hours and poured onto a stirred mixture of crushed ice (100 g) and concentrated hydrochloric acid (50 ml) when a pale brown precipitate was obtained. This was filtered, washed with water, 10% aqueous sodium hydroxide solution

water and dried. This material was chromatographed on silica gel and eluted with chloroform. Removal of solvent from eluate afforded a white material which was recrystallised from absolute ethyl alcohol to constant melting point m.p. 101.5°C (3.53 g, 80%),  $\nu_{\text{max}}^{\text{nujol}}$  2230, 1740, 1725, 1604, 1502, 1378, 1254, 1170, 1018, 920 and 755  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 0.9 (t, 3H,  $-\text{CH}_3$ ) 1.1-2.01 (m, 8H, methylenes) 2.33 (s, 3H,  $\text{arCH}_3$ ) 2.73 (t, 2H,  $\text{arCH}_2$ ) 7.13-8.33 (m, 11H, arH)

[Found: C, 76.17; H, 6.05; N, 3.49%  $\text{C}_{28}\text{H}_{27}\text{O}_4\text{N}$  requires C, 76.19; H, 6.12; N, 3.17%].

The physical data of the cognate preparations of other 4-cyanophenyl-3'-methyl-4'-(4''-n-alkylbenzoyloxy)benzoates are given below.

4-Cyanophenyl-3'-methyl-4'-(4''-methylbenzoyloxy)benzoate

Yield 76%, m.p. 157.0°C,  $\nu_{\text{max}}^{\text{nujol}}$  2225, 1740, 1720, 1604, 1460, 1254, 1175, 1058 and 738  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 2.33 (s, 3H,  $-\text{CH}_3$ ) 2.5 (s, 3H,  $-\text{CH}_3$ ) 7.16-8.33 (m, 11H, arH)

[Found: C, 74.57; H, 4.80; N, 3.89%  $\text{C}_{23}\text{H}_{17}\text{O}_4\text{N}$  requires C, 74.39; H, 4.58; N, 3.77%].

4-Cyanophenyl-3'-methyl-4'-(4''-ethylbenzoyloxy)benzoate

Yield 79%, m.p. 99°C,  $\nu_{\text{max}}^{\text{nujol}}$  2228, 1740, 1720, 1604, 1510, 1252, 1175, 1016 and 752  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 1.3 (t, 3H,  $-\text{CH}_3$ ) 2.33 (s, 3H,  $\text{arCH}_3$ ) 2.78 (q, 2H,  $\text{arCH}_2$ ) 7.2-8.33 (m, 11H, arH)

[Found: C, 74.53; H, 4.51; N, 3.80%  $C_{24}H_{19}O_4N$  requires  
C, 74.80; H, 4.93; N, 3.63%].

4-Cyanophenyl-3'-methyl-4'-(4"-n-propylbenzoyloxy)benzoate

Yield 84%, m.p. 105.5°C;  $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 2230, 1738, 1603, 1510, 1250, 1210, 1125, 1016 \text{ and } 757 \text{ cm}^{-1}; \delta (\text{CDCl}_3) 0.96$   
(t, 3H,  $-\text{CH}_3$ ) 1.33-2.0 (m, 2H, methylene) 2.35 (s, 3H,  $\text{arCH}_3$ )  
2.73 (t, 2H,  $\text{arCH}_2$ ) 7.23-8.33 (m, 11H, arH)

[Found: C, 74.88; H, 5.0; N, 3.61%  $C_{25}H_{21}O_4N$  requires  
C, 75.18; H, 5.26; N, 3.50%].

4-Cyanophenyl-3'-methyl-4'-(4"-n-butylbenzoyloxy)benzoate

Yield 86%, m.p. 92°C;  $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 2230, 1738, 1603, 1505, 1378, 1204, 1018 \text{ and } 757 \text{ cm}^{-1}; \delta (\text{CDCl}_3) 0.96$  (t, 3H,  $-\text{CH}_3$ )  
1.16-2.0 (m, 4H, methylenes) 2.35 (s, 3H,  $\text{arCH}_3$ ) 2.76 (t,  
2H,  $\text{arCH}_2$ ) 7.16-8.33 (m, 11H, arH)

[Found: C, 75.26; H, 5.77; N, 3.44%  $C_{26}H_{23}O_4N$  requires  
C, 75.54; H, 5.56; N, 3.38%].

4-Cyanophenyl-3'-methyl-4'-(4"-n-pentylbenzoyloxy)benzoate

Yield 81%, m.p. 108.5°C;  $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 2232, 1733, 1603, 1504, 1378, 1165, 1018, 920 \text{ and } 756 \text{ cm}^{-1}; \delta (\text{CDCl}_3) 0.91$   
(t, 3H,  $-\text{CH}_3$ ) 1.1-2.03 (m, 6H, methylenes) 2.36 (s, 3H,  $\text{arCH}_3$ )  
2.76 (t, 2H,  $\text{arCH}_2$ ) 7.26-8.36 (m, 11H, arH)

[Found: C, 75.86; H, 5.60; N, 3.45%  $C_{27}H_{25}O_4N$  requires  
C, 75.87; H, 5.85; N, 3.27%].



4-Cyanophenyl-3'-methyl-4'-(4''-n-heptylbenzoyloxy)benzoate

Yield 87%, m.p. 103.5°C;  $\nearrow$   $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$  2232, 1738, 1606, 1505, 1216, 1018, 925 and 754  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 0.88 (t, 3H,  $-\text{CH}_3$ ) 1.06-2.0 (m, 10H, methylenes) 2.35 (s, 3H,  $\text{arCH}_3$ ) 2.73 (t, 2H,  $\text{arCH}_2$ ) 7.16-8.35 (m, 11H,  $\text{arH}$ )

[Found: C, 76.98; H, 6.32; N, 3.14%  $\text{C}_{29}\text{H}_{29}\text{O}_4\text{N}$  requires C, 76.43; H, 6.37; N, 3.07%].

4-Cyanophenyl-3'-methyl-4'-(4''-n-octylbenzoyloxy)benzoate

Yield 90%, m.p. 106°C;  $\nearrow$   $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$  2235, 1740, 1606, 1503, 1380, 1205, 1020, 877 and 758  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 0.88 (t, 3H,  $-\text{CH}_3$ ) 1.08-2.05 (m, 12H, methylenes) 2.35 (s, 3H,  $\text{arCH}_3$ ) 2.73 (t, 2H,  $\text{arCH}_2$ ) 7.16-8.35 (m, 11H,  $\text{arH}$ )

[Found: C, 76.55; H, 6.78; N, 2.91%  $\text{C}_{30}\text{H}_{31}\text{O}_4\text{N}$  requires C, 76.75; H, 6.60; N, 2.98%].

4-Cyanophenyl-3'-methyl-4'-(4''-n-nonylbenzoyloxy)benzoate

Yield 88%, m.p. 104.5°C;  $\nearrow$   $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$  2235, 1740, 1603, 1502, 1378, 1018, 878 and 758  $\text{cm}^{-1}$ ; ( $\text{CDCl}_3$ ) 0.9 (t, 3H,  $-\text{CH}_3$ ) 1.06-2.0 (m, 14H, methylenes) 2.33 (s, 3H,  $\text{arCH}_3$ ) 2.75 (t, 2H,  $\text{arCH}_2$ ) 7.26-8.33 (m, 11H,  $\text{arH}$ )

[Found: C, 77.17; H, 7.10; N, 3.10%  $\text{C}_{31}\text{H}_{33}\text{O}_4\text{N}$  requires C, 77.01; H, 6.83; N, 2.89%].

4-Cyanophenyl-3'-methyl-4'-(4''-n-decylbenzoyloxy)benzoate

Yield 83%, m.p. 100.5°C;  $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 2230, 1740, 1725, 1603, 1502, \text{ rye. } 1210 \text{ and } 754 \text{ cm}^{-1}; 6 \text{ (CDCl}_3\text{)} 0.88 \text{ (t, 3H, -CH}_3\text{)} 1.03\text{-}2.0 \text{ (m, 16H, methylenes)} 2.33 \text{ (s, 3H, arCH}_3\text{)} 2.73 \text{ (t, 2H, arCH}_2\text{)} 7.11\text{-}8.33 \text{ (m, 11H, arH)}$

[Found: C, 77.44; H, 7.50; N, 2.93%  $\text{C}_{32}\text{H}_{35}\text{O}_4\text{N}$  requires C, 77.26; H, 7.04; N, 2.81%].

4-Cyanophenyl-3'-methyl-4'-(4''-n-undecylbenzoyloxy)benzoate

Yield 79%, m.p. 103°C;  $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 2230, 1740, 1725, 1603, 1504, 1418, 1018, 879 \text{ and } 753 \text{ cm}^{-1}; 8 \text{ (CDCl}_3\text{)} 0.89 \text{ (t, 3H, -CH}_3\text{)} 1.06\text{-}2.0 \text{ (m, 18H, methylenes)} 2.36 \text{ (s, 3H, arCH}_3\text{)} 2.75 \text{ (t, 2H, arCH}_2\text{)} 7.23\text{-}8.4 \text{ (m, 11H, arH)}$

[Found: C, 77.35; H, 7.05; N, 3.00%  $\text{C}_{33}\text{H}_{37}\text{O}_4\text{N}$  requires C, 77.49; H, 7.24; N, 2.73%].

4-Cyanophenyl-3'-methyl-4'-(4''-n-dodecylbenzoyloxy)benzoate

Yield 82%, m.p. 100.2°C;  $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 2230, 1738, 1602, 1502, 1378, 1202, 1017, 877 \text{ and } 756 \text{ cm}^{-1}; 6 \text{ (CDCl}_3\text{)} 0.86 \text{ (t, 3H, -CH}_3\text{)} 1.03\text{-}2.0 \text{ (m, 20H, methylenes)} 2.35 \text{ (s, 3H, arCH}_3\text{)} 2.73 \text{ (t, 2H, arCH}_2\text{)} 7.16\text{-}8.33 \text{ (m, 11H, arH)}$

[Found: C, 77.71; H, 7.72; N, 2.96%  $\text{C}_{34}\text{H}_{39}\text{O}_4\text{N}$  requires C, 77.71; H, 7.42; N, 2.66%].

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