

CHAPTER V

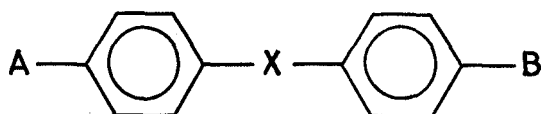
GENERAL PROCEDURE FOR THE PREPARATION OF 4-n-ALKYL-4'- CYANOBIPHENYLS AND 4-n-ALKYL-4"-CYANO-p-TERPHENYLS

5.1 Introduction

With the discovery of the use of liquid crystals in display devices utilising various electro-optical effects,¹ viz., (i) Freedericksz effect, (ii) the dynamic scattering effect, (iii) the twisted nematic effect, (iv) the cholesteric memory effect, (v) the cholesteric-nematic phase change effect, etc., the attention of the chemists was directed towards particular types of liquid crystals with specific characteristics. In addition to certain physical properties such as dielectric anisotropy, resistivity, etc. the compounds had to satisfy various other conditions in order to find applications. These requirements are (a) the compounds must be low melting - the crystal-nematic transition temperature should be -10°C or lower, (b) the mesophase should persist till about $+70^{\circ}\text{C}$, (a) the compounds must be chemically stable to hydrolysis, oxidation, etc., (d) they must be colourless, photochemically and electrochemically stable and, finally (e) the compounds used should be safe chemicals which do not pose health problems to those handling them either during their manufacture or filling up of the cells.

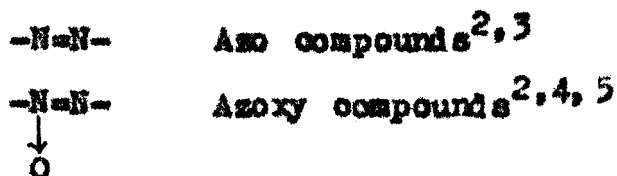
As discussed in chapter I, compounds with both positive and negative dielectric anisotropy are required and the response times and relaxation times in these electrically operated devices are also dependent on the chemical nature of the mesogen. Therefore, from the chemists point of view the task is not easy and to-date no single compound has satisfied all these conditions.

A survey of the majority of known nematogens, which have a fairly low crystal-nematic temperatures shows that such chemicals have the general formula,



where two *p*-phenylene rings are linked through a central group X. In most of the cases the group X contains a double or a triple bond to maintain the rigidity and linearity of the molecules. The *p*, *p'* substituents A and B may vary widely and the lowest crystal-nematic temperatures have been obtained when A = *n*-alkyl and B = *n*-alkoxy or vice versa or A and B = *n*-alkyl.

Examples of central group represented by X in the general formula are



$-\text{CH}=\text{N}-$	Schiff's bases ^{5,6,7}
$-\text{C}=\text{C}-$	Stilbenes ^{8,9,10}
$-\text{C}\equiv\text{C}-$	Tolanes ^{11,12,13}
$-\text{CH}=\text{N}-$ ↓ O	Nitrones. ^{14,15,16}

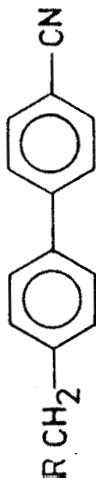
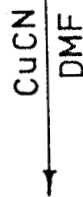
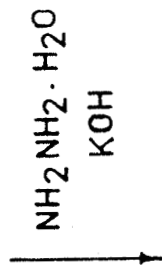
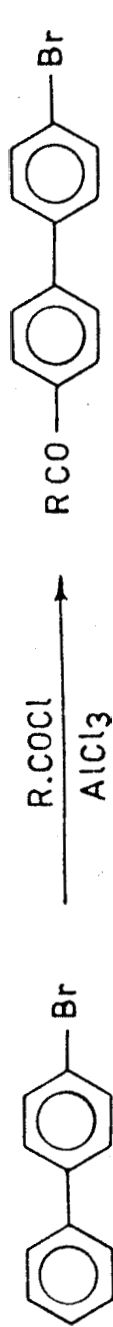
Azo compounds are highly coloured and are susceptible to oxidation and isomerisation. Azoxy compounds are also coloured. Schiff's bases are generally yellow in colour and undergo oxidation and hydrolysis rather easily. It should however be mentioned here that 4-methoxybenzylidene-4'-n-butylaniline (MBBA) was the most widely used compound in electro-optical devices until a few years ago. The stilbenes and tolans are colourless materials but the former compounds are highly photochemically unstable especially to ultraviolet light. However, the tolans seem to be, quite stable. Aldonitrones are colourless substances but tend to decompose thermally and photochemically. In addition to the above central linkage groups, an ester

linkage $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ 17,18,19 which has been used in 4,4'-disubstituted phenylbenzoates and related esters has been found to be very useful. In fact, a large proportion of the compounds that are being reported of late belong to this class. These esters are colourless compounds and give fairly low crystal-nematic temperatures when suitable mixtures are prepared.¹⁹

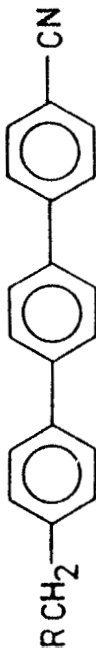
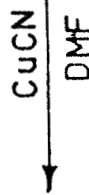
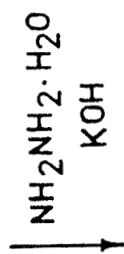
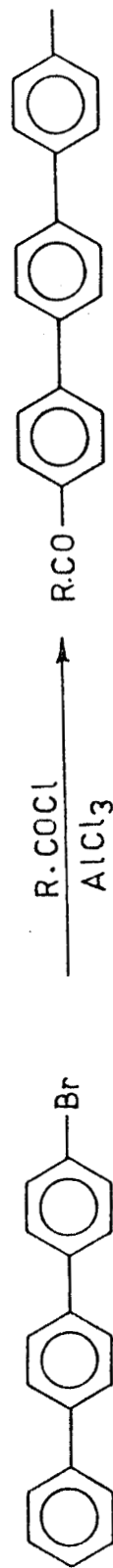
Gray et al²⁰ synthesised a new class of liquid crystals, in which the problems of colour, instabilities due to chemical and photochemical reactions were eliminated by not having any central linkage group. They prepared a number of 4,4'-disubstituted biphenyls of which some are the 4-n-alkyl-4'-cyanobiphenyls (Chart VIIa) are nematic at room temperature. These, individually, do not have the desired temperature range for use in display devices. Later Gray et al²¹ extended this work to synthesise 4-n-alkyl-4'-cyano-p-terphenyls by a similar route (Chart VIIb). These compounds are also stable but have higher melting points and wide nematic thermal ranges. Suitable mixtures of these two systems give excellent temperature ranges and can be used in twisted nematic or phase change effect displays, since the materials are of positive dielectric anisotropy.

Because of their wide utility, these compounds have become important commercially. The procedure of Cade and Pilbeam²² which was adopted by Gray et al²¹ for the preparation of 4-bromo-p-terphenyl, an intermediate compound, presented some problems. These two groups of workers have reported a yield of 48.5% and 25-45% respectively, for several runs. Moreover, isolation of the pure monobromo derivative in good yield has been a difficulty. Further the use of hazardous bromine or the poisonous cuprous

CHART VII



(a)



R = n-Alkyl

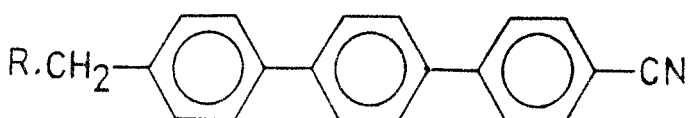
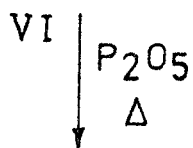
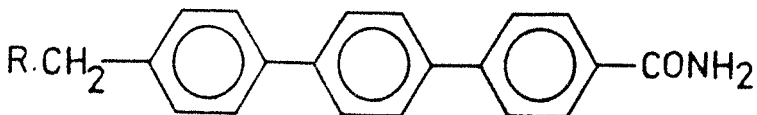
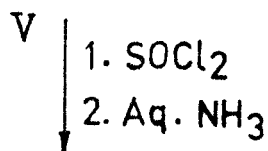
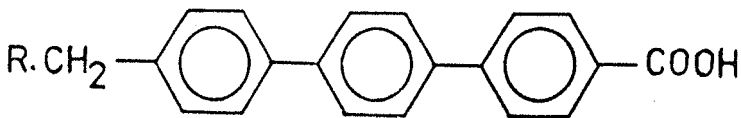
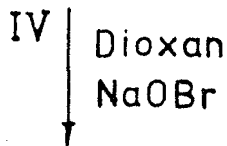
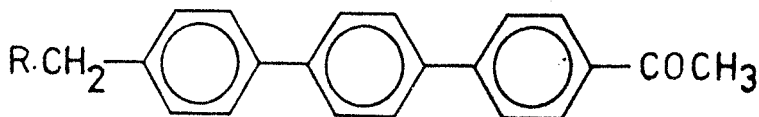
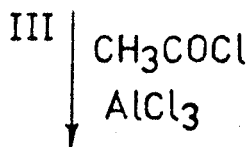
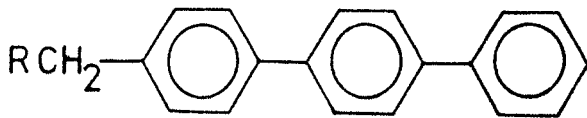
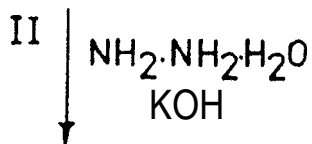
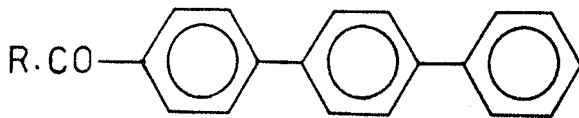
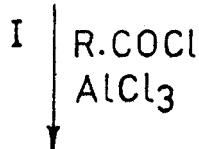
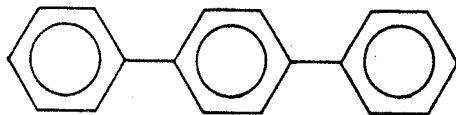
cyanide may not be desirable, especially when working on a large scale. These difficulties prompted us to develop a convenient general procedure²³ for the preparation of both 4-n-alkyl-4''-cyano-p-terphenyls and 4-n-alkyl-4'-cyanobiphenyls. The procedure has been described below for the former compounds and is shown schematically (Charts VIII and IX).

5.2 Synthesis of 4-n-alkyl-4''-cyano-p-terphenyl

This method consists of the Friedel-Crafts reaction on p-terphenyl I (Chart VIII), with an n-acyl halide to furnish 4-n-acyl-p-terphenyl II. Amongst the various solvents suitable for this reaction, nitrobenzene has been found to be the best solvent. This ketone 33 on Huang-Minlon reduction afforded the 4-n-alkyl-p-terphenyl III, which was again acylated with acetyl chloride to yield 4-n-alkyl-4''-cyano-p-terphenyl IV. Oxidation of IV with sodium hypobromite gave the corresponding carboxylic acid V, which on treatment with thionyl chloride gave the acid chloride. Next, the acid chloride was reacted with liquor ammonia to afford the carboxamide VI, which was conveniently dehydrated using phosphorus pentoxide to yield the desired 4-n-alkyl-4''-cyano-p-terphenyl VII. The yields were good in all the steps.

The same series of reactions were performed on biphenyl VIII (Chart IX) to obtain the desired 4-n-alkyl-

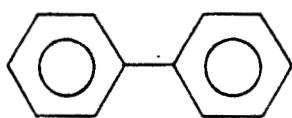
CHART VIII



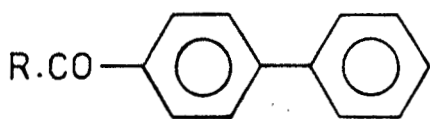
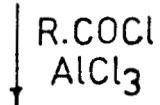
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R = n-Alkyl

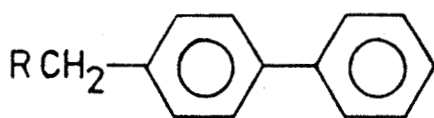
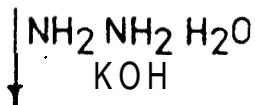
CHART IX



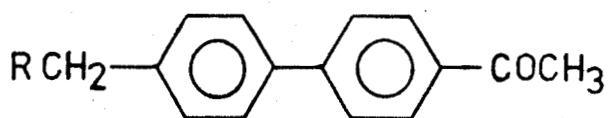
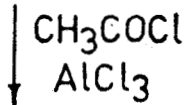
VIII



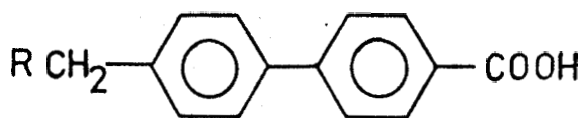
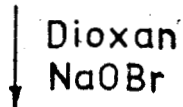
IX



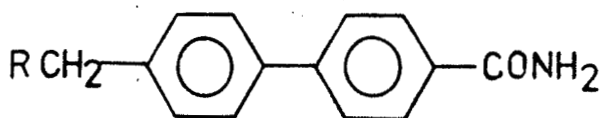
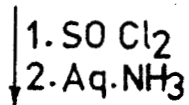
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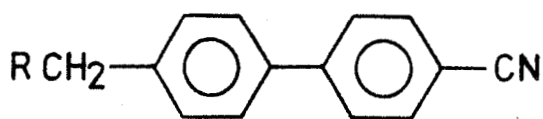
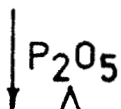
XI



XII



XIII



XIV

R = n-Alkyl

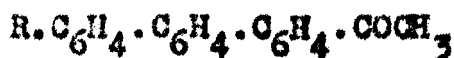
4'-cyanobiphenyl XIV. This general procedure is economical and quite safe in so far as the handling of the chemicals at various stages is concerned. A recent report of Oh²⁴ involves a slight modification of the above procedure and he has also compared the costs of production of 4-n-alkyl-4'-cyanobiphenyls by conventional and the modified procedures. It is heartening to note that this route is far more economical than the conventional one.

5.3 Mesomorphic properties of p-terphenyl derivatives

During this study, it was found that 4-n-alkyl-4''-acetyl-p-terphenyls also exhibit mesomorphic properties. Their transition temperatures are summarised in table 5.1 below.

Table 5.1

Transition temperatures of 4-n-alkyl-4''-acetyl-p-terphenyls



R	K $\xrightarrow{\quad}$ S °C	S $\xrightarrow{\quad}$ I °C	ΔT °C Thermal range
n-C ₅ H ₁₁	231.5	258.5	27.0
n-C ₆ H ₁₃	229.0	253.0	24.0
n-C ₇ H ₁₅	233.5	258.0	24.5
n-C ₈ H ₁₇	230.5	249.5	19.0

All the four compounds melt to a smectic phase which on further heating goes over to this isotropic phase without the formation of a nematic phase. This is not surprising, as it may be mentioned that even the first members of a series of 4-n-alkyl- and 4-n-alkoxy-4'-n-alkanoylbiphenyls²⁵ show a similar behaviour. This is probably due to the strong dipole moment of the carbonyl group operating across the major molecular axis of the molecules, which would increase the lateral attractive forces between molecules. The smectic phase of these compounds shows a mosaic texture which is shown in plate 3. However, the kind of smectic phase has not yet been identified. A plot of the transition temperatures against the number of carbon atoms in the alkyl chain is shown in figure 5.1. It can be seen that both the crystal-smectic and smectic-isotropic transition points alternate.

Based on structural features, the 4-n-alkyl-p-terphenyl-4''-carboxylic acids are expected to show mesomorphic properties. All the four acids are indeed mesomorphic, but the melting points are around 300°C (see Experimental). As a consequence the compounds undergo thermal decomposition in the mesophase. The mesophase-isotropic transition points appear to be >350°C. However, the transition temperatures are not quite reversible and have not been given. The transition temperatures for the



Plate 3

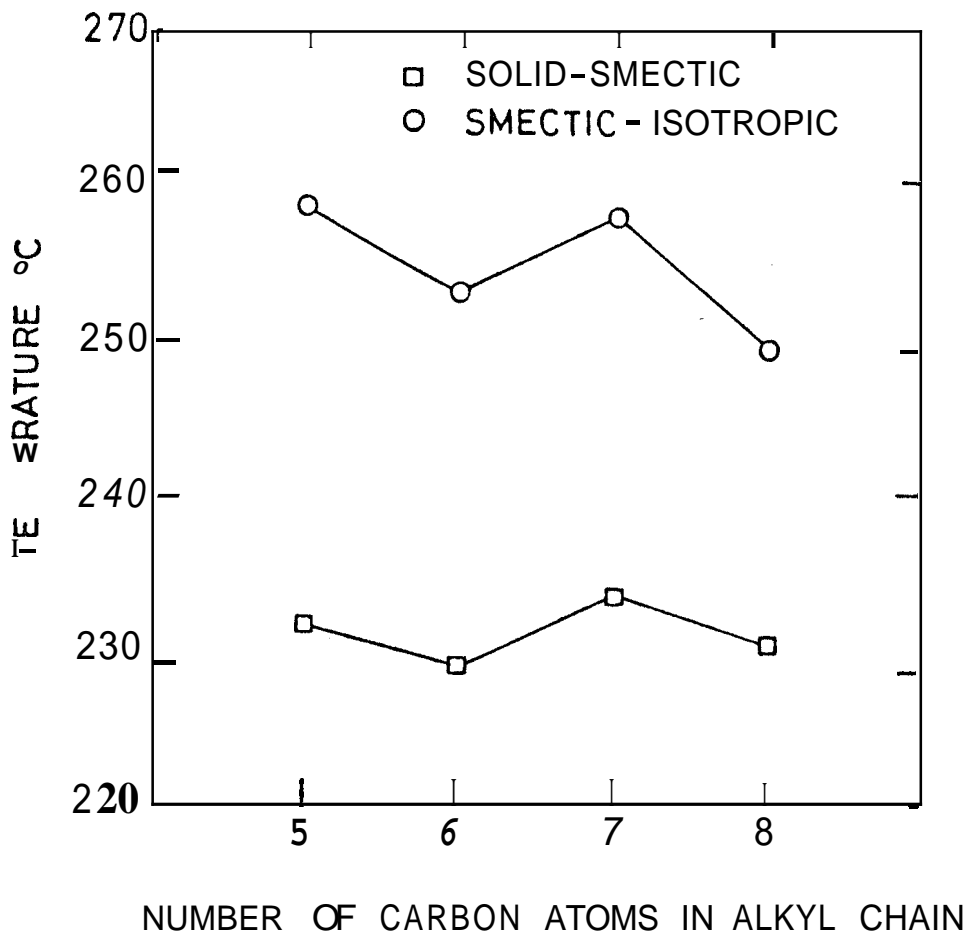


Fig. 5.1

Plot of transition temperatures against number of carbon atoms in the alkyl group for 4-n-alkyl-4''-acetyl-p'-terphenyls.

4-n-alkyl-4''-cyano-p-terphenyls obtained by the above method agree quite well with those reported by Gray et al²⁶ and are given in table 5.2 below.

Table 5.2

Transition temperatures of 4-n-alkyl-4''-cyano-p-terphenyls

R = <i>n</i> -Alkyl	K → N or S ₃ °C	S ₃ → S ₂ °C	S ₂ → S ₁ °C	S ₁ → N °C	N → I °C
n-C ₅ H ₁₁	130	-	-	-	239
n-C ₆ H ₁₃	124.5	-	-	-	227
n-C ₇ H ₁₅	134.0	-	-	(124.5)	222
n-C ₈ H ₁₇	126.0	127.0	131.5	195.0	215

Regarding the smectic phases of the octyl derivative, no miscibility studies were made to establish the identity of various smectic phases. The following sequence of texture pattern change was observed from the nematic phase as the sample was cooled. A fan-shaped texture to a schlieren texture and then to a mosaic texture before the sample crystallised. These changes at the temperatures mentioned, indicated the polymesomorphism in this compound. Gray²⁶ on the basis of miscibility studies has assigned smectic A, B and modifications to these three S₁, S₂ and S₃ phases respectively. A plot of the transition temperatures against

the number of carbon atoms in the alkyl chain is shown in figure 5.2. Although there is an alternation in the melting points, the N-I transition temperature continuously decreases for these four homologues.

5.4 Mesomorphic properties of biphenyl derivatives

As mentioned earlier some of the simplest 4,4'-disubstituted biphenyls show mesomorphic properties. 4-n-Alkyl-4'-acetylbiphenyls exhibit mesomorphism. Their transition temperatures are summarised in table 5.3. As can be seen the pentyl derivative is not mesomorphic whereas the hexyl and heptyl derivatives are enantiotropic smectic and the octyl and nonyl derivatives are monotropic smectic. The latter two compounds are metastable, because they have somewhat higher melting points. All the four compounds show a mosaic texture and a typical texture is shown in plate 4.

Table 5.3: Transition temperatures of 4-n-alkyl-4'-acetylbiphenyls, $R.C_6H_4.C_6H_4.COCH_3$

R	K \longrightarrow S or I	S \longrightarrow I
n-C ₅ H ₁₁	66.5	-
n-C ₆ H ₁₃	74.0	83.5
n-C ₇ H ₁₅	74.0	85.0
n-C ₈ H ₁₇	85.0	(83)
n-C ₉ H ₁₉	85.5	(82.5)

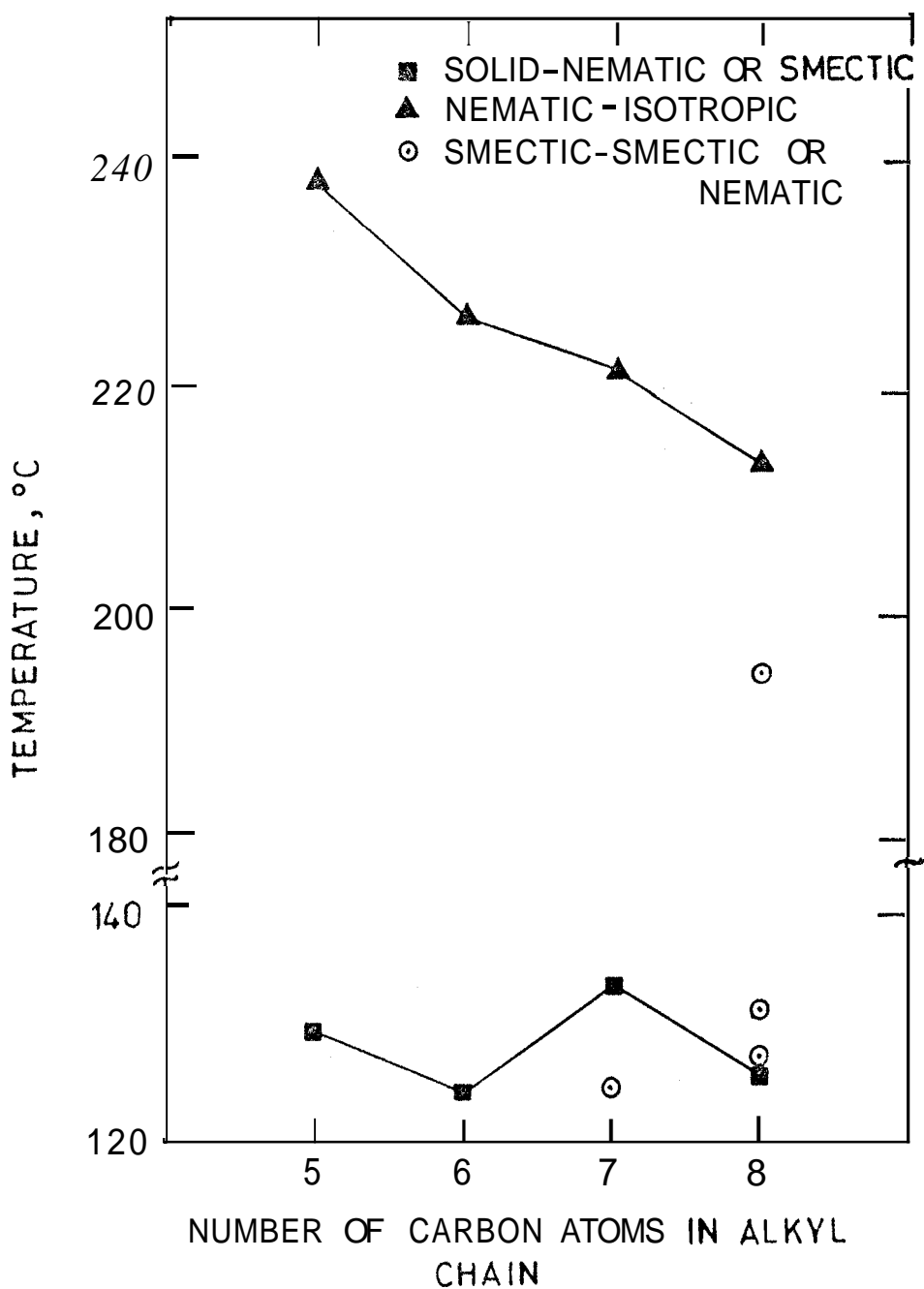


Figure 5.2

Plot of transition temperatures against number of carbon atoms in the alkyl chain for 4-n-alkyl-4''-cyano-p-terphenyls.



Plate 4

4-*n*-Alkylbiphenyl-4'-carboxylic acids are also expected to show mesomorphic properties. All the five acids are enantiotropic smectic and nematic. Their transition temperatures are summarised in table 5.4 below. The acids have wide thermal ranges because of the elongated nature of these molecules which are present in the form of dimers.

Table 5.4

Transition temperatures of 4-*n*-alkylbiphenyl-4'-carboxylic acids

R = <i>n</i> -Alkyl	K → S	S → N	N → I
n-C ₅ H ₁₁	174	200	258
n-C ₆ H ₁₃	178	219.5	257
n-C ₇ H ₁₅	158	232	254
n-C ₈ H ₁₇	156	228	246
n-C ₉ H ₁₉	139	238	250

The 4-*n*-alkyl-4'-cyanobiphenyls, obtained by the dehydration of 4-*n*-alkylbiphenyl-4'-carboxamides, are all colourless, stable room temperature liquid crystals. They have a strong positive dielectric anisotropy²⁷ and are useful compounds in many applications. The transition temperatures of these are given in table 5.5 below and they agree quite well with those reported by Gray et al²⁰ whose values are included in parentheses.

Table 5.5

Transition temperatures of 4-n-alkyl-
4'-cyanobiphenyls

R = <i>n</i> -Alkyl	K \longrightarrow S or N	S \longrightarrow N	N \longrightarrow I
C ₅ H ₁₁	22.5 (22.5)	-	35 (35)
C ₆ H ₁₃	13.5 (13.5)	-	29.5 (27)
C ₇ H ₁₅	28.5 (28.5)	-	42 (42)
C ₈ H ₁₇	21 (21)	32.5 (32.5)	40.5 (40)
C ₉ H ₁₉	40.5 (40.5)	45 (44.5)	48 (47.5)

EXPERIMENTAL4-n-Pentanoyl-p-terphenyl

In a two litre three-necked flask fitted with a reflux condenser, a mercury-sealed stirrer and a dropping funnel were placed p-terphenyl (46 g, 0.2 mol) and 'analar' nitrobenzene (350 ml). Anhydrous aluminium trichloride (29.37 g, 0.22 mol) was added and the mixture stirred at room temperature. n-Pentanoyl chloride (24.1 g, 0.2 mol) was introduced drop by drop to the stirred mixture during 45 minutes. Stirring was continued after addition for 2 hours at room temperature and then at 55-65°C for 2 more hours and left at room temperature overnight. The dark complex was hydrolysed with concentrated hydrochloric acid (100 ml) and ice-water (254 ml) and the reaction mixture steam distilled to remove nitrobenzene. The solid mass was filtered off, washed with water and air-dried.

It was recrystallised from 1,4-dioxan using activated charcoal (57g, 90%), m.p. 177-178°C, $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1686, 1603, 1383, 833 \text{ and } 780 \text{ cm}^{-1}; \delta (\text{CDCl}_3), 0.96(\text{t}, 3\text{H}, -\text{CH}_3) 1.3-1.93 (\text{m}, 4\text{H}, \text{methylenes}) 2.96 (\text{t}, 2\text{H}, -\text{COCH}_2) \text{ and } 7.1-8.05 (\text{m}, 13\text{H}, \text{arH})$

[Found: C, 87.58; H, 7.211% $\text{C}_{22}\text{H}_{32}\text{O}$ requires C, 87.9; H, 7.006%].

The results of the cognate preparations of other 4-n-alkanoyl-p-terphenyls are given below.

4-n-Hexanoyl-p-terphenyl

Yield 86%, m.p. 195-197°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1660, 1585, 1450, 975, 814 \text{ and } 757 \text{ cm}^{-1}$; δ (CDCl₃) 0.92 (t, 3H, -CH₃) 1.2-2.03 (m, 6H, methylenes) 3.0 (t, 2H, -COCH₂) 7.23-8.03 (m, 13H, arH)

[Found: C, 87.50; H, 7.6% $\text{C}_{24}\text{H}_{24}\text{O}$ requires C, 87.80; H, 7.32%].

4-n-Heptanoyl-p-terphenyl

Yield 92%, m.p. 194-197°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1665, 1593, 1460, 1370, 1190, 1000, 825 \text{ and } 763 \text{ cm}^{-1}$; δ (CDCl₃) 0.9 (t, 3H, -CH₃) 1.1-2.16 (m, 8H, methylenes) 3.03 (t, 2H, -COCH₂) 7.21-8.33 (m, 13H, arH)

[Found: C, 87.64; H, 7.50% $\text{C}_{25}\text{H}_{26}\text{O}$ requires C, 87.72; H, 7.60%].

4-n-Octanoyl-p-terphenyl

Yield 88%, m.p. 190-193°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1658, 1585, 1450, 1186, 997, 814 \text{ and } 758 \text{ cm}^{-1}$; δ (CDCl₃) 0.9 (t, 3H, -CH₃) 1.13-2.13 (m, 10H, methylenes) 3.01 (t, 2H, -COCH₂) 7.2-8.26 (m, 13H, arH)

[Found: C, 87.56; H, 7.88% $\text{C}_{26}\text{H}_{28}\text{O}$ requires C, 87.64; H, 7.86%].

4-n-Pentyl-p-terphenyl

A mixture of 4-n-pentanoyl-p-terphenyl (53.38 g, 0.17 mol), diethylene glycol (300 ml), potassium hydroxide pellets (28.77 g, 0.51 mol) and 90% hydrazine hydrate (36 ml) was heated at 110°C for 2 hours. The temperature was gradually raised to 180°C, distilling off the volatile matter in the process, and held at this temperature for 4 hours. The mixture was cooled when it became a solid mass. This was dissolved in chloroform (250 ml), wa— (200 ml) added and the mixture extracted with chloroform (3 x 100 ml). The combined organic phase was washed with water (4 x 100 ml) and dried, ^(Na₂SO₄). Removal of solvent afforded a pale brown material which was crystallised from isopropyl alcohol using activated charcoal to yield 4-n-pentyl-p-terphenyl (39.5 g, 86%) m.p. 177°C, $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1486, 1378, 811, 773 \text{ and } 685 \text{ cm}^{-1}$; 6 (CDCl₃), 0.91 (t, 3H, -CH₃), 1.15-1.91 (m, 6H, methylenes), 2.68 (t, 2H, arCH₂) and 7.11-7.75 (m, 13H, arH)

[Found: C, 92.00; H, 7.998% C₂₃H₂₄ requires
C, 92.00; H, 8.00%].

The results of the cognate preparations of other 4-n-alkyl-p-terphenyls are given below.

4-n-Hexyl-p-terphenyl:

Yield 92%, m.p. 170-172°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1496, 1472, 818,$

762 and 690 cm^{-1} , δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$) 1.06-2.0
(m, 8H, methylenes) 2.66 (t, 2H, arCH_2) 7.1-7.83 (m, 13H, arH)

[Found: C, 91.50; H, 8.39% $\text{C}_{24}\text{H}_{26}$ requires
C, 91.73; H, 8.28%

4-n-Heptyl-p-terphenyl:

Yield 87%, m.p. 170-171°C; \nearrow nujol $\begin{matrix} \text{max} \\ 1493, 1380, 835, \\ 810, 760 \text{ and } 690 \text{ cm}^{-1} \end{matrix}$, δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$)
1.06-2.0 (m, 10 H, methylenes) 2.66 (t, 2H, arCH_2) 7.13-
7.86 (m, 13H, arH)

[Found: C, 91.33; H, 8.41% $\text{C}_{25}\text{H}_{28}$ requires
C, 91.46; H, 8.53%].

4-n-Octyl-p-terphenyl

Yield 89%, m.p. 158-160°C; \nearrow nujol $\begin{matrix} \text{max} \\ 1471, 1380, \\ 815, 760 \text{ and } 746 \text{ cm}^{-1} \end{matrix}$, δ (CDCl_3) 0.86 (t, 3H, $-\text{CH}_3$)
1.03-2.0 (m, 12H, methylenes) 2.66 (t, 2H, arCH_2) 7.1-
7.8 (m, 13H, arH)

[Found: C, 91.45; H, 8.5% $\text{C}_{26}\text{H}_{30}$ requires
C, 91.22; H, 8.77%].

4-n-Pentyl-4''-acetyl-p-terphenyl

In a one litre three-necked flask fitted with a reflux condenser, a mercury-sealed mechanical stirrer and a dropping funnel, were placed 4-n-pentyl-p-terphenyl (42 g, 0.14 mol), 'analar' carbon tetrachloride (300 ml) and anhydrous aluminium chloride (24.03 g, 0.18 mol). The mixture was kept below 20°C and during stirring was added freshly distilled acetyl chloride (10.99 g, 0.14 mol), drop by drop, during 1 hour. Stirring was continued for 4 hours at the same temperature and left to stand for 36 hours. The dark coloured complex was decomposed with concentrated hydrochloric acid (75 ml) and ice-water (150 ml). Chloroform (100 ml) was added and the mixture extracted with chloroform (3 x 100 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Removal of solvent and recrystallisation of the residue from toluene afforded 35.7 g (85%) of the desired acetyl derivate (any unconverted starting material could be recovered by chromatography). m.p. 231.5°C; ν $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 1687, 1608, 1404, 1281, 810 and 683 cm^{-1} ; δ (CDCl_3) 0.91 (t, 3H, $-\text{CH}_3$) 1.18-1.88 (m, 6H, methylenes) 2.48-2.88 (t, 5H, arCH_2 and $-\text{COCH}_3$) and 7.08-8.15 (m, 12H, arH).

[Found: C, 37.46; H, 7.568% $\text{C}_{25}\text{H}_{26}\text{O}$ requires
C, 37.72; H, 7.603%].

The results of the cognate preparations of other 4-n-alkyl-4"-acetyl-p-terphenyls are given below.

4-n-Hexyl-4"-acetyl-p-terphenyl

Yield 87%, m.p. 229°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1690, 1614, 1495, 1405, 1370, 1276, 827, 768 \text{ and } 733 \text{ cm}^{-1}$; δ (CDCl₃) 0.9 (t, 3H, -CH₃) 1.12-2.03 (m, 8H, methylenes) 2.64 (t, 3H, arCH₂) 2.64 [s, 3H, -COCH₃] 7.16-8.26 (m, 12H, arH)

[Found: C, 87.34; H, 7.80% C₂₆H₂₈O requires
C, 87.66; H, 7.85%].

4-n-Heptyl-4"-acetyl-p-terphenyl

Yield 82%, m.p. 233.5°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1690, 1612, 1476, 1332, 1280, 826 \text{ and } 807 \text{ cm}^{-1}$; δ (CDCl₃) 0.91 (t, 3H, -CH₃) 1.1-2.06 (m, 10H, methylenes) 2.63 (t, 3H, arCH₂) 2.63 (s, 3H, -COCH₃) 7.2-8.36 (m, 12H, arH)

[Found: C, 87.82; H, 8.33% C₂₇H₃₀O requires
C, 87.56; H, 8.10%].

4-n-Octyl-4"^{acetyl}-p-terphenyl

Yield 82%, m.p. 230.5°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1688, 1605, 1458, 1270, 808 \text{ and } 785 \text{ cm}^{-1}$; δ (CDCl₃) 0.9 (t, 3H, -CH₃) 1.06-2.0 (m, 12H, methylenes) 2.63 (s, 3H, -COCH₃) 2.63 (t, 2H, arCH₂) 7.13-8.2 (m, 12H, arH)

[Found: C, 87.34; H, 8.42% C₂₈H₃₂O requires
C, 87.5; H, 8.33%].

4-n-Pentyl-p-terphenyl-4''-carboxylic acid

A solution of sodium hypobromite prepared at 0°C by adding bromine (54.6 g, 0.35 mol) to sodium hydroxide (49 g, 1.225 mol) in water (245 ml) was added slowly to a vigorously stirred solution of 4-n-pentyl-4''-acetyl-p-terphenyl (23.94 g, 0.07 mol) in 1,4-dioxan (800 ml) maintained at 30°C during 1 hour. The sodium salt separated out during the addition and stirring was continued for a further 1½ hours during which period the temperature was slowly raised to 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 (1200 ml). About 400 ml of the liquid was distilled and the mixture cooled. Acidification with concentrated hydrochloric acid afforded pale yellow crystals of the acid. This was filtered off, washed with water, dried and recrystallised from 1,4-dioxan to yield a colourless product. (18.3 g, 76.5%) m.p. 308°C; $\left. \begin{array}{l} \text{mujol} \\ \text{max} \end{array} \right\} 1682, 1604, 1432, 1300, 814 \text{ and } 776 \text{ cm}^{-1}$; δ (DMSO-d₆) 0.88 (t, 3H, -CH₃) 1.2-1.7 (m, 6H, methylenes) 2.63 (t, 2H, arCH₂) 7.2-8.1 (m, 12H, arH)

[Found: C, 83.75; H, 6.913% C₂₄H₂₄O₂ requires
C, 83.71; H, 6.976%].

The results of the cognate preparations of other

4-n-alkyl-p-terphenyl-4"-carboxylic acids are given below.

4-n-Hexyl-p-terphenyl-4"-carboxylic acid

Yield 74%, m.p. 287°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 1682, 1614, 1468, 1004,
834 and 775 cm^{-1} ; δ (DMSO- d_6) 0.87 (t, 3H, $-\text{CH}_3$) 1.3-1.65
(m, 8H, methylenes) 2.63 (t, 2H, arCH_2) 7.2-8.1 (m, 12H, arH)
[Found: C, 84.03; H, 7.42% $\text{C}_{25}\text{H}_{26}\text{O}_2$ requires
C, 83.79; H, 7.26%].

4-n-Heptyl-p-terphenyl-4"-carboxylic acid

Yield 70%, m.p. 285°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 1685, 1612, 1498, 1465,
1305, 1005 and 778 cm^{-1} ; δ (DMSO- d_6) 0.86 (t, 3H, $-\text{CH}_3$)
1.2-1.65 (m, 10H, methylenes) 2.63 (t, 2H, arCH_2) 7.2-8.1
(m, 12H, arH)
[Found: C, 84.3; H, 7.40% $\text{C}_{26}\text{H}_{28}\text{O}_2$ requires
C, 83.87; H, 7.52%].

4-n-Octyl-p-terphenyl-4"-carboxylic acid

Yield 76%, m.p. 302°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 1678, 1600, 1460,
1370, 814 and 770 cm^{-1} ; δ (DMSO- d_6) 0.86 (t, 3H, $-\text{CH}_3$)
1.2-1.65 (m, 12H, methylenes) 2.62 (t, 2H, arCH_2) 7.2-8.1
(m, 12H, arH)
[Found: C, 84.3; H, 8.0% $\text{C}_{27}\text{H}_{30}\text{O}_2$ requires
C, 83.93; H, 7.77%].

4-n-Pentyl-p-terphenyl-4''-carboxamide

A mixture of 4-n-pentyl-p-terphenyl-4''-carboxylic acid (13.76 g, 0.04 mol) and redistilled thionyl chloride (60 ml) was refluxed for 4 hours when the evolution of hydrogen chloride gas ceased. Excess thionyl chloride was removed by distillation under reduced pressure and *If*quor ammonia (75 ml, sp.gr.0.9) was added to the crude acid chloride and the mixture agitated for 1/2 hour. The solid material was filtered, washed with water and dried. Recrystallisation from cyclohexanone afforded the desired amide (10.8 g, 78.5%) m.p. 315-317°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 3410, 3180, 1640, 1615, 1466, 1008 \text{ and } 814 \text{ cm}^{-1}$

[Found: C, 84.26; H, 7.21; N, 4.33% $\text{C}_{24}\text{H}_{25}\text{NO}$ requires C, 83.97; H, 7.28; N, 4.08%].

The results of the cognate preparations of other 4-n-alkyl-p-terphenyl-4''-carboxamides are given below.

4-n-Hexyl-p-terphenyl-4''-carboxamide

Yield 90%, m.p. 285-288°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 3420, 3200, 1658, 1612, 1472, 1394 \text{ and } 816 \text{ cm}^{-1}$,

[Found: C, 83.93; H, 7.48; N, 3.86% $\text{C}_{25}\text{H}_{27}\text{NO}$ requires C, 84.03; H, 7.56; N, 3.92%].

4-n-Heptyl-p-terphenyl-4''-carboxamide

Yield 88%, m.p. 312-315°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 3400, 3150, 1642,$

1614, 1003 and 808 cm^{-1} ;

[Found: C, 84.03; H, 7.65; N, 3.87% $\text{C}_{26}\text{H}_{29}\text{NO}$ requires
C, 84.09; H, 7.81; N, 3.77%].

4-n-Octyl-p-terphenyl-4''-carboxamide

Yield 81%, m.p. 308-312°C; $\left. \begin{array}{l} \text{majol} \\ \text{max} \end{array} \right\} 3390, 3180, 1640,$

1614, 1460, 1376 and 814 cm^{-1} ;

[Found: C, 83.85; H, 8.43; N, 3.90% $\text{C}_{27}\text{H}_{31}\text{NO}$ requires
C, 84.15; H, 8.05; N, 3.63%].

4-n-Pentyl-4''-cyano-p-terphenyl

An intimate mixture of 4-n-pentyl-p-terphenyl-4''-carboxamide (8.575 g, 0.025 mol) and phosphorus pentoxide (10.65 g, 0.075 mol) was heated in an electrical heater at 200°C for 2 hours and cooled. The dark brown material was carefully treated with moist chloroform (250 ml). The organic phase was washed with 25% hydrochloric acid (3 x 70 ml), water (75 ml), 10% sodium hydroxide solution (3 x 75 ml) and finally water (2 x 50 ml). It was dried over anhydrous sodium sulphate and the solvent removed to give a pale brown product. This was chromatographed on silica gel and eluted with benzene. Removal of solvent from the eluate afforded a white material which was sublimed under high

vacuum at a bath temperature of 185°C (4.9 g, 60%) m.p. 130°C (reported³⁴ 130°C); ν $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2234, 1602, 1470, 1382, 1004 and 813 cm^{-1} ; δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$), 1.1-1.83 (m, 6H, methylenes) 2.61 (t, 2H, arCH_2) 6.93-7.7 (m, 12H, arH) [Found: C, 88.41; H, 6.92; N, 4.39% $\text{C}_{24}\text{H}_{25}\text{N}$ requires C, 88.61; H, 7.07; N, 4.30%].

The results of the cognate preparations of other 4-n-alkyl-4''-cyano-p-terphenyls are given below.

4-n-Hexyl-4''-cyano-p-terphenyl

Yield 68%, m.p. 124.5 °C (reported²⁶ m.p. 125°C); ν $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2234, 1601, 1504, 1474, 1380, 1006 and 815 cm^{-1} ; δ (CDCl_3) 0.89 (t, 3H, $-\text{CH}_3$) 1.26-1.62 (m, 8H, methylenes) 2.64 (t, 2H, arCH_2) 7.25-7.7 (m, 12H, arH) [Found: C, 88.36; H, 7.32; N, 4.08% $\text{C}_{25}\text{H}_{25}\text{N}$ requires C, 88.49; H, 7.37; N, 4.13%].

4-n-Heptyl-4''-cyano-p-terphenyl

Yield 66%, m.p. 134°C (reported²⁶ m.p. 134°C); ν $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2230, 1601, 1494, 1386, 1004, 827, 806 and 726 cm^{-1} ; δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$) 1.23-1.67 (m, 10H, methylenes) 2.64 (t, 2H, arCH_2) 7.21-7.68 (m, 12H, arH) [Found: C, 88.31; H, 7.58; N, 3.95% $\text{C}_{26}\text{H}_{27}\text{N}$ requires C, 88.38; H, 7.64; N, 3.96%].

4-n-Octyl-4'-cyano-p-terphenyl

Yield 67%, m.p. 127°C (reported²⁶ m.p. 127°C);

ν_{max} (nujol) 2232, 1601, 1498, 1388, 1005, 814 and 775 cm^{-1} ;

δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$) 1.25-1.65 (m, 12H, methylenes)

2.65 (t, 2H, ar-CH_2) 7.23-7.80 (m, 12H, arH)

[Found: C, 88.20; H, 7.92; N, 3.80% $\text{C}_{27}\text{H}_{29}\text{N}$ requires
C, 88.23; H, 7.90; N, 3.81%].

4-n-Pentanoylbiphenyl

This was prepared following the procedure of Long and Herze.²⁸ Thus, anhydrous aluminium trichloride (58.74 g, 0.44 mol) was suspended in dry carbon disulphide (250 ml) in a one litre three-necked flask, fitted with a reflux condenser, a mercury-sealed stirrer and a dropping funnel. n-Pentanoyl chloride (48.2 g, 0.4 mol) and biphenyl (61.6 g, 0.4 mol) were dissolved in carbon disulphide (250 ml) and added to the rapidly stirred suspension over a period of fortyfive minutes. Stirring was continued for thirty minutes at room temperature and the mixture was refluxed for four hours on a steam bath. Carbon disulphide was removed by distillation and the dark residue was hydrolysed by adding it slowly to a mixture of ice (400 g) and concentrated hydrochloric acid (200 ml). A pale yellow solid separated out, which was filtered and recrystallised from methyl alcohol

using activated charcoal to give 4-n-pentanoylbiphenyl
(80 g, 84%), m.p. 78-79°C (reported²⁸ yield 63%, m.p. 76-78°C);

$\nu_{\text{max}}^{\text{nujol}}$ 1676, 1602, 1400, 850, 762, 743 and 690 cm^{-1} ;
 δ (CDCl_3) 0.95 (t, 3H, $-\text{CH}_3$) 1.13-2.1 (m, 4H, methylenes)
3.0 (t, 2H, $-\text{COCH}_2-$) 7.23-8.26 (m, 9H, arH).

The results of the cognate preparations of other
4-n-alkanoylbiphenyls are given below.

4-n-Hexanoylbiphenyl

Yield 87%, m.p. 95-97°C (reported²⁸ yield 67%, m.p.
96.5°C); $\nu_{\text{max}}^{\text{nujol}}$ 1678, 1603, 1462, 1260, 1200, 989, 828 and
757 cm^{-1} ; δ (CDCl_3) 0.91 (t, 3H, $-\text{CH}_3$) 1.1-2.43 (m, 6H,
methylenes) 2.96 (t, 2H, $-\text{COCH}_2-$) 7.13-8.33 (m, 9H, arH).

4-n-Heptanoylbiphenyl

Yield 86.5%, m.p. 87-88°C (reported²⁸ yield 52%,
m.p. 85.5-86.5°C); $\nu_{\text{max}}^{\text{nujol}}$ 1678, 1603, 1405, 985, 849 and
764 cm^{-1} ; δ (CDCl_3) 0.9 (t, 3H, $-\text{CH}_3$) 1.06-2.16 (m, 8H,
methylenes) 2.95 (t, 2H, $-\text{COCH}_2-$) 7.23-8.16 (m, 9H, arH).

4-n-Octanoylbiphenyl

Yield 90%, m.p. 101-102°C; $\nu_{\text{max}}^{\text{nujol}}$ 1678, 1604, 1463,
1378, 1202, 825 and 758 cm^{-1} ; δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$)
1.03-2.13 (m, 10H, methylenes) 3.0 (t, 2H, $-\text{COCH}_2-$) 7.13-
8.26 (m, 9H, arH)

[Found: C, 85.62; H, 8.52% $\text{C}_{20}\text{H}_{24}$ requires
C, 85.71; H, 8.57%]

4-n-Nonanoylbiphenyl

Yield 69.5%, m.p. 93-94.5°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\} 1670, 1601, 1482$
 1367, 1004, 833 and 748 cm^{-1} ; $\delta(\text{CDCl}_3)$ 0.88 (t, 3H, $-\text{CH}_3$)
 1.05-2.13 (a, 12H, methylenes) 2.98 (t, 2H, $-\text{COCH}_2$) 7.16-
 8.33 (m, 9H, arH)

[Found: C, 85.92; H, 8.61% $\text{C}_{21}\text{H}_{26}\text{O}$ requires
 C, 85.71; H, 8.84%].

4-n-Pentylbiphenyl

A mixture of 4-n-pentanoylbiphenyl (71.4 g, 0.3 mol),
 diethylene glycol (375 ml), potassium hydroxide pellets (50.4g,
 0.9 mol) and 90% hydrazine hydrate (50 ml) was heated at
 110°C in an oil bath for two hours. The temperature was
 gradually raised to 180°C, distilling off the volatile matter
 in the process and held at this temperature for four hours.
 The mixture was cooled, water (200 ml) and chloroform (250 ml)
 were added. The aqueous phase was extracted with chloroform
 (3 x 100 ml) and the combined organic phase was washed with
 water and dried (Na_2SO_4). Removal of solvent and distilling
 the residue under reduced pressure gave a colourless liquid
 (51.0 g, 74.5%), b.p. 147-155/2 mm (reported²⁴ yield 65%,
 b.p. 106-109/0.1 mm); $\left. \begin{array}{l} \text{neat} \\ \text{max} \end{array} \right\} 2936, 2864, 1601, 1488, 1006,$
 760 and 697 cm^{-1} ; $\delta(\text{CDCl}_3)$ (t, 3H, $-\text{CH}_3$) 1.08-1.98 (m, 6H,
 methylenes) 2.61 (t, 2H, ar CH_2) 6.9-7.76 (m, 9H, arH).

The results of the cognate preparations of other 4-n-alkylbiphenyls are given below.

4-n-Hexylbiphenyl

Yield 79%, b.p. 168-170/2 mm (reported²⁹ b.p. 175-176/3 mm); $\left. \begin{array}{l} \text{neat} \\ \text{max} \end{array} \right\}$ 2900, 2850, 1601, 1485, 1408, 1072, 1006, 763 and 695 cm^{-1} ; δ (CDCl_3) 0.89 (t, 3H, $-\text{CH}_3$) 1.1-2.0 (m, 8H, methylenes) 2.59 (t, *an.* arCH_2) 7.0-7.7 (m, 9H, arH).

4-n-Heptylbiphenyl

Yield 76%, bop* 165-170/2 mm (reported²⁴ yield 65%, b.p. 124-127/0.1 mm); $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 1601, 1488, 1377, 1004, 760 and 694 cm^{-1} ; δ (CDCl_3) 0.86 (t, 3H, $-\text{CH}_3$) 1.05-2.03 (m, 10H, methylenes) 2.66 (t, 2H, arCH_2) 7.05-7.85 (m, 9H, arH).

4-n-Octylbiphenyl

Yield 72.5%, b.p. 192-199/3 mm (reported²⁹ b.p. 187-188/2 mm); $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 1601, 1490, 1480, 1377, 1005, 757 and 695 cm^{-1} ; δ (CDCl_3) 0.86 (t, 3H, $-\text{CH}_3$) 1.05-2.01 (m, 12H, methylenes) 2.63 (t, 2H, arCH_2) 7.0-7.7 (m, 9H, arH).

4-n-Nonylbiphenyl

Yield 73.5%, m.p. 42-43°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 1602, 1490, 1462, 1378, 1006, 760 and 695 cm^{-1} ; δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$) 1.03-1.93 (m, 14H, methylenes) 2.61 (t, 2H, arCH_2) 7.0-7.66 (m, 9H, arH)

[Found: C, 89.8; H, 9.92% $\text{C}_{21}\text{H}_{28}$ requires
C, 90.0; H, 10.0%].

4-n-Pentyl-4'-acetylbiphenyl

This was prepared following the procedure of Byron, Gray and Wilson³⁰. Thus, a mixture of anhydrous aluminium trichloride (30.74 g, 0.23 mol), dry carbon disulphide (300 ml) and 4-n-pentylbiphenyl (44.8 g, 0.2 mol) was placed in a one litre three-necked flask fitted with a reflux condenser, a mercury sealed stirrer and a dropping funnel. Freshly distilled acetyl chloride (15.7 g, 0.2 mol) was added *drop by drop* to the stirred reaction mixture during thirty minutes. This was stirred for one hour at room temperature, refluxed for three hours on a steam bath and left overnight. Carbon disulphide was removed by distillation and the dark coloured complex was hydrolysed by adding carefully a mixture of ice cold concentrated hydrochloric acid (100 ml) and water (100 ml). More water (100 ml) was added and the mixture stirred in order to obtain the solid material in a finely divided form. It was filtered off, washed with water and dried. Recrystallisation from methyl alcohol gave 4-n-pentyl-4'-acetylbiphenyl (32 g, 60%) m.p. 66.5°C (reported³¹ m.p. 77°C); ν $\left. \begin{array}{l} \text{neat} \\ \text{max} \end{array} \right\} 1670, 1601, 1470, 1273 \text{ and } 809 \text{ cm}^{-1}$; δ (CDCl₃) $\left. \begin{array}{l} 0.93 \\ \end{array} \right\} (t, 3H, -CH_3) 1.1-2.0$ (m, 6H, methylenes) 2.63 (s, 3H, -COCH₃) 2.7 (t, 2H, arCH₂) 7.1-8.23 (m, 8H, arH).

The results of the cognate preparations of other 4-n-alkyl-4'-acetylbiphenyls are given below.

4-n-Hexyl-4'-acetylbiphenylYield 65%, m.p. 74°C (reported³¹ m.p. 79°C);

ν_{max} nujol 1676, 1601, 1462, 1360, 1270, 960, 813 and 774 cm^{-1} ;
 δ (CDCl_3) 0.86 (t, 3H, $-\text{CH}_3$) 1.05-2.01 (m, 8H, methylenes)
 2.61 (s, 3H, $-\text{COCH}_3$) 2.63 (t, 2H, arCH_2) 7.05-8.15 (m, 8H,
 arH).

4-n-Heptyl-4'-acetylbiphenylYield 72%, m.p. 74°C (reported³¹ m.p. 76.5°C);

ν_{max} nujol 1672, 1601, 1461, 1390, 1137, 828 and 803 cm^{-1} ; δ (CDCl_3)
 0.86 (t, 3H, $-\text{CH}_3$) 1.03-2.03 (m, 10H, methylenes) 2.61 (s, 3H,
 $-\text{COCH}_3$) 2.64 (t, 2H, arCH_2) 7.06-8.23 (m, 8H, arH).

4-n-Octyl-4'-acetylbiphenylYield 71%, m.p. 85°C (reported³¹ m.p. 86.5°C);

ν_{max} nujol 1672, 1603, 1460, 1262, 812 and 783 cm^{-1} ; δ (CDCl_3)
 0.86 (t, 3H, $-\text{CH}_3$) 1.05-2.0 (m, 12H, methylenes) 2.60 (s, 3H,
 $-\text{COCH}_3$) 2.61 (t, 2H, arCH_2) 7.1-8.18 (m, 8H, arH).

4-n-Nonyl-4'-acetylbiphenylYield 82%, m.p. 85.5°C (reported³¹ m.p. 85°C);

nujol 1680, 1603, 1465, 1378, 1270, 826 and 805 cm^{-1} ;
 δ (CDCl_3) 0.93 (t, 3H, $-\text{CH}_3$) 1.1-2.03 (m, 14H, methylenes)
 2.53 (s, 3H, $-\text{COCH}_3$) 2.65 (t, 2H, arCH_2) 7.03-8.16 (m, 8H, arH).

4-n-Pentylbiphenyl-4'-carboxylic acid

This was prepared following the procedure of Johnson, Gutsche and Offenbauer.³² Thus, a solution of sodium hypobromite prepared at 0°C, by dissolving bromine (93.6 g, 0.6 mol) in a solution of sodium hydroxide (84 g, 2.1 mol) in water (420 ml) was added to a vigorously stirred solution of 4-n-pentyl-4'-acetylbiphenyl (31.92 g, 0.12 mol) in dioxan (300 ml). The addition was carried out at room temperature during one hour. The temperature was slowly raised to 50°C and held there for half hour to ensure completion of reaction. Enough aqueous sodium metabisulphite solution was added to destroy the excess of sodium hypobromite. Water (2000 ml) was added and 400ml of the liquid was boiled off. The residue was cooled and acidified with concentrated hydrochloric acid. The product so obtained was filtered, washed with water thoroughly and air-dried. Recrystallisation from glacial acetic acid gave colourless crystals of 4-n-pentylbiphenyl-4'-carboxylic acid (22.35 g, 69.5%), m.p. 176°C (reported³¹ m.p. 176°C); $\nu_{\text{max}}^{\text{nujol}}$ 1670, 1603, 1428, 1180, 1005 and 775 cm^{-1} , δ (DMSO- d_6) 0.9 (t, 3H, $-\text{CH}_3$) 1.08-2.11 (m, 6H, methylenes) 2.68 (t, 2H, arCH_2) 7.15-8.45 (m, 8H, arH).

The results of the cognate preparations of other 4-n-alkylbiphenyl-4'-carboxylic acids are given below.

4-n-Hexylbiphenyl-4'-carboxylic acidYield 75%, m.p. 178°C (reported³¹ m.p. 165°C);
 $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 1668, 1603, 1430, 1126, 1002 and 775 cm^{-1} ;
 δ (DMSO- d_6) 0.88 (t, 3H, $-\text{CH}_3$) 1.05-2.0 (m, 8H, methylenes)2.65 (t, 2H, arCH_2) 7.1-8.33 (m, 8H, arH).4-n-Heptylbiphenyl-4'-carboxylic acidYield 65%, m.p. 158°C (reported³¹ m.p. 156°C);
 $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 1668, 1602, 1422, 1002 and 774 cm^{-1} ; δ (DMSO- d_6)
0.86 (t, 3H, $-\text{CH}_3$) 1.06-2.03 (m, 8H, methylenes) 2.6 (t, 2H, arCH_2) 7.03-8.3 (m, 8H, arH).4-n-Octylbiphenyl-4'-carboxylic acidYield 68%, m.p. 156°C (reported³¹ m.p. 147°C);
 $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 1667, 1601, 1460, 1371, 1001 and 737 cm^{-1} ;
 δ (DMSO- d_6) 0.86 (t, 3H, $-\text{CH}_3$) 1.03-2.0 (m, 10H, methylenes)2.6 (t, 2H, arCH_2) 7.1-8.33 (m, 8H, arH).4-n-Nonylbiphenyl-4'-carboxylic acidYield 78%, m.p. 139°C (reported³¹ m.p. 135°C);
 $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 1666, 1601, 1422, 1282, 1001 and 763 cm^{-1} ;
 δ (DMSO- d_6) 0.83 (t, 3H, $-\text{CH}_3$) 1.0-2.0 (m, 12H, methylenes)2.5 (t, 2H, arCH_2) 7.0-8.16 (m, 8H, arH).

4-n-Pentylbiphenyl-4'-carboxamide

A mixture of 4-n-pentylbiphenyl-4'-carboxylic acid (21.44 g, 0.08 mol) and redistilled thionyl chloride (100 ml) was refluxed for five hours when the evolution of gas ceased. Excess of thionyl chloride was removed by distillation under reduced pressure. Liquor ammonia (125 ml, sp.gr. 0.9) was added to the crude acid chloride and the mixture agitated for thirty minutes. The white solid so obtained was filtered off, washed with water and air-dried. Recrystallisation from 1,4-dioxan afforded the pure amide (18g, 84%) m.p. 234-235°C (reported²⁴ yield 86%, m.p. 231-233°C); ν_{max} (nujol) 3400, 3200, 1645, 1618, 1574, 1408, 1145, 1005 and 848 cm^{-1} ; δ (DMSO- d_6) 0.88 (t, 3H, $-\text{CH}_3$) 1.08-2.03 (m, 6H, methylenes) 2.56 (t, 2H, arCH_2) 3.33 (s, 2H, $-\text{CONH}_2$) 6.9-8.36 (a, 8H, arH).

The results of the cognate preparations of other 4-n-alkylbiphenyl-4'-carboxylic acids are given below.

4-n-Hexylbiphenyl-4'-carboxamide

Yield 83%, m.p. 218-220°C; ν_{max} (nujol) 3395, 3194, 1640, 1617, 1574, 1460, 1409, 1003 and 820 cm^{-1} ; δ (DMSO- d_6) 0.9 (t, 3H, $-\text{CH}_3$) 1.1-2.36 (m, 8H, methylenes) 2.6 (t, 2H, arCH_2) 3.36 (s, 2H, $-\text{CONH}_2$) 6.93-8.43 (m, 8H, arH).

4-n-Heptylbiphenyl-4'-carboxamide

Yield 90%, m.p. 225-228°C (reported²⁴ yield 82%, m.p.

m.p. 223-225°C); $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 3400, 3200, 1645, 1618, 1582, 1416, 1150, 1005 and 788 cm^{-1} ; δ (DMSO- d_6) 0.88 (t, 3H, $-\text{CH}_3$) 1.06-2.03 (m, 10H, methylenes) 2.6 (t, 2H, arCH_2) 3.36 (s, 2H, $-\text{CONH}_2$) 7.05-8.53 (m, 8H, arH).

4-n-Octylbiphenyl-4'-carboxamide

Yield 88%, m.p. 224-227°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 3395, 3192, 1645, 1612, 1462, 1371, 1004 and 818 cm^{-1} ; δ (DMSO- d_6) 0.86 (t, 3H, $-\text{CH}_3$) 1.0-2.03 (m, 12H, methylenes) 2.53 (t, 2H, arCH_2) 3.4 (s, 2H, $-\text{CONH}_2$) 7.03-8.3 (m, 8H, arH).

4-n-Honylbiphenyl-4'-carboxamide

Yield 79%, m.p. 227-229°C; $\left. \begin{array}{l} \text{nujol} \\ \text{max} \end{array} \right\}$ 3400, 3180, 1642, 1612, 1460, 1408, 1408, 1378 and 832 cm^{-1} ; δ (DMSO- d_6) 0.86 (t, 3H, $-\text{CH}_3$) 1.06-2.06 (m, 14H, methylenes) 2.53 (t, 2H, arCH_2) 3.33 (s, 2H, $-\text{CONH}_2$) 7.06-8.16 (m, 8H, arH).

4-n-Pentyl-4'-cyanobiphenyl

An intimate mixture of 4-n-pentylbiphenyl-4'-carboxamide (16.02 g, 0.06 mol) and phosphorus pentoxide (24.08 g, 0.24 mol) was heated at 200°C in an electrical heater for two hours and cooled. The brown material was carefully decomposed with moist chloroform (100 ml). Water (125 ml) and concentrated hydrochloric acid (50 ml) were added to this mixture and extracted with chloroform (3 x 100 ml). The combined organic

phase was washed with water, 10% aqueous sodium hydroxide solution (2 x 60 ml) and water (2 x 100 ml) and dried (Na_2SO_4). Removal of solvent afforded a pale brown material, which was chromatographed on silica gel using benzene as eluent to give a white product. Further purification by sublimation at 180°C under high vacuum afforded 11.0 g of pure product (73.5%), m.p. 22.5°C (reported^{20(b)} m.p. 22.5°C); $\left. \begin{array}{l} \text{neat} \\ \text{max} \end{array} \right\} 2950, 2250, 1605, 1500 \text{ and } 1008 \text{ cm}^{-1}$; δ (CDCl_3) 0.9 (t, 3H, $-\text{CH}_3$) 1.1-1.86 (m, 6H, methylenes) 2.65 (t, 2H, arCH_2) 7.06-7.8 (m, 8H, arH).

The results of the cognate preparations of other 4-n-alkyl-4'-cyanobiphenyls are given below.

4-n-Hexyl-4'-cyanobiphenyl

Yield 80%, m.p. 13.5°C (reported^{20(b)} m.p. 13.5°C); $\left. \begin{array}{l} \text{neat} \\ \text{max} \end{array} \right\} 2931, 2856, 2228, 1603, 1493, 1005 \text{ and } 815 \text{ cm}^{-1}$; δ (CDCl_3) 0.9 (t, 3H, $-\text{CH}_3$) 1.06-2.0 (m, 8H, methylenes) 2.63 (t, 2H, arCH_2) 7.03-7.86 (m, 8H, arH).

4-n-Heptyl-4'-cyanobiphenyl

Yield 76%, m.p. 28.5°C (reported^{20(b)} m.p. 28.5°C); $\left. \begin{array}{l} \text{neat} \\ \text{max} \end{array} \right\} 2938, 2868, 2235, 1610, 1498 \text{ and } 1006 \text{ cm}^{-1}$; δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$) 1.03-2.0 (m, 10H, methylenes) 2.65 (t, 2H, arCH_2) 7.03-7.86 (m, 8H, arH).

4-n-Octyl-4'-cyanobiphenyl

Yield 79%, m.p. 21°C (reported^{20(b)} m.p. 21°C);

$\nu_{\text{max}}^{\text{neat}}$ 2938, 2868, 2236, 1610, 1498, 1472, 1006 and 815 cm^{-1} ;

δ (CDCl_3) 0.86 (t, 3H, $-\text{CH}_3$) 1.05-2.0 (m, 12H, methylenes)

2.63 (t, 2H, arCH_2) 7.0-7.86 (m, 8H, arH).

4-n-Nonyl-4'-cyanobiphenyl

Yield 83%, m.p. 40°C (reported^{20(b)} m.p. 40°C);

$\nu_{\text{max}}^{\text{nujol}}$ 2234, 1610, 1498, 1470, 1378, 1005, 853 and 830 cm^{-1} ;

δ (CDCl_3) 0.86 (t, 3H, $-\text{CH}_3$) 1.03-2.0 (m, 14H, methylenes)

2.66 (t, 2H, arCH_2) 7.1-7.8 (m, 8H, arH).

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