CHAPTER IV

SYNTHESIS AND MESOMORPHIC PROPERTIES OF SOME BIPHENYLYL-BENZOATES

4.1 Survey of the liquid crystalline properties of compounds containing a biphenyl moiety

As pointed out in chapter 1, the fundamental requirements for a compound to exhibit liquid crystalline properties are that the constituent molecules should have shape anisotropy and that the anisotropy of the cohesive forces between molecules must be of suitable magnitude. The influence of molecular structure upon liquid crystalline properties is varied and often interesting. The introduction of a lateral substituent in a liquid crystalline substance may have profound effects on the transition temperatures. The effects of changing a terminal substituent are also interesting as a given substituent may alter the smectic and nematic thermal stabilities to different extents.

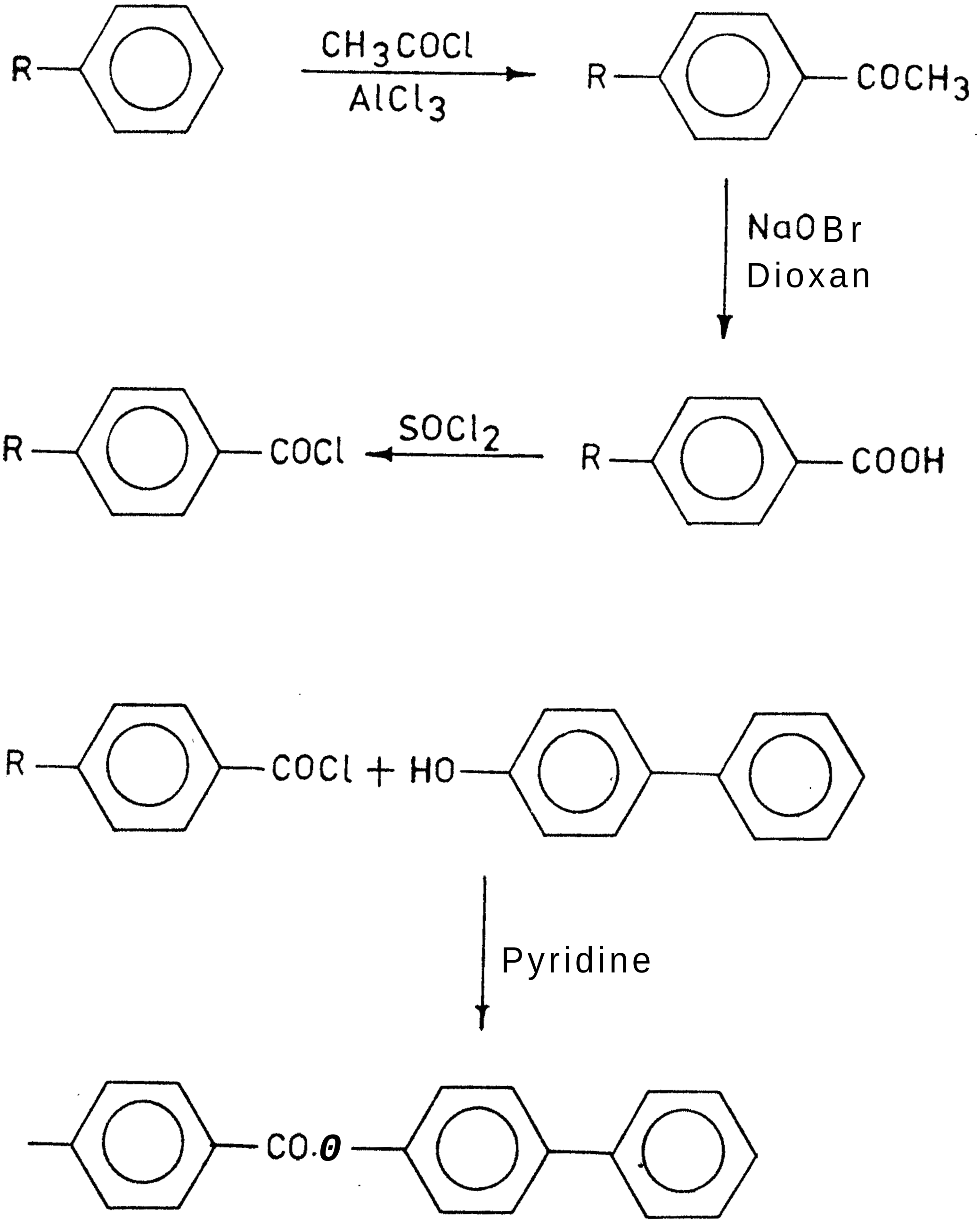
The biphenyl molecule is well suited to form the central core of a potential liquid crystalline substance because of its geometrical shape. The tendency to form liquid crystals by biphenyl derivatives is so marked that even very simple 4,4'-substituents[1] give rise to mesogenic compounds. A large number of compounds containing a biphenyl moiety have been studied by Gray and his co-workers[2] and most of these are 4,4'-disubstituted derivatives. Gray _et al_[3] synthesised a series of 4-n-alkoxybiphenyl-4'-carboxylic acids and compared the mesomorphic properties with those exhibited by 4-n-alkoxybenzoic acids. The former compounds have relatively higher thermal stabilities and this has been attributed to the enhanced molecular cohesions arising from the second aromatic ring and to the greater molecular length of the biphenyl compounds. The mesomorphic properties of 4-n-alkoxybiphenyl-4'-carboxylic acids are typical of a homologous series of mesogenic compounds and are similar to other alkoxyarenecarboxylic acids like 4-n-alkoxybenzoic acids,[4] _trans_-_p_-n-alkoxycinnamic acids[5] and 6-n-alkoxy-2-naphthoic acids.[6] However, simple alkyl _esters_ of the last three series of compounds do not show mesophases, whereas those of 4-n-alkoxybiphenyl-4'-carboxylic acids do show them. Carboxylic acid molecules exist as dimers, which are the effective units in the mesophase. The absence of mesophase in alkyl esters of the above three series of acids may be explained as due to insufficient cohesive forces between the shortened monomeric ester molecules. In view of the relatively higher thermal stability of the biphenyl carboxylic acids, even their simple alkyl esters[2] exhibit mesophases.

4-Substituted and 4,4'-disubstituted biphenyls provide a rich source of liquid crystals, which are thermally stabler and have wider mesophase ranges than many other systems. This has led to various studies such the effect of different types of lateral and terminal substituents on the mesomorphic behaviour, and of the group efficiency order of the three types of mesophases. Most of the compounds studied, however, belong to the Schiff's base class of compounds which are rather labile to oxidation and hydrolysis and tend to undergo decomposition on repeated heating. However, esters are comparatively more stable than the schiff's bases. Moreover, there are relatively few homologous series of compounds containing a biphenyl moiety in which one of the *para* positions is free.[7,8,9] In order to study such compounds, we have synthesised two homologous series of biphenylylbenzoates. Their mesomorphic properties are characterised and compared with other similar series of compounds.

4.2 Synthesis and mesomorphic properties of 4-biphenylyl 4"-n-alkylbenzoates

The 4-biphenylyl 4"-n-alkylbenzoates were conveniently prepared from commercially available 4-hydroxybiphenyl and prepared *p*-n-alkylbenzoyl chlorides and the reaction sequence is shown schematically (Chart V). The transition temperatures for this series are summarised in table 4.1. It is

CHART V



R = n-Alkyl

Table 4.1

Melting and clearing temperatures of 4-biphenylyl 4"-n-alkylbenzoates

Compound number	R = n-Alkyl	Temperature of transition to	
		Nematic, °C	Isotropic, °C
1	CH_3	-	155.5
2	C_2H_5	-	153
3	C_3H_7	(108.5)	114.2
4	C_4H_9	-	133.4
5	C_5H_{11}	(106.5)	137.5
6	C_6H_{13}	(96.4)	130.3
7	C_7H_{15}	(102.5)	120.3
8	C_8H_{17}	(96.3)	112.6
9	C_9H_{19}	(99.2)	105.5
10	$C_{10}H_{21}$	(96)	106
11	$C_{11}H_{23}$	(96.5)	105.5
12	$C_{12}H_{25}$	(94)	103

seen that only nine of the twelve compounds show mesomorphic properties, all of them exhibiting a monotropic nematic phase. This type of behaviour is rather rare and is attributed to the fact that the molecules pack themselves efficiently in the crystal lattice and require fairly high temperature for the solid to melt to give the isotropic liquid. However, supercooling of these melts gives rise to the mesophase in nine of the twelve homologues.

Figure 4.1 is a plot of the transition temperatures versus the number of carbon atoms in the alkyl chain. T_{N-I} decreases on ascending the homologous series. This is the general trend that has been observed by a number of workers for homologous series of compounds with relatively high transition points. These points lie on two smooth curves, the curve for the odd homologues lying above that for the even ones. Compounds 1, 2 and 4 (table 4.1) do not supercool sufficiently to show the mesophase. They tend to crystallise about 10° below their melting points whereas from figure 4.1 it may be estimated that they would have to supercool by about 30° below their melting points in order to exhibit a monotropic mesophase.

It is interesting to compare the mesomorphic properties of 4-biphenylyl 4"-n-alkylbenzoates with those of *p*-n-alkylbenzoic acids.[10] It must be remembered that these

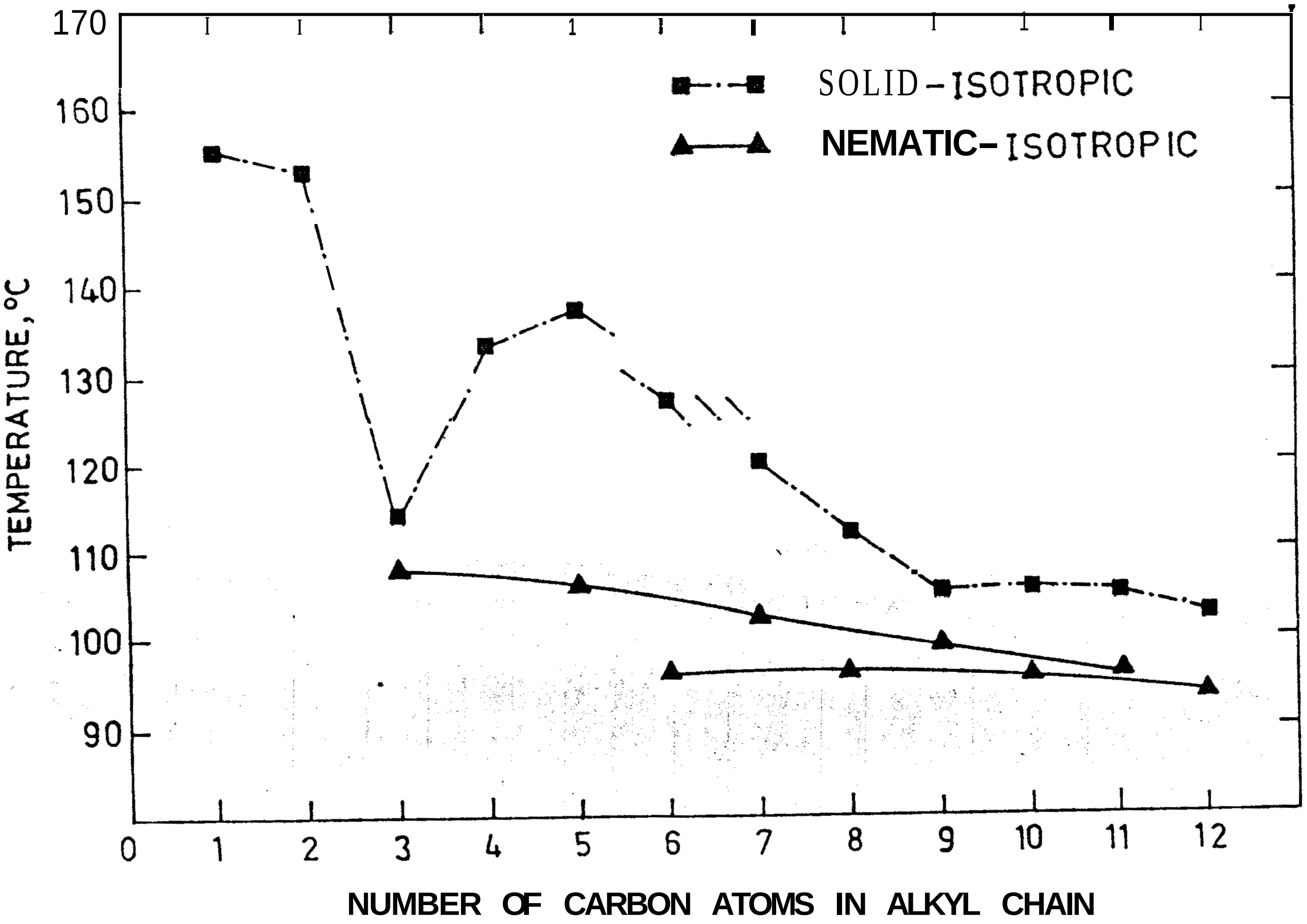
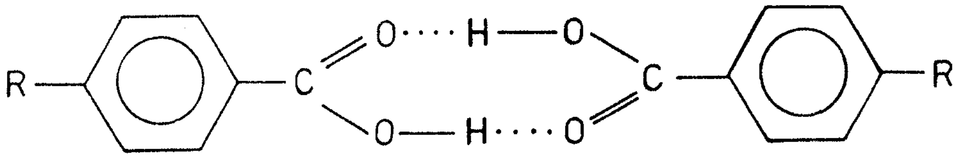


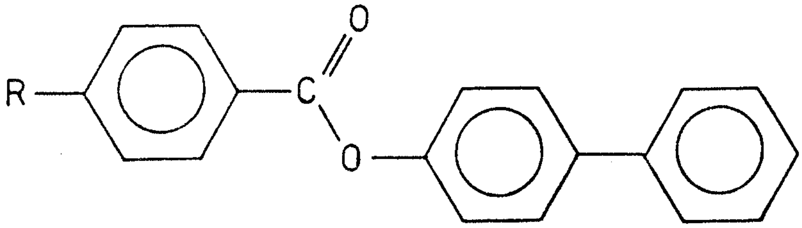
Figure 4.1

Plot of transition temperatures against number of carbon atoms in the alkyl group for 4-bfphenylyl 4"-n-alkylbenzoates.

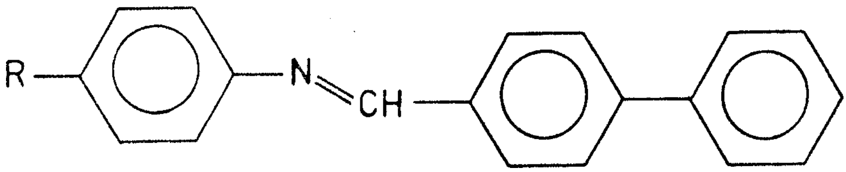
acids are present as dimers as shown in A. The first three members of this series are non-mesomorphic but from p-n-butylbenzoic acid up to p-n-dodecylbenzoic acid, they are all enantiotropic nematic. In the ester molecule B, we have added a biphenyl nucleus which, in addition to lengthening the molecule would contribute to the polarisability of the molecule in the direction of the long molecular axis. Therefore, one would expect the esters to have higher thermal stability for the mesophases. On the other hand, three of the esters are non-mesomorphic and the rest are all monotropic nematic. The average N-I transition temperature (C_5 to C_{12}) for series A is 114.7°C whereas those for series B is 98.4°C. However, this reduction in T_{N-I} can be explained by considering the two structures A and B. In series A, we have a symmetrical dimeric system which is conducive to liquid crystal formation whereas in series B the three phenyl rings are not collinear because of the bridging $O-\overset{O}{\overset{\|}{C}}-$ group. Thus, the added biphenyl moiety broadens the resulting monomeric ester molecule, reduces the length to breadth ratio thereby reducing the thermal stability of the mesophases considerably. The liquid crystalline properties of series B can be compared to those of p-phenylbenzylidene-p'-alkylanilines,[9] C, as the structures of the two are similar. However, the properties are striking in series C, where polymorphic smectic phases are present. In both series of compounds the first two



A



B



C

R = n-Alkyl

homologues are non-mesomorphic. The average T_{N-I} (C_5 to C_{10}) for series C is 134.1°C. This higher value, as compared to that for series B may be attributed to the fact that the azomethine linkage group in series C, imparts a greater rigidity and polarisability than the ester linkage group in series B. The length-breadth ratio in series B is lower than that for series C. The appearance of the enantiotropic smectic phase from C_3 onwards in series C may also be attributed to these factors.

4.3 Thermodynamic properties of 4-biphenylyl 4''-n-alkylbenzoates

The transition enthalpies (ΔH) and transition entropies (ΔS) for 4-biphenylyl 4''-n-alkylbenzoates are summarised in table 4.2. The enthalpies for N-I transition were obtained by reheating the supercooled mesophases. These enthalpies are typically in the range of 0.1 to 0.25 kcal/mole. The effect of the alkyl chain length on the solid to isotropic liquid transition entropy and the mesophase transition entropies are shown in figure 4.2. As can be seen there is no regular trend in the solid to isotropic liquid transition entropy. There is an odd-even alternation in the ΔS values for N-I transition up to C_9 after which there is a sharp rise for C_{10} and then again a decrease for C_{11} and C_{12}. However such decreases have been observed

Table 4.2

Transition enthalpies and entropies of 4-biphenylyl 4"-n-alkylbenzoates

n-Alkyl group	Transition	Transition heat ΔH, kcal mol^{-1}	Transition entropy ΔS, cal/mole/°K
Methyl	K ⟶ I	7.71	23.49
Ethyl	K ⟶ I	8.18	19.22
Propyl	K ⟶ I	6.75	17.44
	N ⟶ I	0.126	0.32
Butyl	K ⟶ I	8.32	20.49
Pentyl	K ⟶ I	11.62	28.28
	N ⟶ I	0.143	0.37
Hexyl	K ⟶ I	8.56	21.23
	N ⟶ I	0.111	0.33
Heptyl	K ⟶ I	8.50	21.60
	N ⟶ I	0.140	0.37
Octyl	K ⟶ I	8.35	21.68
	N ⟶ I	0.111	0.30
Nonyl	K ⟶ I	9.77	25.82
	N ⟶ I	0.154	0.41
Decyl	K ⟶ I	11.92	31.50
	N ⟶ I	0.232	0.62
Undecyl	K ⟶ I	9.60	25.34
	N ⟶ I	0.219	0.59
Dodecyl	K ⟶ I	9.66	25.68
	N ⟶ I	0.202	0.55

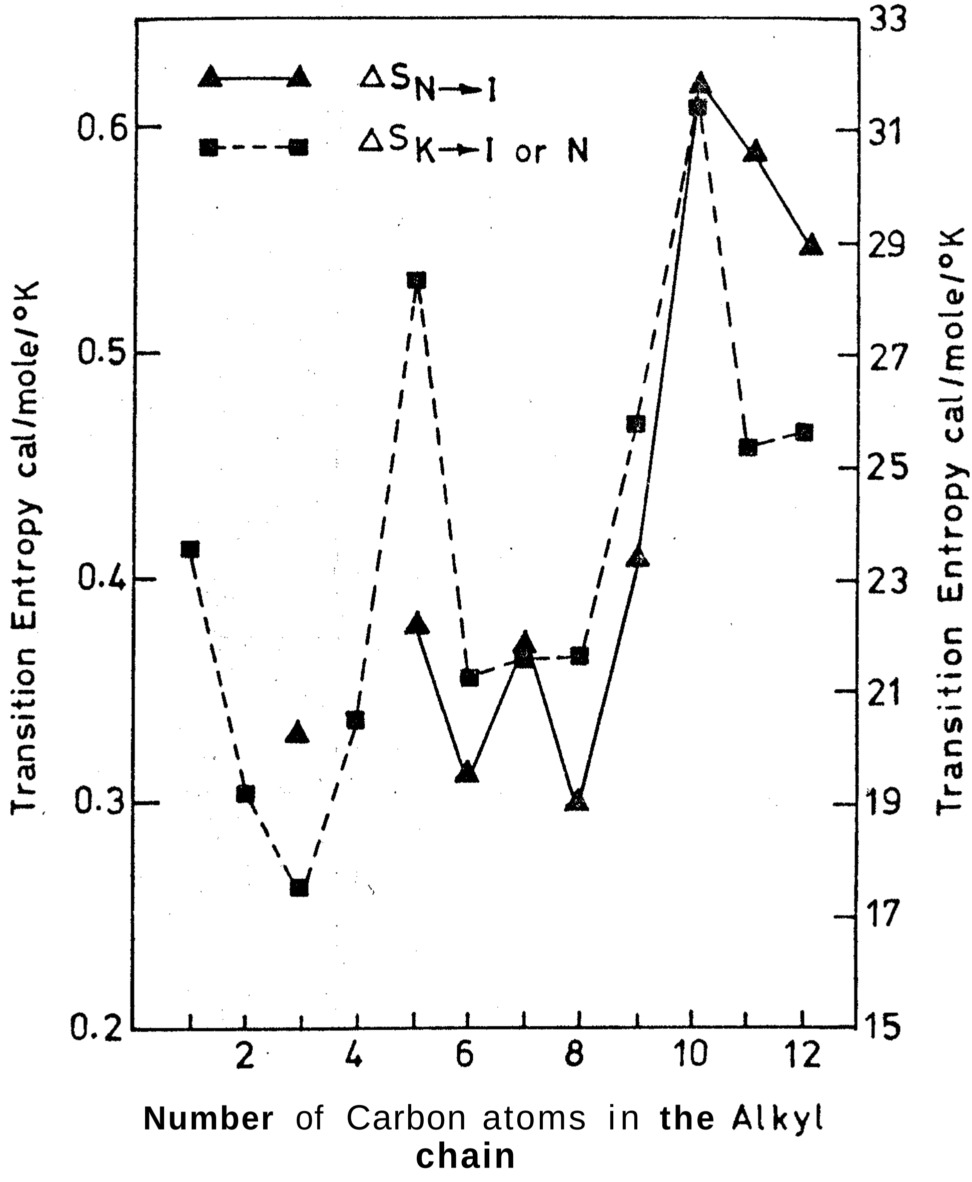


Figure 4.2

Transition entropies for 4-biphenylyl 4"-n-alkylbenzoates.

in some homologous series of compounds, e.g., cholestanyl S-alkyl thiocarbonates.[11]

4.4 Synthesis and mesomorphic properties of 4-biphenylyl 4"-n-alkoxybenzoates

The 4-biphenylyl 4"-n-alkoxybenzoates were prepared from commercially available 4-hydroxybiphenyl and prepared p-n-alkoxybenzoyl chlorides (Chart VI). The transition temperatures for this series are given in table 4.3. As can be seen all the twelve compounds exhibit mesophases. The first five homologues, C_1 to C_5, are monotropic nematic. The hexyl and heptyl derivatives, C_6 and C_7, are enantiotropic nematic and the smectic phase commences as a monotropic phase with the octyloxy derivative, C_8. The smectic phase of this and the higher homologues shows a simple fan-shaped texture as shown in plate 2 and is believed to be smectic A. Figure 4.3 shows a plot of the transition temperatures against the number of carbon atoms in the alkoxy chain. The odd-even effect is evident from this figure. These points lie on two smooth falling curves, the curve for the even homologues lying above that for the odd ones. The curve for the smectic-nematic transition points shows the usual initial upward trend and these lie on a smooth curve. It is interesting to note that there is alternation in the crystal-isotropic liquid transition temperatures of

CHART VI

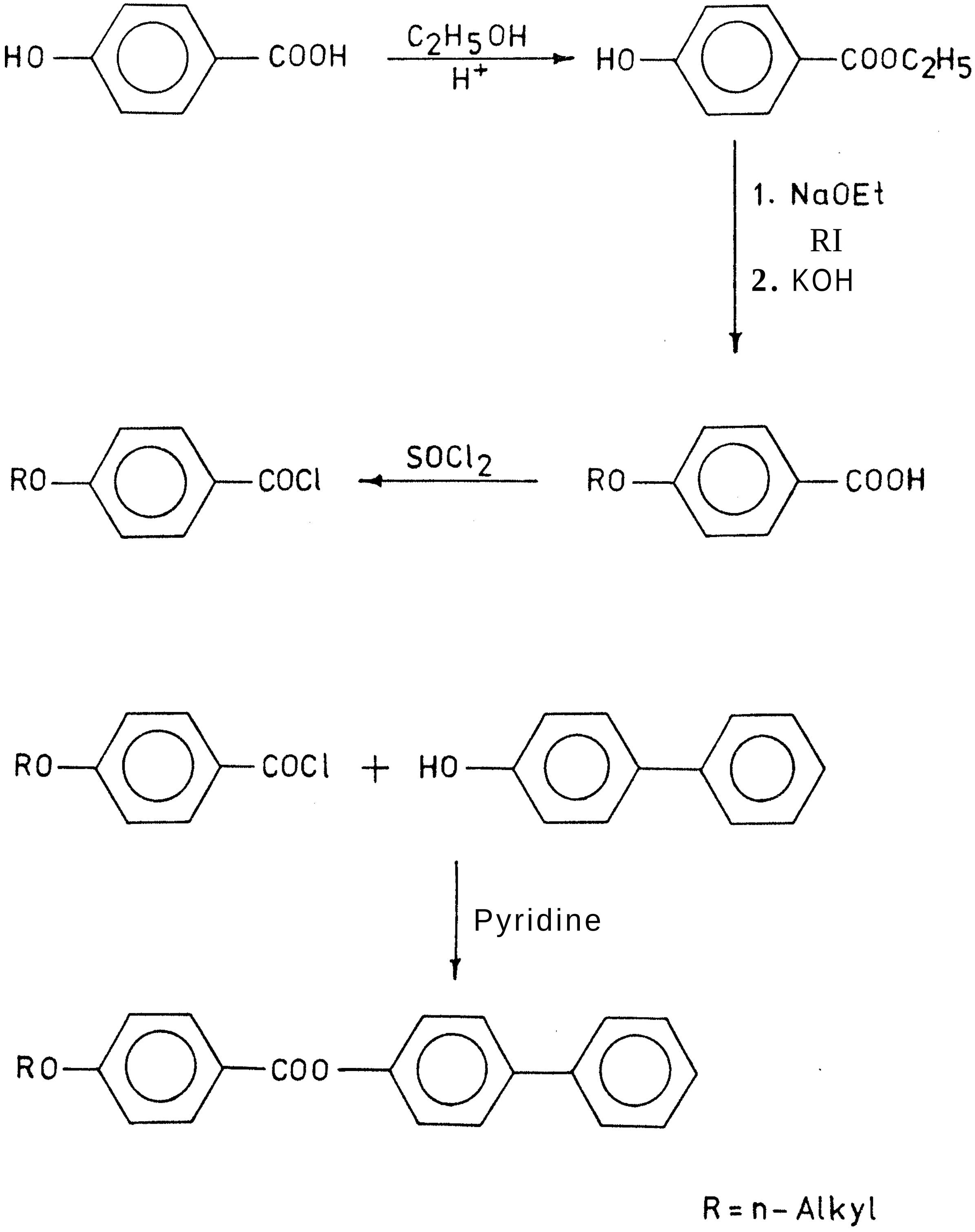

HO
COOH
C2H5OH
H+
HO
COOC2H5
1. NaOEt
RI
2. KOH
RO
COCl
SOCl2
RO
COOH
RO
COCl
+
HO
Pyridine
RO
COO
R = n- Alkyl

Table 4.3

Melting and clearing temperatures of 4-biphenylyl 4''-n-alkoxybenzoates

Compound number	R=n-Alkyl	Temperature of transition to		
		Smectic,°C	Nematic,°C	Isotropic,°C
1	CH_3	-	(145.3)	156.5
2	C_2H_5	-	(157.5)	160
3	C_3H_7	-	(136.2)	146
4	C_4H_9	-	(142.4)	156.5
5	C_5H_{11}	-	(132.3)	154.5
6	C_6H_{13}	-	132.5	135.3
7	C_7H_{15}	-	126	130
8	C_8H_{17}	(98)	120	130.8
9	C_9H_{19}	(101)	117.1	127.5
10	$C_{10}H_{21}$	(106)	110	127
11	$C_{11}H_{23}$	98.5	109.5	125
12	$C_{12}H_{25}$	109.7	113.2	124

Plate 2

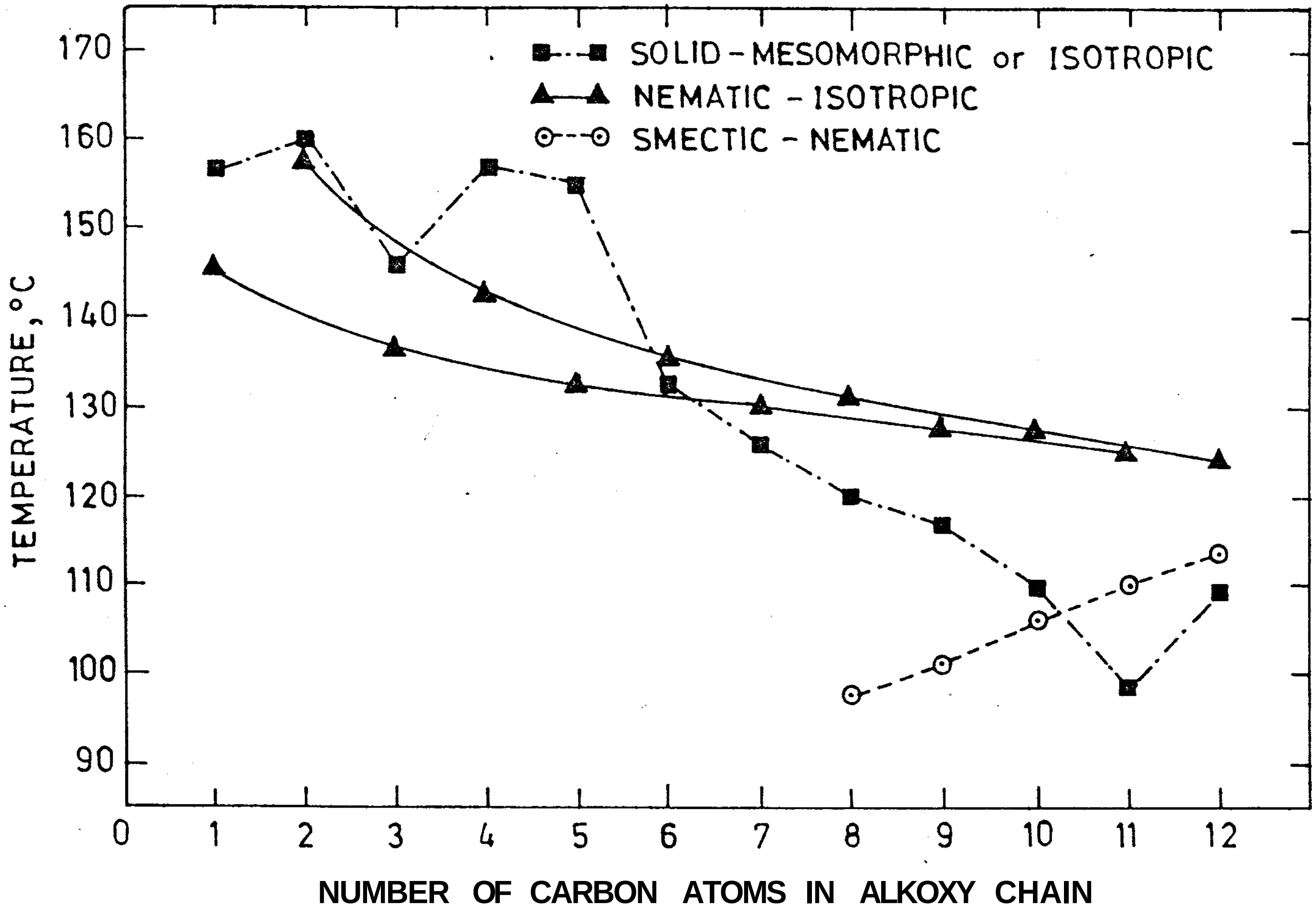


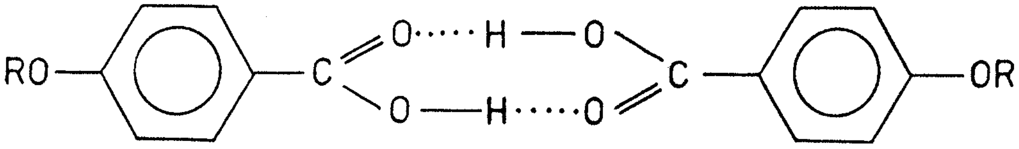
Figure 4.3

an

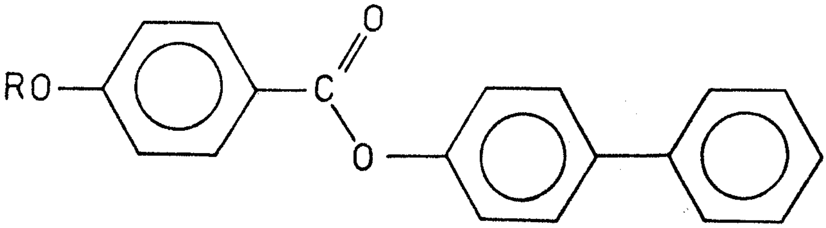
Plot of tr sition temperatures against number of carbon atoms in the alkaxy group for 4-biphenylyl 4"-n-alkoxybenzoates.

the first five members of this series. A similarity in crystal structure would be expected to give some trend in the crystal-mesophase or isotropic liquid transitions. X-ray studies[12] on p-n-alkoxybenzoic acids showed that, although no similarities were found for tha crystal structures of lower homologues, a similarity was found from p-n-heptyloxybenzoic acid onwards. The alternation found in the present series may be attributed to a possible similarity in the crystal structure of the first five homologues, C_1 to C_5.

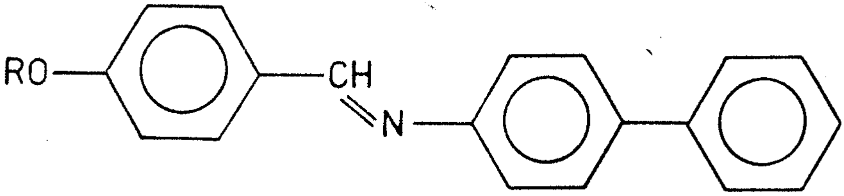
A comparison of the liquid crystalline properties of 4-biphenylyl 4"-n-alkoxybenzoates, E with those of p-n-alkoxybenzoic acids,[4] D, is similar to that discussed in section 4.2. The average N-I transition temperature (C_1 to C_{12}) for series D is 136°C and those lor series E is 128.5°C. This decrease has been attributed to the same arguements putforward to in section 4.2. However, as the series is ascended the smectic phase appears as an enantiotropic phase from the p-n-heptyloxybenzoic acid in series D and as a monotropic phase from the 4-biphenylyl 4"-n-octyloxybenzoate in series E. The mesomorphic properties of series E can be compared to the series 4-p-n-alkoxybenzylideneaminobiphenyls,[7] F, as the two are very similar. In series F, all the homologues are enantiotropic mesomorphic whereas in series E, only from C_6 onwards the mesophase



D



E



F

R = n-Alkyl

is enantiotropic. The average H-I transition temperature for series F is 169.2°C which is very much higher than that for series E. This is due to the fact that $-CH=N-$ bridging group in F is more polarisable than the $-\overset{O}{\overset{\|}{C}}-O-$ bridging group In E and also the latter broadens the molecule to a somewhat greater extent than the former. Moreover, the azomethine linkage group confers more rigidity to the molecule than the ester linkage group. This is reflected in the commencement of the smectic phase in the two series of compounds. In series E it commences as a metastable phase from C_8 whereas in series F it appears as an enantiotropic phase from C_5. However, it must be emphasised that it is difficult to predit the onset of the smectic phase in a homologous series, as this depends on various parameters like the geometry of the molecule, the length to breadth ratio and the relative strengths of the lateral and terminal attractions.

4.5 Thermodynamic properties of 4-biphenylyl 4"-n-alkoxybenzoates

The transition enthalpies and transition entropies for 4-biphenylyl 4"-n-alkoxybenzoates are summarised in table 4.4. As mentioned earlier, the transition enthalpies for compounds exhibiting a monotropic phase, was obtained by reheating these supercooled mesophases. The enthalpies of the nematic-isotropic transition, ΔH_{N-I} are typically in the range of 0.1 to 0.3 kcal/mole. Figure 4.4 shows the

Table 4.4

Transition enthalpies and entropies of 4-biphenylyl 4"-n-alkoxybenzoates

n-Alkyl group	Transition	Transition heat ΔH kcal/mole	Transition entropy ΔS, cal/mole/°K
Methyl	K ⟶ I	8.50	19.78
	N ⟶ I	0.137	0.32
Ethyl	K ⟶ I	7.56	17.48
	N ⟶ I	0.160	0.37
Propyl	K ⟶ I	7.66	18.31
	N ⟶ I	0.137	0.33
Butyl	K ⟶ I	10.05	23.41
	N ⟶ I	0.160	0.38
Pentyl	K ⟶ I	10.17	23.78
	N ⟶ I	0.137	0.34
Hexyl	K ⟶ N	9.24	22.77
	N ⟶ I	0.171	0.42
Heptyl	K ⟶ N	9.35	23.42
	N ⟶ I	0.130	0.32
Octyl	K ⟶ N	8.81	22.44
	N ⟶ I	0.204	0.506
	S ⟶ N	-	-
Nonyl	K ⟶ N	12.52	32.10
	N ⟶ I	0.178	0.44
	S ⟶ N	0.223	0.59
Decyl	K ⟶ N	11.24	29.34
	N ⟶ I	0.190	0.47
	S ⟶ N	0.213	0.56
Undecyl	K ⟶ S	12.72	34.23
	S ⟶ N	0.336	0.87
	N ⟶ I	0.221	0.55
Dodecyl	K ⟶ S	12.86	33.62
	S ⟶ N	0.466	1.21
	N ⟶ I	0.302	0.73

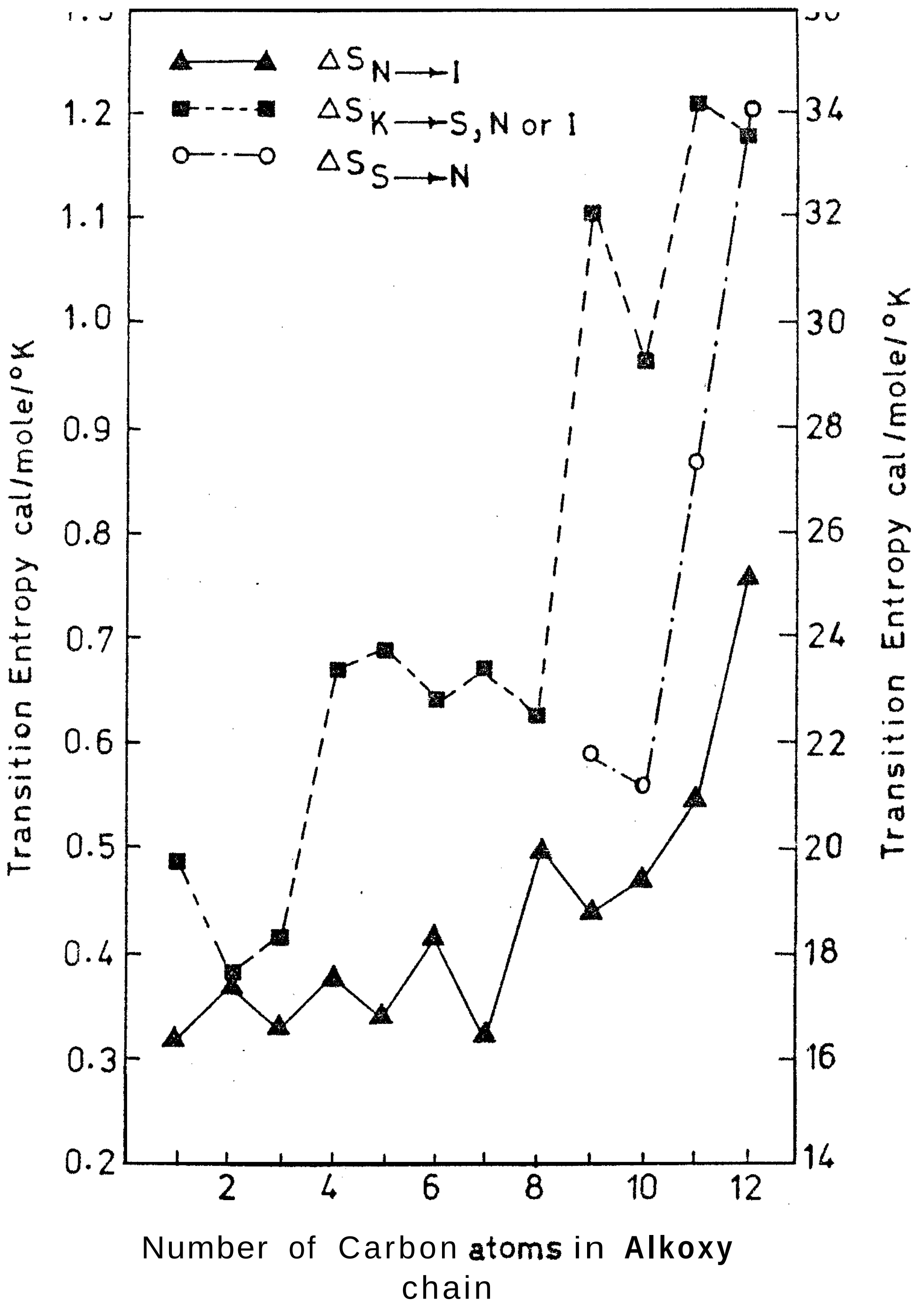


Figure 4.4

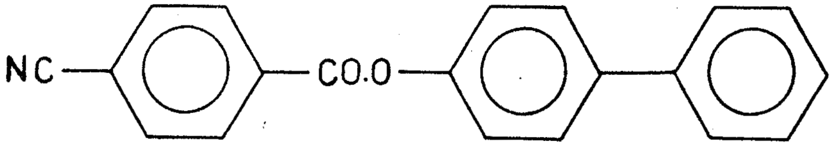
Transition entropies for 4-bfphenylyl 4"-n-alkoxy-benzoates.

relationship between the transition entropies, ΔS, and the alkoxy chain length for the various transitions. There is an alternation in the ΔS_{N-I} values between successive homologues up to C_9 after which there is a sharp increase. Beyond C_8 the compounds show a smectic phase also, and hence the increase in ΔS_{N-I} beyond C_8 may be due to the onset of smectic-like short range order in the nematic phase. For the smectic-nematic transition there is a small initial decrease in the entropy followed by a continuous increase as the series is ascended.

4.6 Effect of terminal substituent on biphenylyl-benzoates

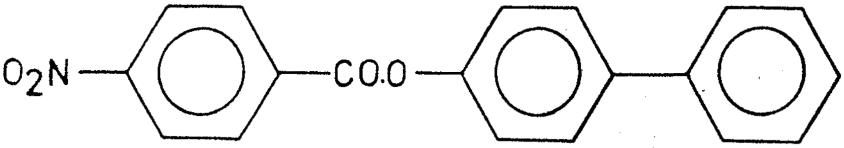
It is known from a number of studies that a large number of molecules forming liquid crystals contain moderately dipolar terminal groups. The effect of such terminal substituents on liquid crystal behaviour varies from one mesogenic system to another. It is therefore of interest to study such effects in different systems and to understand the function of such substituents. It has also been fairly well established that replacement of a terminal hydrogen in a molecule by a different substituent enhances the mesogenic order of the resultant molecule. In other words if the unsubstituted parent compounds show liquid crystal behaviour then the substituted compounds also show this behaviour but generally of higher thermal stability. However, it should be pointed out that certain terminal substituents lower the thermal stability of smectic liquid crystals.[13]

The role of a terminal substituent is important in some systems in which the unsubstituted parent compound is not mesomorphic. The 4-biphenylylbenzoates belong to this class. For example, the unsubstituted 4-biphenylylbenzoate, is non-mesomorphic whereas 4-biphenylyl 4"-cyanobenzoate is enantiotropic nematic. The cyano group in this compound not only increases the rigid core of tho molecule but also increases the anisotropy of polarisability considerably which contributes to the formation of the mesophase. Similarly methoxy and nitro groups impart liquid crystallinity to the 4-biphenylylbenzoate system although they exhibit metastable nematic phases. On the other hand substituents like chloro, bromo and methyl do not lead to mesomorphism. The introduction of a terminal substituent generally raises the melting point of the compound but the thermal stability of the mesophase is increased even more. This is clearly demonstrated by comparison of the transition temperatures of 4-cyanophenyl biphenylyl 4'-carboxylate and 4-cyanophenyl 4"-methoxy-biphenylyl-4'-carboxylate. Although both compounds are enantiotropic nematic, the terminal methoxy substituent



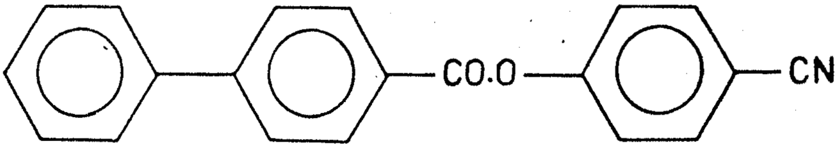
4-Biphenylyl 4″-cyanobenzoate

K 159.5 N 182.5 I



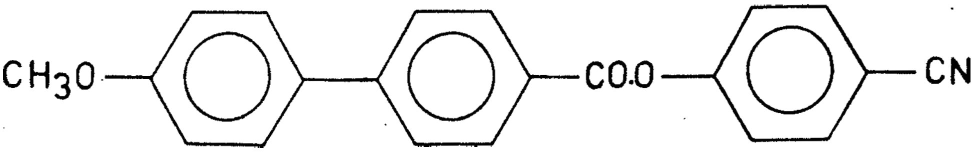
4-Biphenylyl 4″-nitrobenzoate

K 172 N (156) I



4-Cyanophenyl biphenylyl 4′-carboxylate

K 155 N 179 I



4-Cyanophenyl 4″-methoxybiphenylyl-4′-carboxylate

K 167 N 305 I

has a profound effect on the thermal stability of the mesophase. The melting point is raised by 12° but the clearing temperature is increased by 126°.

Finally, a comparison of the two series of compounds, i.e., 4-biphenylyl 4"-n-alkylbenzoates versus 4-biphenylyl 4"-n-alkoxybenzoates reveals that alkoxy substitution favours the thermal stabilisation of all phases. This is possibly due to the oxygen atom adjacent to the phenyl ring undergoing an electronic interaction with it, which in turn stabilises the mesophases. The smectic properties observed in the alkoxy series may also be explained in terms of strong dipole moments operating across the major axis of the molecules which enhance the lateral attractive forces.

EXPERIMENTAL

n-Propylphenyl ketone

This was prepared following the procedure described by Vogel.[14] Thus, by Friedel-Crafts reaction using n-butyroyl chloride (60.25 g, 0.5 mol) and benzene (200 ml), n-propylphenyl ketone (76.3 g, 94%), b.p. 97°C/5 mm was obtained (reported[14] b.p. 227-230°C/680 mm; yield 52%).

By a similar procedure the other required ketones were prepared and their physical data are given in table 4.5.

n-Butylbenzene

This was prepared following the procedure described by Vogel.[17] Thus, by Huang-Minlon reduction of n-propyphenyl ketone (60.0 g, 0.40 mol), n-butylbenzene (50.0 g, 92%), b.p. 179-181°/690 mm was obtained (reported[17] b.p. 181-184°, yield 59%).

The other n-alkylbenzenes were prepared by a similar procedure and their physical data are given in table 4.6.

4-n-Butylacetophenone

In a one litre three-necked flask fitted with a mercury sealed stirrer, a reflux condenser and a dropping funnel, were placed carbon tetrachloride (400 ml), anhydrous aluminium trichloride (73.42 g, 0.55 mol) and n-butylbenzene

Table 4.5

Boiling and melting points of n-alkylphenyl ketones, $R.CO.C_6H_5$

R=n-Alkyl	Observed		Reported			
	b.p.°C/mm	% Yield	b.p.°C/mm	m.p.°C	% Yield	Reference
C_2H_5	75/3	80	214–217/760		60	14
C_4H_9	75/1	85	144–145/35		75	15
C_5H_{11}	95–100/2	83	-	27	60	16
C_6H_{13}	125/2	90	-	17	85	16
C_7H_{15}	126/2	92	-	22.2–23.2	88	16
C_8H_{17}	128–132/2	86	-	17	81	16
C_9H_{19}	140–145/3	78	-	34.4–35.4	88	16
$C_{10}H_{21}$	157–160/2	80	-	29.5–30.2	60	16
$C_{11}H_{23}$	148/1	75	-	45.8–47	90	16

Table 4.6

Bailing points of n-alkylbenzenes, R.C_6H_5.

R = n-alkyl	Observed b.p. °C/mm	Reported	
		b.p. °C/mm	Reference
C_3H_7	153-155/690	158-159/760	17
C_5H_{11}	200-202/690	198-203/760	17
C_6H_{13}	62-70/3	220-225/760	17
C_7H_{15}	80-82/3	240/760	18
C_8H_{17}	90-93/3	257/760	18
C_9H_{19}	103-108/3	275/760	18
$C_{10}H_{21}$	120-122/4	-	-
$C_{11}H_{23}$	135-140/4	-	-
$C_{12}H_{25}$	138/1-2	138	19

(60 g, 0.44 mol). The mixture was stirred and cooled in ice-water (0-5°C) and freshly distilled acetyl chloride (34.54 g, 0.44 mol) was added drop by drop during thirty minutes. It was stirred for an additional two hours and left at room temperature overnight. The dark coloured reaction mixture was poured into a mixture of concentrated hydrochloric acid (300 ml) and crushed ice (500 g). The organic layer was separated, washed with water (2x100 ml) and dried (Na_2SO_4). The solvent was removed and the residue distilled under vacuum to give 4-n-butylacetophenone (40.0 g, 51%), b.p. 96-98°/1 mm. (reported[20] 91%, b.p. 101.5-102/1.5 mm).

The physical data of the cognate preparations of other 4-n-alkylacetophenones are given in table 4.7.

<u>4-n-Butylbenzoic acid</u>

This was prepared following the procedure of Johnson, Outsche and Offenhauer.[21] A solution of sodium hypobromite prepared at 0-5°C by adding bromine (128 g, 0.8 mol) to sodium hydroxide (64 g, 1.6 mol) in water (400 ml), was added slowly to a stirred solution of 4-n-butylacetophenone (35.2 g, 0.2 mol) in dioxan (350 ml) maintained at 20°C during one hour. The sodium salt separated out during the addition and stirring was continued for a further one hour

Table 4.7

Physical data for a series of 4-n-alkylacetophenones, $R.C_6H_4COCH_3$

R = n-Alkyl	Observed		Reported		
	b.p. °C/mm	% Yield	b.p. °C/mm	% Yield	Reference
C_2H_5	90/4	80	86/3	95.7	20
C_3H_7	98/2	83	82-90/1	88	22
C_5H_{11}	120/4	70	106-109/1.1		22
C_6H_{13}	118-20/2	64	120/1	90.6	20
C_7H_{15}	132/2	72	165-75/10	45	23
C_8H_{17}	140-45/1	60	149-50/1	94.8	20
C_9H_{19}	165-68/3	83	159-62/2-3	56.6	20
$C_{10}H_{21}$	160-65/1	62	166-68/1.5	94	20
$C_{11}H_{23}$	180-85/3	80	-	-	-
$C_{12}H_{25}$	197-98/2	76	47-48 (m.p.)	69.7	20

during which period the temperature was gradually raised fa 55°C to ensure completion of reaction. Enough aqueous sodium metabisulphite solution was added to remove the excess of hypobromite and the mixture was diluted with water (1500 ml). About 300ml of the liquid was distilled and the mixture cooled. Acidification with concentrated hydrochloric acid afforded white crystals, which was filtered off, washed with water and air dried. Recrystallisation of the solid afforded pure 4-n-butylbenzoic acid (29.7 g, 84.5%) m.p. 99.5°C (reported[10] m.p. 99.5°C); ν_{max}^{nujol} 1680, 1603, 1320, 1180, 1009, 855 and 763 cm^{-1}.

The results of the cognate preparations of other 4-n-alkylbenzoic acids are given in table 4.8.

4-Biphenylyl 4"-n-butylbenzoate

A mixture of 4-n-butylbenzoic acid (5.34 g, 0.03 mol) and redistilled thionyl chloride (12 ml) was refluxed for five hours and the excess of thionyl chloride was removed by distillation under reduced pressure. 4-Hydroxybiphenyl (5.1 g, 0.03 mol) in anhydrous pyridine (30 ml) was added to the crude acid chloride and the mixture stirred magnetically at room temperature and left overnight. It was poured into a stirred mixture of concentrated hydrochloric acid (50 ml) and crushed ice (100 g) when a precipitate was obtained. It was filtered, washed with 10% aqueous

Table 4.8

Physical data of 4-n-alkylbenzoic acids

$R.C_6H_4.COOH$

R=n-Alkyl	Observed		Reported		
	m.p.°C	% Yield	m.p.°C	% Yield	Reference
C_2H_5	113-113.5	81	113.5	-	24
C_3H_7	141-42	94	141	-	25
C_5H_{11}	92	81	88	91	26
C_6H_{13}	98	71	97	89	26
C_7H_{15}	103.5	84	101.5	88	26
C_8H_{17}	100	81	100	85	26
C_9H_{19}	99	94	98.5	-	10
$C_{10}H_{21}$	97	75	94.5	-	10
$C_{11}H_{23}$	98	70	-	-	-
$C_{12}H_{25}$	96	72	-	-	-

odium hydroxide solution (200 ml) and water (250 ml) and dried. This was chromatographed on silica gel and eluted with benzene. Removal of solvent from the eluate afforded a white material which was recrystallised from absolute ethyl alcohol to constant melting point (9.2 g, 82.5%) m.p. 133.4°C; ν_{max}^{nujol} 1725, 1603, 1454, 1370, 1218, 1168, 1005, 875 and 760 cm^{-1}; δ ($CDCl_3$) 0.93 (t, 3H, $-C\underline{H}_3$) 1.1-2.0 (m, 4H, methylenes) 2.7 (t, 2H, $arC\underline{H}_2$) 7.16-8.3 (m, 13H, $ar\underline{H}$)

[Found: C, 83.99; H, 6.58% $C_{23}H_{22}O_2$ requires
C, 83.64; H, 6.66%].

The physical data of the cognate preparations of other biphenylyl 4"-n-alkylbenzoates are given below.

<u>4-Biphenylyl 4"-methylbenzoate</u>

Yield 92%, m.p. 155.5°C; ν_{max}^{nujol} 1725, 1603, 1486, 1220, 1076, 1005, 875 and 757 cm^{-1}; δ ($CDCl_3$) 2.4 (s, 3H, $-C\underline{H}_3$) 7.0-8.16 (m, 13H, $ar\underline{H}$)

[Found: C, 83.36; H, 5.83% $C_{20}H_{16}O_2$ requires
C, 83.33; H, 5.55%].

<u>4-Biphenylyl 4"-ethylbenzoate</u>

Yield 82%, m.p. 153°C; ν_{max}^{nujol} 1725, 1608, 1462, 1215, 1078, 1005, 850 and 755 cm^{-1}; δ ($CDCl_3$) 1.26 (t, 3H, $-C\underline{H}_3$)

2.66 (q, 2H, arC$\underline{H}_2$-) 7.1-8.3 (m, 13H, ar$\underline{H}$)

[Found: C, 83.77; H, 6.18% $C_{21}H_{18}O_2$ requires
C, 83.41; H, 5.96%].

4-Biphenylyl 4"-n-propylbenzoate

Yield 87%, m.p. 114.2°C; ν_{max}^{nujol} 1726, 1604, 1460, 1220, 1077, 1005, 878 and 762 cm^{-1}; δ ($CDCl_3$) 0.93 (t, 3H, -C$\underline{H}_3$) 1.33-2.0 (m, 2H, -C$\underline{H}_2$-) 2.66 (t, 2H, arC$\underline{H}_2$) 7.13-8.5 (m, 13H, ar$\underline{H}$)

[Found: C, 83.75; H, 6.59% $C_{22}H_{20}O_2$ requires
C, 83.54; H, 6.35%].

4-Biphenylyl 4"-n-pentylbenzoate

Yield 89%, m.p. 137.5°C; ν_{max}^{nujol} 1725, 1602, 1485, 1220, 1074, 1005, 875 and 757 cm^{-1}; δ ($CDCl_3$) 0.9 (t, 3H, -C$\underline{H}_3$) 1.06-2.03 (m, 6H, methylenes) 2.7 (t, 2H, arC$\underline{H}_2$) 7.16-8.3 (m, 13H, ar$\underline{H}$)

[Found: C, 83.41; H, 7.19% $C_{24}H_{24}O_2$ requires
C, 83.71; H, 6.97%].

4-Biphenylyl 4"-n-hexylbenzoate

Yield 85%, m.p. 130.3°C; ν_{max}^{nujol} 1730, 1605, 1490, 1218, 1270, 1005, 878 and 758 cm^{-1}; δ ($CDCl_3$) 0.9 (t, 3H, -C$\underline{H}_3$) 1.1-2.1 (m, 8H, methylenes) 2.7 (t, 2H, arC$\underline{H}_2$) 7.1-8.23 (m, 13H, ar$\underline{H}$)

[Found: C, 83.89; H, 7.00% $C_{25}H_{26}O_2$ requires
C, 83.79; H, 7.26%].

4-Biphenylyl 4"-n-heptylbenzoate

Yield 77%, m.p. 120.3°C; ν_{max}^{nujol} 1725, 1606, 1460, 1218, 1070, 1005, 875 and 762 cm^{-1}; δ ($CDCl_3$) 0.9 (t, 3H, $-C\underline{H}_3$) 1.06-2.0 (m, 10H, methylenes) 2.73 (t, 2H, ar$C\underline{H}_2$) 7.16-8.3(m, 13H, ar$\underline{H}$)

[Found: C, 83.56; H, 7.79% $C_{26}H_{28}O_2$ requires
C, 83.89; H, 7.52%].

4-Biphenylyl 4"-n-Octylbenzoate

Yield 83%, m.p. 112.6°C; ν_{max}^{nujol} 1725, 1604, 1470, 1218, 1075, 1006, 878 and 760 cm^{-1}; δ ($CDCl_3$) 0.9 (t, 3H, $-C\underline{H}_3$) 1.1-2.03 (m, rat, methylenes) 2.71 (t, 2H, ar$C\underline{H}_2$) 7.16-8.3 (m, 13H, ar$\underline{H}$)

[Found: C, 83.51; H, 7.61% $C_{27}H_{30}O_2$ requires
C, 83.92; H, 7.77%].

4-Biphenylyl 4"-n-nonylbenzoate

Yield 76%, m.p. 105.5°C; ν_{max}^{nujol} 1725, 1606, 1468, 1218, 1072, 1005, 876 and 760 cm^{-1}; δ ($CDCl_3$) 0.9 (t, 3H, $-C\underline{H}_3$) 1.1-2.03 (m, 14H, methylenes) 2.73 (t, 2H, ar$C\underline{H}_2$) 7.2-8.35 (m, 13H, ar$\underline{H}$)

[Found: C, 83.56; H, 8.19% $C_{28}H_{32}O_2$ requires
C, 83.99; H, 7.99%].

4-Biphenylyl 4"-n-decylbenzoate

Yield 79%, m.p. 106°C; ν_{max}^{nujol} 1725, 1604, 1462, 1213 1076, 1005, 878 and 759 cm^{-1}; δ (CDCl$_3$) 0.9 (t, 3H, $-C\underline{H}_3$) 1.06-2.03 (m, 16H, methylenes) 2.73 (t, 2H, ar$C\underline{H}_2$) 7.23-8.33 (m, 13H, ar$\underline{H}$)

[Found: C, 84.09; H, 8.56% $C_{29}H_{34}O_2$ requires
C, 84.07; H, 8.21%].

4-Biphenylyl 4"-n-undecylbenzoate

Yield 74%, m.p. 105.5°C; ν_{max}^{nujol} 1725, 1608, 1469, 1218, 1064, 1004, 877 and 760 cm^{-1}; δ (CDCl$_3$) 0.9 (t, 3H, $-C\underline{H}_3$) 1.06-2.0 (m, 18H, methylenes) 2.75 (t, 2H, ar$C\underline{H}_2$) 7.23-8.36 (m, 13H, ar$\underline{H}$)

[Found: C, 84.33; H, 8.80% $C_{30}H_{36}O_2$ requires
C, 84.12; H, 8.41%].

4-Biphenylyl 4"-n-dodecylbenzoate

Yield 83%, m.p. 103°C; ν_{max}^{nujol} 1725, 1604, 1465, 1374, 1218, 1075, 1005, 878 and 758 cm^{-1}; δ (CDCl$_3$) 0.86 (t, 3H, $-C\underline{H}_3$) 1.03-2.0 (m, 20H, methylenes) 2.7 (t, 2H, ar$C\underline{H}_2$) 7.16-8.33 (m, 13H, ar$\underline{H}$)

[Found: C, 84.45; H, 8.70% $C_{31}H_{38}O_2$ requires
C, 84.16; H, 8.59%].

Ethyl 4-hydroxybenzoate

A mixture of 4-hydroxybenzoic acid (41.4 g, 0.3 mol), absolute ethyl alcohol (200 ml) and concentrated sulphuric acid (5 ml) was refluxed on a water bath for eight hours and the excess alcohol was removed by distillation. The mixture was cooled, diluted with water (200 ml) and extracted with ether (3 x 100 ml). The combined ethereal solution was washed with 10% sodium bicarbonate solution (2x100 ml) and water (2x100 ml) and dried (Na_2SO_4). Removal of solvent afforded the required eater (47.9 g, 99%) m.p. 116°C (reported[27] m.p. 116°C).

4-n-Butoxybenzoic acid

This was prepared following the procedure of Lauer *et al.*[28] Thus, from ethyl 4-hydroxybenzoate (16.6 g, 0.1 mol), sodium (2.3 g, 0.1 mol), n-butyl iodide (20.24 g, 0.11 mol) absolute ethyl alcohol (100 ml), and hydrolysing the product with ethanolic potassium hydroxide, 4-n-butoxybenzoic acid (13.6 g, 82%) m.p. 147°C was obtained (reported[28] m.p. 147-148°C); ν_{max}^{nujol} 1668, 1602, 1504, 1170, 854 and 775 cm^{-1}.

The physical data of the cognate preparations of other 4-n-alkoxybenzoic acids are given table 4.9.

Table 4.9

Melting points of 4-n-alkoxybenzoic acids

$RO.C_6H_4.COOH$

R = n-Alkyl	Observed		Reported[28]
	m.p.°C	% Yield	m.p.°C
CH_3	184	92	180–182
C_2H_5	195.5	95	195
C_3H_7	145	90	145.5–147
C_5H_{11}	124	94	123–124
C_6H_{13}	105	92	105.5–107
C_7H_{15}	92	95	92
C_8H_{17}	101	91	100
C_9H_{19}	94	90	92
$C_{10}H_{21}$	96.5	90	92
$C_{11}H_{23}$	84	92	84.5 (ref.29)
$C_{12}H_{25}$	95	95	95

4-Biphenylyl 4"-n-butoxybenzoate

A mixture of 4-n-butoxybenzoic acid (3.88 g, 0.02 mol) and freshly distilled thionyl chloride (12 ml) was refluxed for three hours and the excess of thionyl chloride was removed by distillation under reduced pressure. 4-Hydroxybiphenyl(3.4 g, 0.02 mol) in anhydrous pyridine (60 ml) was added to the crude acid chloride and stirred magnetically at room temperature and left overnight. The reaction mixture was poured onto a stirred mixture of concentrated hydrochloric acid (100 ml) and crushed ice (200 g) when a precipitate was obtained. This was filtered, washed with 10% aqueous sodium hydroxide solution (200 ml) and water (250 ml) and dried. The crude material was chromatographed on neutral alumina and was eluted with benzene. Removal of solvent from the eluate afforded a white material which was crystallised from benzene-petroleum ether (40-60°) to constant melting point (6.4 g, 90%) m.p. 156.5°C; ν_{max} 1725, 1602, 1580, 1460, 1170, 1078, 856 and 763 cm^{-1}; δ ($CDCl_3$) 1.0 (s, 3H, $-CH_3$) 1.2-2.0 (m, 4H, methylenes) 4.18 (t, 2H, $-OCH_2-$) 7.0 (d, 2H, arH, J=9 Hz) 7.2-7.6 (m, 9H, arH) 8.2 (d, 2H, arH, J=9Hz).

[Found: C, 79.64; H, 6.45% $C_{22}H_{23}O_3$ requires
C, 79.77; H, 6.35%].

The physical data of the cognate preparations of other 4-biphenylyl 4"-n-alkoxybenzoates are given below.

4-Biphenylyl 4"-methoxybenzoate

Yield 86%, m.p. 156.5°C; ν_{max}^{nujol} 1725, 1604, 1518, 1454, 1260, 1164, 1072, 1004, 879 and 759 cm^{-1}; δ ($CDCl_3$) 3.63 (a, 3H, $-OCH_3$) 6.8 (d, 2H, arH, J=9Hz) 6.9-7.6 (m, 9H, arH) 8.16 (d, 2H, arH, J=9 Hz)

[Found: C, 78.78; H, 5.50% $C_{20}H_{16}O_3$ requires
a, 70.94, H, 5.26%].

4-Biphenylyl 4"-ethoxybenzoate

Yield 82%, m.p. 160°C; ν_{max}^{nujol} 1725, 1603, 1518, 1260, 1178, 1074, 1005, 855 and 759 cm^{-1}; δ ($CDCl_3$) 1.43 (t, 3H, $-CH_3$) 4.1 (q, 2H, $-OCH_2-$) 7.0 (d, 2H, arH, J=9 Hz) 7.16-7.75 (m, 9H, arH) 8.23 (d, 2H, arH, J=9 Hz)

[Found: C, 79.52; H, 5.76% $C_{21}H_{18}O_3$ requires
C, 79.25; H, 5.66%].

4-Biphenylyl 4"-n-propoxybenzoate

Yield 81%, m.p. 146°C; ν_{max}^{nujol} 1725, 1603, 1510, 1460, 1258, 1163, 1072, 1005, 878 and 757 cm^{-1}; δ ($CDCl_3$) 1.03 (t, 3H, $-CH_3$) 1.43-2.16 (m, 2H, $-CH_2-$) 4.0 (t, 2H, $-OCH_2-$) 6.91 (d, 2H, arH, J=9Hz) 7.18-7.8 (m, 9H, arH) 8.11 (d, 2H, arH, J=9 Hz)

[Found: C, 79.50; H, 6.28% $C_{22}H_{20}O_3$ requires
C, 79.52; H, 6.02%].

4-Biphenylyl 4"-n-pentyloxybenzoate

Yield 79%, m.p. 154.5°C; ν_{max}^{nujol} 1725, 1603, 1510, 1458, 1260, 1170, 1074, 1005 and 759 cm^{-1}; δ ($CDCl_3$) 0.95 (t, 3H, $-C\underline{H}_3$) 1.13-2.23 (m, 6H, methylenes) 4.05 (t, 2H, $-OC\underline{H}_2$) 6.98 (d, 2H, ar$\underline{H}$, J=9Hz) 7.2-7.96 (m, 9H, ar$\underline{H}$) 8.2 (d, 2H, ar$\underline{H}$, J = 9 Hz)

[Found: C, 80.00; H, 6.94% $C_{24}H_{24}O_3$ requires
C, 80.00; H, 6.76%].

4-Biphenylyl 4"-n-hexyloxybenzoate

Yield 87%, m.p. 132.5°C; ν_{max}^{nujol} 1725, 1603, 1510, 1463, 1250, 1164, 1070, 1005, 875 and 758 cm^{-1}; δ ($CDCl_3$) 0.93 (t, 3H, $-C\underline{H}_3$) 1.1-2.16 (m, 8H, methylenes) 4.1 (t, 2H, $-OC\underline{H}_2$) 7.0 (d, 2H, ar$\underline{H}$, J=9Hz) 7.23-7.9 (m, 9H, ar$\underline{H}$) 8.26 d, 2H, ar$\underline{H}$, J=9Hz)

[Found: C, 80.19; H, 7.18% $C_{25}H_{26}O_3$ requires
C, 80.21; H, 6.95%].

4-Biphenylyl 4"-n-heptyloxybenzoate

Yield, 79%, m.p. 126°C; ν_{max}^{nujol} 1725, 1602, 1490, 1254, 1168, 1673, 1004, 844 and 759 cm^{-1}; δ ($CDCl_3$) 0.91 3H, $-C\underline{H}_3$) 1.1-2.11 (a, 10H, methylenes) 4.05 (t, 2H, $-OC\underline{H}_2$) 7.0 (d, 2H, ar$\underline{H}$, J=9Hz) 7.13-7.8 (m, 9H, ar$\underline{H}$) 8.18 (d, 2H, ar$\underline{H}$, J=9Hz)

[Found: C, 80.55; H, 7.57% $C_{26}H_{28}O_3$ requires
C, 80.42; H, 7.22%].

4-Biphenylyl 4"-n-octyloxybenzoate

Yield, 81%, m.p. 120°C; ν_{max}^{nujol} 1725, 1603, 1491, 1255, 1168, 1072, 1005, 880 and 760 cm^{-1}; δ ($CDCl_3$) 0.91 (t, 3H, $-C\underline{H}_3$) 1.06–2.1 (m, 12H, methylenes) 4.03 (t, 2H, $-OC\underline{H}_2-$) 6.93 (d, 2H, ar$\underline{H}$, J=9Hz) 7.1–7.8 (m, 9H, ar$\underline{H}$) 8.16 (d, 2H, ar$\underline{H}$, J=9Hz)

[Found: C, 80.22; H, 7.63% $C_{27}H_{30}O_3$ requires
C, 80.60; H, 7.46%].

4-Biphenylyl 4"-n-nonyloxybenzoate

Yield 76%, m.p.117. 1°C; ν_{max}^{nujol} 1725, 1604, 1492, 1258, 1170, 1072, 1005, 881 and 762 cm^{-1}; δ ($CDCl_3$) 0.9 (t, $-C\underline{H}_3$) 1.1–2.1 (m, 14H, methylenes) 4.08 (t, 2H, $-OC\underline{H}_2-$) 7.03 (d, 2H, ar$\underline{H}$, J=9 Hz) 7.2–7.9 (m, 9H, ar$\underline{H}$) 8.26 (d, 2H, ar$\underline{H}$, J=9Hz)

[Found: C, 80.60; H, 7.90% $C_{28}H_{32}O_3$ requires
C, 80.77; H, 7.69%].

4-Biphenylyl 4"-n-decyloxybenzoate

Yield 79%, m.p. 110°C; ν_{max}^{nujol} 1725, 1603, 1483, 1315, 1190, 1070, 1003, 877 and 757 cm^{-1}; δ ($CDCl_3$) 0.88 (t, 3H, $-C\underline{H}_3$) 1.05–2.15 (m, 16H, methylenes) 4.0 (t, 2H, $OC\underline{H}_2-$) 6.9 (d,2H, ar$\underline{H}$, J=9Hz) 7.06–7.75 (m, 9H, ar$\underline{H}$) 8.1 (d, 2H, ar$\underline{H}$, J=9Hz)

[Found: C, 81.14; H, 7.98% $C_{29}H_{34}O_3$ requires
C, 80.93; H, 7.90%].

4-Biphenylyl 4''-n-dodecyloxybenzoate

Yield 77%, m.p. 109.7°C; ν_{max}^{nujol} 1725, 1603, 1485, 1315, 1192, 1070, 1005, 878 and 760 cm^{-1}; δ ($CDCl_3$) 0.88 (t, 3H-$C\underline{H}_3$) 1.06-2.1 (m, 20H, methylenes) 4.03 (t, 2H,-$OC\underline{H}_2$) 6.96 (d, 2H, ar$\underline{H}$, J=9Hz) 7.16-7.8 (m, 9H, ar$\underline{H}$) 8.2 (d, 2H, ar$\underline{H}$, J=9Hz)

[Found: C, 81.32; H, 8.28% $C_{31}H_{38}O_3$ requires
C, 81.21; H, 8.29%].

4-Cyanobenzoic acid

A mixture of 4-bromobenzoic acid (8.04 g, 0.04 mol), anydrous cuprous cyanide (5.372 g, 0.06 mol) and anhydrous dimethyl formamide (125 ml) was refluxed for 12 hours and cooled. The reaction mixture was poured onto a stirred mixture of hydrated ferric chloride (6.5 g), concentrated hydrochloric acid (5 ml) and water (200 ml). This was heated to 60°C and maintained at that temperature for about 30 minutes. The cooled reaction mixture was extracted with ether (4x100 ml) and the combined ethereal solution was washed with water (2x100 ml) and dried over anhydrous sodium sulfate. Removal of solvent afforded a white material which was recrystallised from glacial acetic acid (5.4 g, 92%) m.p. 218-219°C (reported^{30} m.p. 219°C); ν_{max}^{nujol} 2250, 1700, 1620, 1440, 1325, 1020, 866 and 773 cm^{-1}.

4-Biphenylyl 4"-cyanobenzoate

This was prepared following the method adopted for 4-biphenylyl 4"-n-butoxybenzoate as described earlier. Thus, from 4-cyanobenzoic acid (2.94 g, 0.02 mol), thionyl chloride (15 ml), 4-hydroxybiphenyl (3.4 g, 0.02 mol), and anhydrous pyridine (35 ml), 4-biphenylyl 4"-cyanobenzoate (5.5 g, 90%) m.p. 160°C was obtained; ν_{max}^{nujol} 2250, 1745, 1495, 1210, 1085, 1010 and 764 cm^{-1}; δ(CDCl$_3$) 7.25–8.55 (m, 13H, ar$\underline{H}$).

[Found: C, 80.2; H, 4.31; N, 4.62% $C_{20}H_{13}O_2N$ requires C, 80.26; H, 4.34; N, 4.68%].

4-Biphenylyl 4"-nitrobenzoate

From 4-nitrobenzoic acid (3.34 g, 0.02 mol) thionyl chloride (15 ml), 4-hydroxybiphenyl (3.4 g, 0.02 mol) and anhydrous pyridine (40 ml), 4-biphenylyl 4"-nitrobenzoate (6.2 g, 94.5%) was obtained. m.p. 172–173°C; ν_{max}^{nujol} 1735, 1604, 1520, 1355, 1085, 1010, 853 and 766 cm^{-1}; δ (CDCl$_3$) 7.2–8.6 (m, 13H, ar$\underline{H}$)

[Found: C, 71.51; H, 4.1; N, 4.24% $C_{19}H_{13}O_4N$ requires C, 71.47; H, 4.07; N, 4.38%].

4-Biphenylyl 4"-chlorobenzoate

From 4-chlorobenzoic acid (3.13 g, 0.02 mol), thionyl chloride (15 ml), 4-hydroxybiphenyl (3.4 g, 0.02 mol) and anhydrous pyridine (40 ml), 4-biphenylyl 4"-chlorobenzoate (5.8 g, 91%) was obtained. m.p. 170-171.5°C; ν_{max}^{nujol} 1725, 1590, 1490, 1195, 1095, 1015, 875 and 760 cm^{-1}; δ (CDCl$_3$) 7.3-8.5 (m, 13H, ar<u>H</u>)

[Found: C, 74.22; H, 4.40% $C_{19}H_{13}O_2Cl$ requires
C, 73.90; H, 4.21; Cl, 11.50%].

4-Biphenylyl 4"-bromobenzoate

From 4-bromobenzoic acid (4.02 g, 0.02 mol), thionyl chloride (20 ml), 4-hydroxybiphenyl (3.4 g, 0.02 mol) and anhydrous pyridine (40 ml), 4-biphenylyl 4"-bromobenzoate (6.3 g, 87%) was obtained, m.p. 187°C; ν_{max}^{nujol} 1725, 1590, 1490, 1196, 1010, 875 and 758 cm^{-1}; δ (CDCl$_3$) 7.3-8.4 (m, 13H, ar<u>H</u>)

[Found: C, 64.42; H, 3.80% $C_{19}H_{13}O_2Br$ requires
C, 64.58; H, 3.68; Br, 22.66%].

4-Acetylbiphenyl

This was prepared following the procedure of Long and Henze.[31] Thus, from biphenyl (61.6 g, 0.4 mol), acetyl chloride (31.4 g, 0.4 mol), anhydrous aluminium chloride (58.74 g, 0.44 mol) and carbon disulphide (300 ml), 4-acetylbiphenyl was obtained. This was recrystallised from ethyl alcohol (yield 69.0 g, 88%) m.p. 121°C (reported[31] yield 90%, m.p. 121°C).

Biphenyl-4-carboxylic acid

This was prepared following the procedure of Byron, Gray and Wilson.[32] Thus from 4-acetylbiphenyl (19.6 g, 0.1 mol), dioxan (210 ml), sodium hydroxide (32.0 g, 0.8 mol), bromine (64 g, 0.4 mol) and water (400 ml), biphenyl-4-carboxylic acid was obtained. This was recrystallised from ethyl alcohol (16 g, 80%) m.p. 228°C (reported[33] yield 79%, m.p. 228°C).

4-Cyanophenyl biphenylyl-4'-carboxylate

a mixture of biphenyl-4-carboxylic acid (2.97 g, 0.15 mol) and thionyl chloride (15 ml) was refluxed for twelve hours and the excess thionyl chloride was removed by distillation under reduced pressure. 4-Hydroxybenzonitrile (1.785 g, 0.15 mol) in anhydrous pyridine (30 ml) was addedto the crude acid chloride and stirred magnetically at room temperature for twentyfour hours. The reaction mixture was poured on to a stirred mixture of concentrated hydrochloric acid (50 ml) and crushed ice (200 g) and the precipitated solid was filtered, washed with 10% sodium hydroxide solution (150 ml) and water (200 ml) and dried. This was recrystallised from benzene repeatedly until the melting point was constant (4.0g, 87%), m.p. 155°C; ν_{max}^{nujol} 2235, 1725, 1603, 1461, 1272, 1165, 1005, 857 and 744 cm^{-1}; δ ($CDCl_3$) *7.2–0.5* (m, 13H, ar$\underline{H}$)

[Found: C, 80.13; H, 4.3; N, 4.54% $C_{20}H_{13}O_2N$ requires
C, 80.26; H, 4.34; N, 4.68%].

4'-Methoxybiphenyl-4-carboxylic acid

This was prepared according to tho procedure of Gray, Hartley and Jones.[34] Thus, from 4-methoxybiphenyl (15.0 g), 4'-methoxybiphenyl-4-carboxylic acid (10.8g) was obtained. m.p. 258°C (reported[34] m.p. 258°C).

4-Cyanophenyl 4"-methoxybiphenylyl-4'-carboxylate

From 4'-methoxybiphenyl-4-carboxylic acid (2.28 g, 0.01 mol), redistilled thionyl chloride (12 ml), 4-hydroxybenzonitrile (1.19 g, 0.01 mol) and anhydrous pyridine (30 ml), was obtained 4-cyanophenyl 4"-methoxybiphenylyl-4'-carboxylate (2.8 g, 85%), m.p.167°C; ν_{max}^{nujol} 2232, 1740, 1601, 1500, 1303, 1209, 1065, 900, 838 and 770 cm^{-1}; δ ($CDCl_3$) 3.86 (s, 3H, $-OC\underline{H}_3$) 6.8-8.4 (m, 12H, ar$\underline{H}$)

[Found: C, 76.42; H, 4.56; N, 4.21% $C_{21}H_{15}O_3N$ requires
C, 76.58; H, 4.59; N, 4.25%].

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